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RESEARCH ARTICLE

Quantifying annual groundwater recharge and storage in the central Sierra Nevada using naturally occurring ^{35}S

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Abstract

Identifying aquifer vulnerability to climate change is of vital importance in the Sierra Nevada and other snow-dominated basins where groundwater systems are essential to water supply and ecosystem health. Quantifying the component of new (current year's) snowmelt in groundwater and surface water is useful in evaluating aquifer vulnerability because significant annual recharge may indicate that streamflow will respond rapidly to annual variability in precipitation, followed by more gradual decreases in recharge as recharge declines over decades. Hydrologic models and field-based studies have indicated that young (<1 year) water is an important component of streamflow. The goal of this study was to utilize the short-lived, naturally occurring cosmogenic isotope sulfur-35 (^{35}S) to quantify new snowmelt contribution to groundwater and surface waters in Sagehen Creek Basin (SCB) and Martis Valley Groundwater Basin (MVGB) located within the Tertiary volcanics of the central Sierra Nevada, CA. Activities of ^{35}S were measured in dissolved sulfate ($^{35}\text{SO}_4^{2-}$) in SCB and MVGB snowpack, groundwater, springs, and streamflow. The percent of new snowmelt (PNS) in SCB streamflow ranged from $0.2 \pm 6.6\%$ during baseflow conditions to $14.0 \pm 3.4\%$ during high-flow periods of snowmelt. Similar to SCB, the PNS in MVGB groundwater and streamflow was typically <30% with the largest fractions occurring in late spring or early summer following peak streamflow. The consistently low PNS suggests that a significant fraction of annual snowmelt in SCB and MVGB recharges groundwater, and groundwater contributions to streamflow in these systems have the potential to mitigate climate change impacts on runoff.

KEYWORDS

groundwater recharge, mountain groundwater, snowmelt infiltration, sulfur-35

1 | INTRODUCTION

Groundwater vulnerability to climate change in high-elevation basins has widespread implications for ecosystem health and water supply (Earman & Dettinger, 2011; Earman et al., 2015). In the mountains of the western United States, groundwater is a major component of streamflow, even during peak snowmelt conditions (e.g., Frisbee et al., 2011; Liu et al., 2004). Spatial and temporal changes in snow dynamics, such as declines in snowpack accumulation (Mote 2003; Mote et al., 2005) and earlier onset of snowmelt (Hamlet et al., 2005; Knowles et al., 2006; Mote et al., 2005), are of particular concern for Sierra Nevada basins because groundwater recharge is mainly derived from snowpack for most of the southwest (Earman et al., 2006; Winograd et al., 1998). Groundwater recharge in high-elevation basins in the western United States is important for aquifer replenishment

(Wilson & Guan, 2004; Manning & Solomon, 2005) and ecosystem health, yet the impact of climate change on groundwater recharge is poorly understood (Earman & Dettinger, 2011; Earman et al., 2015; Viviroli et al., 2011).

Understanding climate change impacts on groundwater resources in the Sierra Nevada and other high-elevation basins is difficult because of a weak understanding of direct and indirect effects of climate change on mountain recharge processes (Earman & Dettinger, 2011; Earman et al., 2015). Current forecasts of the effects of climate change vary widely. In snow-dominated basins that are predicted to experience a shift in precipitation from snow to rain, groundwater recharge may decrease because snow is a more efficient recharging mechanism than rain (Earman et al., 2006; Meixner et al., 2016; Winograd et al., 1998). However, reductions in snowpack or shifts from snow to rain may have little effect on groundwater recharge in

fractured rock aquifers that are permeability limited (Manning et al., 2012). Under either condition, investigating groundwater response times would reduce the uncertainty of how mountain basins respond to changing precipitation patterns.

Groundwater transit time, defined as the time elapsed between the input of water to the basin and the time of water sampling, is useful in evaluating groundwater sensitivity to climate change by providing insight into recharge processes, storage capacity, and flow characteristics of groundwater reservoirs. Shallow groundwater basins are likely to have lower buffering capacity and greater sensitivity to climate change (Singleton & Moran, 2010). Short transit times indicate shallow groundwater reservoirs and relatively small storage capacities. Because groundwater storage capacity inferred from groundwater transit time distributions in high-elevation basins such as the Sierra Nevada has important implications for groundwater vulnerability to climate change, an accurate basin study typically requires the use of groundwater tracer techniques.

Environmental groundwater tracers, such as dissolved gases and isotopic tracers, are useful for characterizing the transit time or “apparent age” of groundwater in high-elevation basins (e.g. Plummer et al., 2001; Manning & Solomon, 2005; Manning et al., 2012; Segal et al., 2014). In the Sierra Nevada, dissolved noble gas concentrations (Ne, Ar, Kr, and Xe) combined with tritium–helium ($^3\text{H}/^3\text{He}$) age dating have been useful in determining apparent groundwater ages of <50 years in various basins such as Martis Valley Groundwater Basin (MVGB) and Olympic Valley Basin (Singleton & Moran, 2010; Segal et al. 2014). For the nearby Sagehen Creek Basin (SCB), Manning et al. (2012) used time-series measurements of chlorofluorocarbons (CFCs), sulfur hexafluoride, and tritium (^3H) to determine apparent groundwater ages of springs and found that most springs are best characterized by a bimodal mixture of <1-year-old water and water recharged after 1950. Recharge studies using CFCs, sulfur hexafluoride, and $^3\text{H}/^3\text{He}$ tracer methods have determined groundwater ages of <1 year; however, the uncertainties of these methods are typically greater than or equal to 1 year (Singleton & Moran, 2010; Manning et al., 2012).

Field-based and hydrologic modeling studies have indicated that young (<1 year) water is a substantial component of streamflow, which has important implications for groundwater recharge and storage. A review of field studies using a lumped parameter approach revealed that mean transit time of water in diverse catchments ranged from <1 to 5 years (McGuire & McDonnell, 2006). Stable water isotope investigations have also shown that approximately one third of global river discharge is derived from young streamflow (Jasechko et al., 2016). In the western U.S., hydrologic modeling demonstrated that young water component is most vulnerable to changing recharge conditions under a drier climate (Engdahl & Maxwell, 2015). Dry conditions cause immediate responses in rapid vadose pathways by cutting off rapid flowpaths resulting in significantly older composite age distributions (Engdahl & Maxwell, 2015). The development and application of new groundwater tracer methods that can quantify seasonal fluxes of precipitation on <1-year timescales would improve our understanding of groundwater residence times and storage capacities in mountain basins.

An infrequently utilized environmental tracer that captures the timescale of <1 year is the radioisotope sulfur-35 (^{35}S). ^{35}S is produced

by cosmic ray spallation of atmospheric argon above the troposphere and eventually enters the hydrologic cycle as dissolved $^{35}\text{SO}_4^{2-}$ through precipitation (Tanaka & Turekian, 1991). The half life of 87.5 days (Lal & Peters, 1967) is ideal for investigating groundwater recharge and cycling of $^{35}\text{SO}_4^{2-}$ on timescales of <1.2 years (five half lives). Hydrologic studies in high-elevation basins such as the Rocky Mountain Range have successfully used $^{35}\text{SO}_4^{2-}$ to determine mean residence times of SO_4^{2-} and groundwater in basins where the hydrologic SO_4^{2-} budget is dominated by atmospheric inputs, and biogeochemical cycling and water–rock interactions are minimal (Cooper et al., 1991; Sueker et al., 1999; Michel et al., 2000; Kester et al., 2003; Shanley et al., 2005; Singleton et al., 2014). Because of its short half life, the $^{35}\text{SO}_4^{2-}$ tracer can be used to characterize basins that have a significant component of total streamflow derived from the current year’s snowmelt (hereon referred to as “new” snowmelt), which would be an important tool in evaluating the vulnerability of water resources to changing precipitation patterns.

This study utilized environmental $^{35}\text{SO}_4^{2-}$ to determine the annual flux of new snowmelt being stored or discharged from two central Sierra Nevada basins: SCB and MVGB. The $^{35}\text{SO}_4^{2-}$ tracer method is used to quantify the fraction of surface water and groundwater derived from new snowmelt to constrain the new snowmelt contribution to groundwater recharge.

2 | SITE DESCRIPTION

SCB and MVGB are located on the eastern slope of the central Sierra Nevada, CA, near the crest of the Sierran divide, northwest of Lake Tahoe (Figure 1). MVGB has an area of approximately 148 km², which is over five times the 27-km² area for SCB. Both SCB and MVGB cover a similar elevation range: 1940–2600 and 1740–2700 m for SCB and MVGB, respectively. The large difference in surface area allows for the investigation of how groundwater recharge from new snowmelt is affected by larger surface area and storage volume.

Both basins have a mean annual precipitation of approximately 80 cm per year, 80% of which falls as snow during the winter months (Snowpack Telemetry [SNOTEL] Site #834 in MVGB and Site #539 located within 2.0 km of SCB; <http://www.wcc.nrcs.usda.gov/snow/>). Peak snowmelt typically occurs in early April, and surface flows are controlled by melting snowpack with peak stream discharge occurring in the late spring to early summer. SCB is drained by Sagehen Creek, which flows from west to east as a tributary to the Truckee River (TR; Figure 2a). Several surface water bodies within MVGB also eventually flow into the TR including Martis Lake (ML) and Donner Creek (DC; Figure 2b). Daily mean streamflow values for Sagehen Creek were obtained from a U.S. Geological Survey gauging station located near the outlet of SCB.

SCB and MVGB basins are underlain by Cretaceous granites and granodiorites typical of the Sierra Nevada batholith. However, Miocene to Pleistocene volcanics comprised mainly of andesitic flows, breccias, and basalts are the predominant rock type in both basins (Sylvester, 2008; California Department of Water Resources, 2006) that presumably contain the shallow aquifer. Surficial Quaternary alluvium, colluvium, and glacial deposits derived from the Tertiary aged

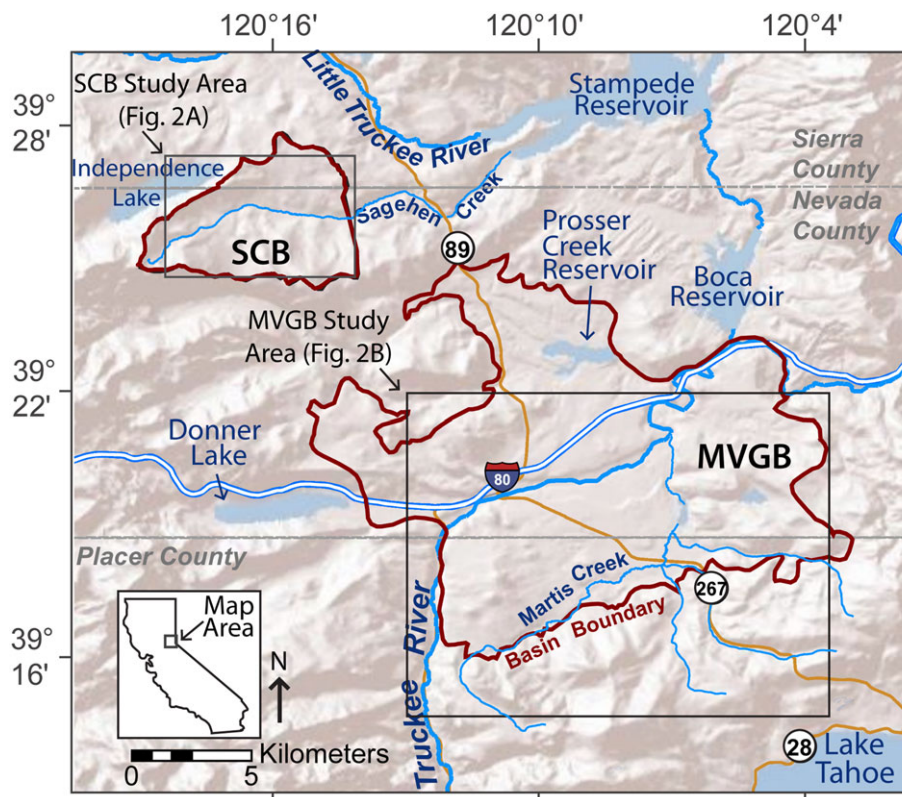


FIGURE 1 Location of Sagehen Creek Basin (SCB) and Martis Valley Groundwater Basin (MVGB) in California. MVGB is generally delineated around the extent of alluvium and basin-fill deposits within the Martis Valley (Hydro-Search, Inc., 1995). Source: USGS National Hydrography Data Set and California Department of Water Resources

volcanic rocks overlies and interfingers with the volcanic sequences. The alluvial and glacial deposits have higher specific storage than the volcanic and basement rocks and likely support surficial aquifers in this region.

SCB and MVGB soils are well-drained soils derived from volcanic parent material. Soils in SCB are generally Andic and Ultic Haploxeralfs (Pacific Southwest Research Station, 2016). The predominant soil series in SCB are Fugawee, Tahoma, and Jorge, which generally consist of sandy or gravelly loam layer up to 13 inches thick overlying a gravelly clay or cobble loam that extends to a depth between 35 and 47 inches (Soil Survey Staff, 2016). MVGB soils are also composed of varying percentages of Martis, Euer, Kyzbur, Trojan, and Aldi soil series (Soil Survey Staff, 2016). Similar to the soils found in SCB, the MVGB soil series are generally gravelly sandy loam of 6–21 inches in thickness overlying a gravelly clay loam that extends up to 67 inches in depth (Soil Survey Staff, 2016).

Groundwater residence times and recharge processes in SCB and MVGB have been studied extensively using noble gas and environmental tracer techniques. On the basis of CFCs and $^3\text{H}/^3\text{He}$ data, Rademacher et al. (2001) found that the apparent groundwater ages of springs in SCB ranged from <2 to 36 years using the simplified piston-flow model. In MVGB, Segal et al. (2014) used $^3\text{H}/^3\text{He}$ and dissolved noble gases to determine groundwater ages and recharge temperatures at various wells throughout MVGB. They found that groundwater recharge generally occurred at lower elevations and that long screened wells were a mixture of groundwater with ages of 50 to over 1,000 years. These studies have characterized the residence time of water on the scale of greater than 2 years, but the uncertainty

inherent in the analytical techniques limits its application on the <1-year timescale making them unsuitable for investigating the transport and storage of new snowmelt. Application of the $^{35}\text{SO}_4^{2-}$ tracer technique will improve our understanding of groundwater residence times and storage capacities in mountain basins on annual timescales.

2.1 | Transport of sulfate in SCB and MVGB

The simplified transport model used in this study assumes that $^{35}\text{SO}_4^{2-}$ moves conservatively through the groundwater system. Characterization of the soil, and potential physical and biogeochemical processes, which may affect the transport of $^{35}\text{SO}_4^{2-}$ in this region, is not well quantified in the Sagehen and Martis Valley basins. Sorption of $^{35}\text{SO}_4^{2-}$ typically occurs in soils with low pH and an abundance of minerals containing iron and aluminum oxyhydroxides (Chao et al., 1964; Parfitt, 1978). Andic soils containing iron and aluminum hydroxides have been identified in SCB and MVGB (Soil Survey Staff, 2016); however, no data exist showing the pH level of the soil, which is critical in understanding SO_4^{2-} sorption capacity. Our measurements of pH in groundwater from the basins show the levels to be neutral (~7), supporting our assumption of limited SO_4^{2-} sorption. To our knowledge, no S stable isotope data for SO_4^{2-} exist for SCB and MVGB, which could provide information on biogeochemical processes.

In an effort to better understand SO_4^{2-} transport in this region, we performed a SO_4^{2-} mass balance calculation for SCB. The SO_4^{2-} mass balance described in Appendix A revealed a net export of SO_4^{2-} from SCB, which may be due to higher atmospheric SO_4^{2-} loading from previous decades or organic matter mineralization in the soil zone. Mean

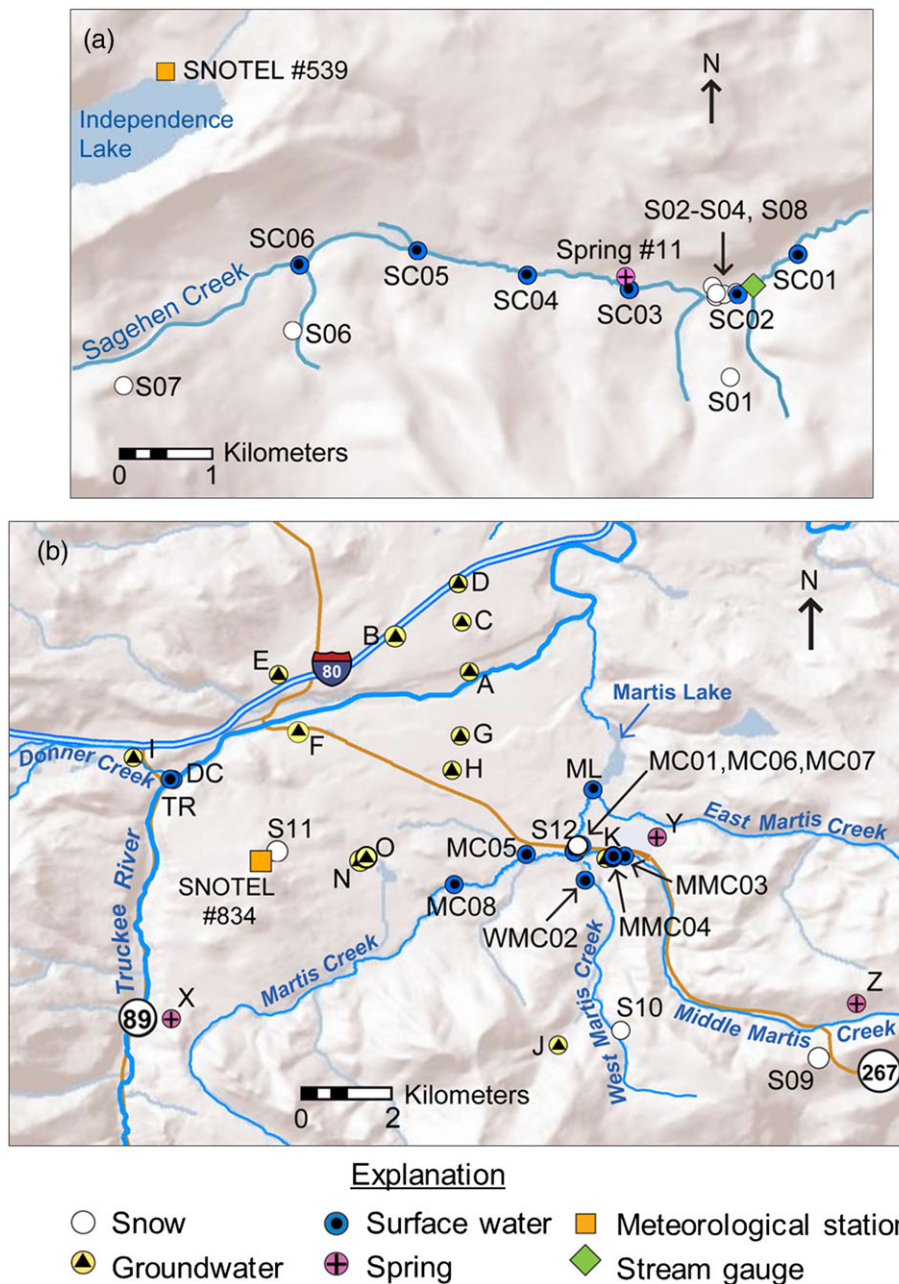


FIGURE 2 ³⁵SO₄²⁻ sampling locations in (a) Sagehen Creek Basin and (b) Martis Valley Groundwater Basin. Source: USGS National Hydrography Data Set and California Department of Water Resources

groundwater ages plotted versus SO₄²⁻ concentrations for springs and wells in both SCB and MVGB reveal a minimal trend between groundwater apparent age and SO₄²⁻ concentrations (Figure 3). Rademacher et al. (2001) did note a trend between major cations and residence time in SCB spring water indicating that water rock interactions are occurring in the subsurface; however, the comparison of SO₄²⁻ concentrations with apparent groundwater ages suggests that chemical weathering in these basins has little influence on stream SO₄²⁻ hydrochemistry at these sites.

Given the limited information available on SO₄²⁻ sorption and biogeochemical cycling in SCB and MVGB, our analysis begins with the assumption that SO₄²⁻ is behaving conservatively in the system, and hence, the fraction of new snowmelt in surface water and groundwater is interpreted as a minimum contribution.

3 | METHODS

3.1 | Snow sampling

SCB snowpacks were collected in winter 2009–2010 and 2010–2011 by shoveling full-depth vertical snow pits until an impermeable layer (i.e., ice layer or ground surface) was reached. Snow was allowed to melt in plastic containers, yielding between 13 and 20 L of melt water per sample. Fifteen snowpack composite samples were collected on three sampling dates (one in winter 2009–2010 and two in winter 2010–2011) from eight sites within SCB (Figure 2a). The sites range in elevation from 1844 m near the basin floor to 2373 m on the western slope of SCB.

Snow collection techniques were modified for MVGB to better characterize temporal and spatial difference of ³⁵SO₄²⁻ snow activity

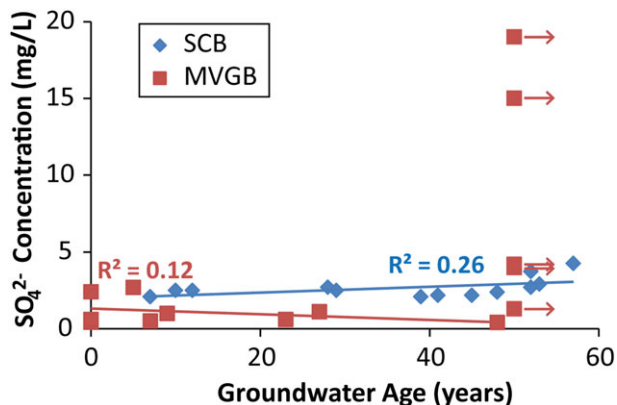


FIGURE 3 Groundwater apparent age versus SO_4^{2-} concentration for Sagehen Creek Basin (SCB) and Martis Valley Groundwater Basin (MVGB) springs and wells. MVGB groundwater ages plotted at 50 years with an arrow to the right represent ages of >50 years and are not included in the calculation of the correlation coefficient. The low correlation coefficient observed for both SCB ($R^2 = 0.26$) and MVGB ($R^2 = 0.12$) suggests a minimal trend between groundwater apparent age and SO_4^{2-} concentrations. Groundwater apparent age data were obtained from Manning et al. (2012) and Segal et al. (2014)

within a season. In November 2011, prior to the first major water year (WY) 2012 winter precipitation event, 210-L containers were placed at four MVGB sampling locations (Figure 2b), which cover the MVGB range in elevation. The contents of each container were transferred into 20-L buckets on four sample collection dates in winter 2011–2012 with the goal of obtaining 20 L of melt water per sampling event. If less than 20 L was obtained over a collection period, the uppermost layers of the surrounding snow, which is representative of the most recent snowfall, was added to the sample container to achieve approximately 20 L of melt water. The May 2, 2012, sampling event yielded between 2.0 and 13.5 L of melt water at each of the four sampling sites because no additional snow was available to augment the melt water. Although both rain and snow were allowed to accumulate in the MVGB containers, approximately 77% of the precipitation over the entire sampling period occurred as snow; therefore, each sample is assumed to represent a composite of snow that was deposited between collection periods.

3.2 | Surface water sampling

Surface water was sampled in SCB and MVGB to determine the contribution of new snowmelt being discharged from the basins. In SCB, Sagehen Creek was sampled approximately every other month from February 2010 to August 2011. On August 28, 2010, six locations along a 5-km reach of lower Sagehen Creek (Figure 2a) were sampled to determine spatial changes in groundwater inflow. For each SCB surface water sampling event, a submersible pump was used to field filter approximately 20 L of water through a 0.45-micron high-capacity filter. For the MVGB study, surface water from 11 locations including ML, DC, TR, and eight locations along several tributaries that discharge into ML (MC01, MC05–MC08, WMC02, MMC03, and MMC04; Figure 2b) was collected periodically in 2012 by submerging and filling

five gallon polyethylene containers. Approximately 20 L of water was collected for each event, and samples were field filtered through a 0.45-micron high-capacity filter.

3.3 | Groundwater sampling

A perennial spring in SCB (Figure 2a) was sampled four times from 2010 to 2011 to provide a snapshot of $^{35}\text{SO}_4^{2-}$ activity in SCB groundwater. The spring was sampled at less frequent intervals compared to Sagehen Creek due to limited access and the difficulty of sampling. In MVGB, 12 production and irrigation wells (wells A to I, K, N, and O) and one cistern (J; Figure 2b) were periodically sampled from January to September 2012. Production and irrigation wells were equipped with a sampling spigot and a submersible pump was used to collect groundwater from the cistern. Three perennial springs in MVGB (springs X, Y, and Z) were sampled on October 29, 2012, using a submersible pump. Similar to surface water sampling, 20 L of water was collected for each spring and groundwater sample. Prior to analysis, all samples were filtered through a 0.45-micron high-capacity filter.

3.4 | Laboratory analysis

Recovery of $^{35}\text{SO}_4^{2-}$ was achieved using a batch method technique summarized in Urióstegui et al. (2015). Because natural concentrations of SO_4^{2-} are low in Sierran surface waters and groundwater, a carrier (100 mg of ^{35}S -free SO_4^{2-} added as dissolved Na_2SO_4) was added to ensure effective recovery of SO_4^{2-} in the sample. Samples were then acidified to pH 3–4 using 5 M HCl, and Amberlite ion exchange resin was added and suspended in each sample for 2 hr, allowing $^{35}\text{SO}_4^{2-}$ to bind to the resin. The resin was collected, and $^{35}\text{SO}_4^{2-}$ was eluted off the resin with a 5% NaCl solution. A $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution was added in excess to form a $\text{Ba}^{35}\text{SO}_4^{2-}$ precipitate, which was subsequently rinsed with deionized water and suspended in a liquid scintillation gel. Samples were analyzed on an ultra low-level liquid scintillation spectrometer at the Lawrence Livermore National Laboratory in Livermore, CA. $^{35}\text{SO}_4^{2-}$ activities are reported in millibecquerel per liter. The minimal detectable activity ranged from 0.3 to 2.8 mBq/L because of variations in counting efficiencies, background count rates, and sample volumes. One sigma counting errors were typically less than 0.3 mBq/L.

Reproducibility of the measurements was evaluated through comparison of field duplicates using the relative error ratio (RER), with RER values at or below 3.0 being considered reproducible. RER is determined by

$$\text{RER} = \left| \frac{S-D}{\sqrt{\sigma_S^2 + \sigma_D^2}} \right|, \quad (1)$$

where S is the sample $^{35}\text{SO}_4^{2-}$ activity (mBq/L); D is the field duplicate $^{35}\text{SO}_4^{2-}$ activity (mBq/L); and σ_S^2 and σ_D^2 are one sigma counting errors for the sample and field duplicate (mBq/L), respectively.

Concentrations of SO_4^{2-} , as well as other anions, were determined in the samples collected from February 2010 to July 2012 by ion chromatograph on a Dionex model DX500 at BC Laboratories, Inc. in Bakersfield, CA. Surface water and groundwater samples collected from September 2012 to October 2012 were analyzed at the

Lawrence Livermore National Laboratory in Livermore, CA, using a Metrohm Model 881 ion chromatograph.

3.5 | Quantification of new snowmelt contribution

In snow-dominated Sierra Nevada midelevation basins such as SCB and MVGB, the majority of precipitation falls as snow during the winter and completely melts by midsummer. Snowmelt in the Western Mountains is a more efficient recharging mechanism than rain, even when snow constitutes a relatively small portion of the total precipitation (Earman et al., 2006). When groundwater is mainly derived from annual snowmelt, new snowmelt containing $^{35}\text{SO}_4^{2-}$ can be treated as an annual pulse input to the groundwater basin. Determining the activity of ^{35}S in this pulse is not straight forward, and the timing of the pulse is a source of uncertainty in the estimation of the ^{35}S activity in the snow end member. The half life of ^{35}S (87.4 days) is sufficiently short that significant decay will occur over the course of a snow season. Melting and recharging snow (as well as samples of accumulated snow) will contain both recent snow with high ^{35}S activity and old snow with lower ^{35}S activity. Furthermore, $^{35}\text{SO}_4^{2-}$ activity of fresh snow changes from one snowfall event to another over the season as demonstrated by the MVGB snow composites (see below).

The bulk input of snow $^{35}\text{SO}_4^{2-}$ activity to the SCB groundwater and surface water was assumed to initiate at the onset of snowmelt (t_0), which was defined as the day after peak snow water equivalence (April 7, 2010, for winter 2009–2010 and April 2, 2011, for winter 2010–2011). Because of data gaps at the SCB weather station during the study period, complementary meteorological data was obtained from SNOTEL #539 located in an adjacent basin to the north of SCB (Figure 2a). This SNOTEL station is located at 2,135 m, which is approximately the mean elevation of SCB.

The percent of new snowmelt (PNS) in SCB groundwater and surface water was determined by

$$\text{PNS}_t = \frac{A_{\text{GW,SW}}}{A_{\text{SNOW}}} * 100, \quad (2)$$

where PNS_t is the PNS in percent in groundwater (GW) or surface water (SW) on collection date t ; $A_{\text{GW,SW}}$ is the groundwater or surface water $^{35}\text{SO}_4^{2-}$ activity (mBq/L) on collection date t , with the mean activity reported for field duplicates; and A_{SNOW} is the mean snow $^{35}\text{SO}_4^{2-}$ activity (mBq/L) on t_0 decay corrected to date t . For SCB, A_{SNOW} on t_0 (April 7, 2010) for winter 2009–2010 was assumed to be the average $^{35}\text{SO}_4^{2-}$ activity for the February 13, 2010, full depth

snow composites; in winter 2010–2011, A_{SNOW} on t_0 (April 2, 2011) was the average $^{35}\text{SO}_4^{2-}$ activity for the March 5, 2011, full depth snow composites.

Although groundwater and surface waters in SCB is primarily derived from winter snowpack, runoff and shallow subsurface flow from precipitation or melt events that occur outside of the primary snowmelt period of spring to early summer may increase the $^{35}\text{SO}_4^{2-}$ activity in surface water, particularly during baseflow conditions. The PNS for surface waters and groundwater collected from t_0 through September 31st (WY day 365) assumes an A_{SNOW} $^{35}\text{SO}_4^{2-}$ activity of t_0 decay corrected to the collection date t ; however, waters collected from October 1st (WY day 1) to t_0 of the following winter are not decay corrected because precipitation and short melt events during this low-flow period could increase the $^{35}\text{SO}_4^{2-}$ activity leading to an overestimation of the PNS in surface waters and shallow groundwater.

This study was expanded to MVGB in 2012 with higher frequency snow sampling in winter 2011–2012 allowing for greater confidence in the snow end member $^{35}\text{SO}_4^{2-}$ activity. Mean $^{35}\text{SO}_4^{2-}$ activity was determined using a depth-weighted approach in which snow $^{35}\text{SO}_4^{2-}$ activity at four snow sampling locations is expressed as

$$S_t = \frac{\sum_{i=1}^4 a_i P_i}{P_{\text{Total}}}, \quad (3)$$

where S_t is the depth-weighted mean snow $^{35}\text{SO}_4^{2-}$ activity (mBq/L) for a given site decay corrected to groundwater or surface water collection date t ; a is the snow $^{35}\text{SO}_4^{2-}$ activity (mBq/L) for the snow sampling event $i = 1-4$ decay corrected to date t ; and P is the precipitation amount (m) deposited between snow sampling events (Table 1). For example, $P_{i=2}$ represents the total precipitation that fell between time $i = 1$ (January 25, 2012) and $i = 2$ (February 24, 2012). MVGB daily precipitation data from SNOTEL #834 near MVGB site S11 (Figure 2b) were assumed for all four snow sampling locations.

The depth-weighted mean snow activity for the entire basin was determined by

$$A_{\text{SNOW}} = \frac{\sum_{i=1}^4 S_i}{S_{\text{Total}}}, \quad (4)$$

where A_{SNOW} is the decay-corrected mean snow $^{35}\text{SO}_4^{2-}$ activity (mBq/L) for snow sampling sites $n = 1$ to 4. Similar to SCB, the PNS in MVGB groundwater or surface water was calculated using Equation 2.

TABLE 1 MVGB precipitation from SNOTEL #834

Sample	Collection date	Sampling period	Precipitation (m)	Amount of total precipitation (%) ^a
P1	Jan. 25, 2012	Nov. 5–Jan. 25	0.16	33
P2	Feb. 24, 2012	Jan. 26–Feb. 24	0.02	4
P3	Apr. 4, 2012	Feb. 25–Apr. 4	0.25	51
P4	May 2, 2012	Apr. 5–May 2	0.06	13
P Total			0.49	

Note. MVGB = Martis Valley Groundwater Basin. The precipitation amount that fell during the sampling period represents 77% of the total precipitation during water year 2012.

^aAmount of total precipitation that fell during sampling period (Nov. 5, 2012–May 2, 2012).

4 | RESULTS AND DISCUSSION

4.1 | Snowpack end member

Concentrations of SO_4^{2-} in SCB snowpack were consistently ≤ 0.5 mg/L, which is typical of precipitation measurements in the Sierra Nevada (e.g., Williams & Melack, 1991, 1997; Williams et al., 1993; Chorover et al., 1994; Meixner et al., 1998). MVGB snow composites also had generally low SO_4^{2-} concentrations of <0.3 mg/L in January and February 2012; higher concentrations in May 2012 may be due to less solute dilution resulting from a decrease in storm size (Williams & Melack, 1997).

The $^{35}\text{SO}_4^{2-}$ activity of SCB snowpack ranged from 5.5 ± 0.3 to 12.4 ± 0.3 mBq/L (Table 2), with an average activity of 8.3 ± 0.1 and 7.4 ± 0.2 mBq/L for winters 2009–2010 and 2010–2011, respectively. The SCB snowpack $^{35}\text{SO}_4^{2-}$ activity is similar to values reported for

TABLE 2 Sulfate concentrations and average $^{35}\text{SO}_4^{2-}$ activity with one sigma counting uncertainties for SCB (Sites S01–S08) and MVGB (Sites S09–S12) winter snowpack

SCB site ID	Collection date	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-} \pm 1\sigma$ (mBq/L)
S01	Feb. 13, 2010	0.5	9.0 ± 0.3
S02	Feb. 13, 2010	0.3	9.3 ± 0.3
S02	Feb. 13, 2010	0.3	12.4 ± 0.3
S03	Feb. 13, 2010	0.3	5.9 ± 0.3
S03	Feb. 13, 2010	0.3	7.8 ± 0.3
S04	Feb. 13, 2010	0.3	5.5 ± 0.3
S05	Jan. 9, 2011	<0.1	8.2 ± 0.6
S05	Jan. 9, 2011	<0.1	6.8 ± 0.6
S06	Mar. 5, 2011	0.2	5.9 ± 0.4
S06	Mar. 5, 2011	0.2	10.0 ± 0.5
S07	Mar. 5, 2011	0.2	10.4 ± 0.5
S04	Mar. 5, 2011	0.2	5.9 ± 0.4
S04	Mar. 5, 2011	0.2	6.5 ± 0.4
S08	Mar. 5, 2011	0.2	6.7 ± 0.4
S08	Mar. 5, 2011	0.2	6.1 ± 0.4
MVGB site ID	Collection date	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-} \pm 1\sigma$ (mBq/L)
S09	Jan. 25, 2012	0.2	10.2 ± 0.3
S10	Jan. 25, 2012	0.3	12.6 ± 0.3
S11	Jan. 25, 2012	0.2	10.5 ± 0.3
S09	Feb. 24, 2012	<0.1	11.0 ± 0.7
S10	Feb. 24, 2012	<0.1	1.1 ± 0.5
S11	Feb. 24, 2012	<0.1	2.8 ± 0.5
S12	Feb. 24, 2012	3.3	15.1 ± 0.6
S09	Apr. 4, 2012	3.1	17.7 ± 0.6
S10	Apr. 4, 2012	<0.1	26.9 ± 0.7
S11	Apr. 4, 2012	<0.1	11.9 ± 0.5
S12	Apr. 4, 2012	4.1	25.4 ± 0.6
S09	May 2, 2012	9.2	34.0 ± 0.8
S10	May 2, 2012	3.2	41.9 ± 1.2
S11	May 2, 2012	1.4	30.9 ± 1.2
S12	May 2, 2012	5.1	52.9 ± 3.4

Note. SCB = Sagehen Creek Basin; MVGB = Martis Valley Groundwater Basin.

snowpack in high-elevation basins in the Rocky Mountains 13.1 ± 0.5 – 25.0 ± 1.7 mBq/L (Sueker et al., 1999; Michel et al., 2000; Michel et al., 2002). The $^{35}\text{SO}_4^{2-}$ activity for the higher frequency MVGB snow composites varied between 1.1 ± 0.5 and 52.9 ± 3.4 mBq/L, with the May 2, 2012, sampling event having the highest activity. Increasing MVGB snow $^{35}\text{SO}_4^{2-}$ activity from the winter to the late spring (Figure 4) may be due to stratosphere-to-troposphere exchange during the spring and summer, which increases the depositional flux of cosmogenic $^{35}\text{SO}_4^{2-}$. Warming of air masses during the spring and summer months results in convective heating and downward transfer of aerosols into the troposphere, with peak stratosphere-to-troposphere exchange of cosmogenic radionuclides such as beryllium-7 occurring in the spring and summer at middle latitudes, especially at high elevations (Brost et al., 1991; Feely et al., 1989).

4.2 | SCB: new snowmelt contribution in surface water and groundwater

Time series measurements of $^{35}\text{SO}_4^{2-}$ activities in Sagehen Creek collected from SCB site SC02 were between 0.0 ± 0.1 and 1.5 ± 0.9 mBq/L, with the exception of one sample collected on August 24, 2010, and one collected on August 7, 2011, that did not have detectable $^{35}\text{SO}_4^{2-}$ activity (Tables 3 and 4). RER values of 0.0–2.2 indicate good reproducibility between sample duplicates. Calculated PNS values ranged from $0.2 \pm 6.6\%$ to $14.0 \pm 3.4\%$, with the errors being the propagated one sigma counting error. For WY 2010, the highest PNS was observed soon after the onset of snowmelt, with PNS increasing from $4.1 \pm 1.6\%$ to $14.0 \pm 3.4\%$ from February to April 2010 in response to snowmelt recession (Table 3, Figure 5). Although stream discharge continued to increase in May 2010, PNS decreased to $4.8 \pm 2.7\%$. As streamflow receded in late spring and early summer, PNS in streamflow was consistently $<15\%$, with no significant difference observed between the high-flow conditions of May 2010 ($4.8 \pm 2.7\%$) and baseflow conditions in August 2010 ($8.4 \pm 4.0\%$). These results suggest that although new meltwater is discharging into the stream via overland flow and/or shallow subsurface flowpaths

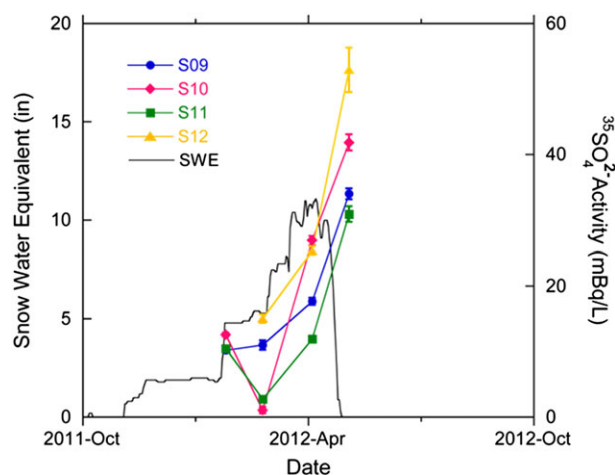


FIGURE 4 $^{35}\text{SO}_4^{2-}$ activities for MVGB snow collected during winter 2011–2012 (January 25, February 24, April 4, and May 5). Error bars represent one sigma counting uncertainties. SWE = snow water equivalent

TABLE 3 Sulfate concentrations, $^{35}\text{SO}_4^{2-}$ activity, and the percent of new snowmelt (PNS) for SCB surface water collected from site SC02 and groundwater collected from Spring #11

Date Collected	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-}$ (mBq/L)	Duplicate $^{35}\text{SO}_4^{2-}$ (mBq/L)	RER	Reported $^{35}\text{SO}_4^{2-}$ (mBq/L)	Snow $^{35}\text{SO}_4^{2-}$ (mBq/L) ^a	PNS (%)
Surface water WY 2010							
Feb. 13, 2010	1.2	0.4 ± 0.2	0.3 ± 0.2	0.3	0.3 ± 0.1	8.3 ± 0.1	4.1 ± 1.6
Apr. 25, 2010	0.3	0.5 ± 0.2	1.5 ± 0.4	0.7	1.0 ± 0.2	7.2 ± 0.1	14.0 ± 3.4
May 23, 2010	0.3	0.3 ± 0.2	NA	-	0.3 ± 0.2	5.8 ± 0.1	4.8 ± 2.7
May 27, 2010	0.3	0.3 ± 0.1	NA	-	0.3 ± 0.1	5.6 ± 0.1	5.1 ± 2.5
Jun. 27, 2010	NA	0.3 ± 0.2	NA	-	0.3 ± 0.2	4.4 ± 0.1	7.5 ± 3.9
Jul. 30, 2010	NA	0.4 ± 0.1	NA	-	0.4 ± 0.1	3.4 ± 0.1	10.9 ± 4.1
Aug. 24, 2010	0.2	ND ^b	0.2 ± 0.1	-	0.2 ± 0.1	2.8 ± 0.0	8.4 ± 4.0
Surface water WY 2011							
Nov. 6, 2010	<0.1	0.6 ± 0.1	0.9 ± 0.1	2.1	0.8 ± 0.1	8.3 ± 0.1	9.1 ± 1.1
Dec. 12, 2010	<0.1	0.6 ± 0.1	0.6 ± 0.1	0.0	0.6 ± 0.1	8.3 ± 0.1	6.9 ± 0.9
Mar. 5, 2011	0.2	0.8 ± 0.3	1.4 ± 0.3	1.4	1.1 ± 0.2	8.3 ± 0.1	12.9 ± 3.0
Apr. 22, 2011	0.3	1.2 ± 0.3	0.4 ± 0.2	2.2	0.8 ± 0.3	6.3 ± 0.1	12.3 ± 4.2
Jun. 8, 2011	0.3	0.2 ± 0.2	0.8 ± 0.2	2.1	0.5 ± 0.2	4.3 ± 0.1	10.8 ± 5.5
Jul. 22, 2011	0.2	0.0 ± 0.1	0.2 ± 0.1	1.4	0.1 ± 0.2	3.1 ± 0.1	3.5 ± 5.3
Aug. 7, 2011	<0.1	ND ^b	0.0 ± 0.2	-	0.0 ± 0.2	2.7 ± 0.1	0.2 ± 6.6
Spring #11							
Aug. 24, 2010	<0.1	0.3 ± 0.1	0.0 ± 0.1	2.1	0.2 ± 0.3	2.8 ± 0.0	6.2 ± 9.9
Mar. 6, 2011	0.2	0.1 ± 0.3	ND ^b	-	0.1 ± 0.3	8.3 ± 0.1	0.8 ± 3.5
Jun. 8, 2011	0.3	ND ^b	0.2 ± 0.2	-	0.2 ± 0.2	4.3 ± 0.1	5.7 ± 3.9

Note. SCB = Sagehen Creek Basin; NA = Not Available; ND = Not Detectable; RER = Relative Error Ratio. When field duplicates were collected and analyzed, the mean activity of the two measurements is reported and used to calculate PNS. Uncertainties represent propagated \pm one sigma counting errors.

^aAverage decay-corrected snow $^{35}\text{SO}_4^{2-}$ activity for the given sample collection date.

^bSample not incorporated into the reported $^{35}\text{SO}_4^{2-}$ activity or calculated PNS.

TABLE 4 Sulfate concentrations, $^{35}\text{SO}_4^{2-}$ activity, and the PNS for surface water collected on August 28, 2010, from six sites along a 5-km reach Sagehen Creek

Site ID	Distance downstream (km)	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-}$ (mBq/L)	Duplicate $^{35}\text{SO}_4^{2-}$ (mBq/L)	RER	Reported $^{35}\text{SO}_4^{2-}$ (mBq/L)	PNS (%)
SC01	4.8	0.2	0.4 ± 0.2	0.0 ± 0.1	1.8	0.2 ± 0.3	7.3 ± 11.5
SC02	3.8	0.2	0.2 ± 0.1	0.4 ± 0.1	1.4	0.3 ± 0.1	12.4 ± 4.1
SC03	3.0	0.2	0.1 ± 0.2	0.1 ± 0.1	0.0	0.1 ± 0.1	4.9 ± 3.9
SC04	2.1	0.4	0.1 ± 0.1	NA	-	0.1 ± 0.1	4.0 ± 4.8
SC05	1.2	<0.1	0.2 ± 0.1	0.0 ± 0.1	1.4	0.1 ± 0.3	4.8 ± 12.4
SC06	0	<0.1	0.3 ± 0.2	0.2 ± 0.1	0.4	0.2 ± 0.1	8.3 ± 4.4

Note. PNS = Percent of new snowmelt; NA = Not Available; RER = Relative Error Ratio. Site SC01 is located furthest downstream whereas site SC06 is furthest upstream. The average decay-corrected snow end member activity on August 28, 2010, was 2.8 ± 0.0 mBq/L. Uncertainties represent propagated \pm 1 σ counting errors.

during both high-flow and baseflow conditions, streamflow is primarily derived from groundwater recharged during previous winters.

To determine spatial variability of new snowmelt contribution to streamflow along Sagehen Creek, we sampled six sites along a 5-km reach on August 28, 2010 (Figure 2a). The average $^{35}\text{SO}_4^{2-}$ activity for the six sites (0.1 ± 0.1–0.3 ± 0.1 mBq/L) was not significantly different during this baseflow period, with PNS being <15% (Table 4). The low PNS throughout the reach is consistent with estimated groundwater input to streamflow using a numerical model based on $\delta^{18}\text{O}$ and CFC-12 concentrations for samples collected on August 28, 2010, at the same six sites (Earman et al., 2015). The lowest PNS calculated in

this study was observed at Site SC04, which is located about 2 km downstream in the transect and is the site with the highest modeled groundwater input based on $\delta^{18}\text{O}$ and CFC-12 concentrations. Although the calculated groundwater inflows varied significantly through the reach, total groundwater input was 76% of the total flow, with the remaining 24% being derived from recent precipitation (Earman et al., 2015).

Similar trends of consistently low PNS in Sagehen Creek was observed throughout WY 2011, despite total precipitation increasing from 0.67 to 1.22 m (82% increase) and peak snow water equivalence increasing from 0.47 to 0.89 m (53% increase) from WY 2010 to WY 2011. Prior to the onset of snowmelt in WY 2011, the average

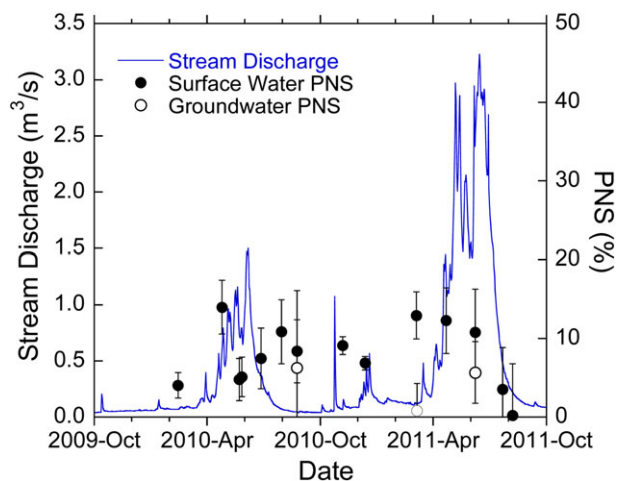


FIGURE 5 Sagehen Creek stream discharge and time series measurements of percent new snowmelt (PNS) in Sagehen Creek and Sagehen Creek Basin groundwater measured from Spring #11. Error bars represent propagated \pm one sigma counting errors. Stream discharge data from US Geological Survey National Water Information System

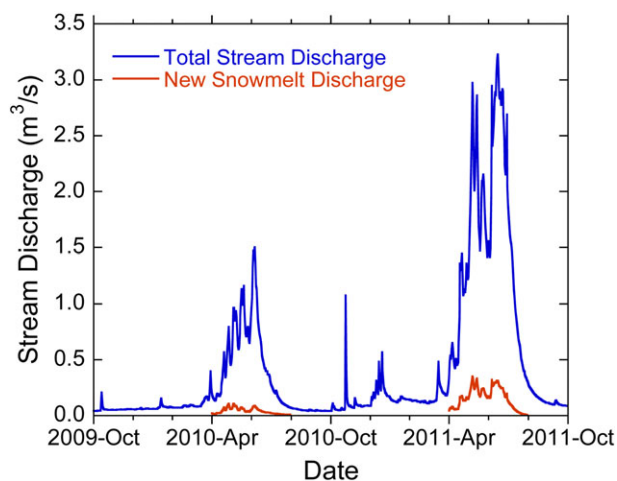


FIGURE 6 Hydrograph separation of Sagehen Creek discharge derived from new snowmelt during the primary discharge period of April, May, June, and July. The orange line represents the contribution of new snowmelt to the total stream discharge based on the calculated PNS

TABLE 5 Summary of Sagehen Creek discharge derived from new snowmelt for the primary snowmelt period of April, May, June, and July (AMJJ) and estimated change in groundwater storage

Water year	Total annual precipitation		AMJJ total discharge (m^3)	AMJJ new snowmelt	
	(m)	(m^3) ^a		Discharge (m^3)	% of total discharge
2010	0.7	1.8×10^7	5.4×10^6	$4.3 \times 10^5 \pm 0.2 \times 10^5$	8.0 ± 0.3
2011	1.2	3.3×10^7	16.5×10^6	$16.3 \times 10^5 \pm 0.9 \times 10^5$	9.9 ± 0.5
	Markstrom et al. (2008)			Tague and Peng (2013)	
Water year	Groundwater recharge (m^3) ^b	Change in storage (m) ^c	Groundwater recharge (m^3) ^b	Change in storage (m) ^c	
2010	1.2×10^5	0	3.9×10^6	1.0–1.8	
2011	1.4×10^7	3.4–6.3	1.4×10^7	3.4–6.3	

^aBased on Sagehen Creek Basin drainage area of 27 km².

^bGroundwater recharge is determined by $R = T_p - S_{AMJJ} - ET$; where R is groundwater recharge, T_p is total annual precipitation, S_{AMJJ} is the new snowmelt discharged from the basin in AMJJ, and ET is the annual evapotranspiration. Markstrom et al. (2008) report an average daily ET for SCB of 1.8 mm/day, whereas Tague and Peng (2013) estimate ET to be 1.4 mm/day for WY 2010 and 1.8 mm/day for WY 2011.

^cChange in storage is the equivalent change in groundwater head based on the calculated annual groundwater recharge assuming an specific yield of 0.08–0.15 (Markstrom et al., 2008).

$^{35}\text{SO}_4^{2-}$ activity for streamflow in March 2011 was 1.1 ± 0.2 mBq/L resulting in $12.9 \pm 3.0\%$ PNS (Table 3, Figure 5). The June 8, 2011, sampling event during the peak flow period was collected within one week of the peak discharge for WY 2011 ($3.23 \text{ m}^3/\text{s}$ on June 15, 2011), and PNS for this sampling event was $10.8 \pm 5.5\%$. During streamflow recession in July and August 2011, $^{35}\text{SO}_4^{2-}$ activities declined, and PNS values were $3.5 \pm 5.3\%$ and $0.2 \pm 6.6\%$, respectively (Table 3). Minimal interannual variability of PNS in stream discharge suggests that even during a year with significantly above average precipitation, such as the 50% above average precipitation in WY 2011, Sagehen Creek stream discharge is dominated by deeper groundwater flowpaths that were recharged in previous winters.

In contrast to hydrologic model predicting that groundwater discharge to streams is inversely correlated to streamflow due to snowmelt runoff, interflow filling stream channels, and elevating stream head (Huntington & Niswonger, 2012), the trend of decreasing PNS during high flow suggests that groundwater discharge was not suppressed during the high-flow period of WY 2010 or WY 2011 and that overland flow and shallow subsurface flow was minimal relative to significant melt water storage and displacement of groundwater derived from previous winters.

Using the times series measurements of $^{35}\text{SO}_4^{2-}$ activity and calculated PNS during the high-flow period, a hydrograph separation provides an estimate of the volumetric contribution of new snowmelt to stream discharge and groundwater recharge. The high-flow period of April to July (AMJJ) represents 79% of the total annual discharge from Sagehen Creek for WY 2010 and 84% of the total discharge for WY 2011, with the larger snowpack in WY 2011 resulting in approximately three times the AMJJ discharge ($16.5 \times 10^6 \text{ m}^3$) compared to WY 2010 ($5.4 \times 10^6 \text{ m}^3$; Figure 6, Table 5). During AMJJ, new snowmelt (as defined by PNS calculated from $^{35}\text{SO}_4^{2-}$ activities) contributes $8.0 \pm 0.3\%$ of total stream discharge in WY 2010 and $9.9 \pm 0.5\%$ in WY 2011. The difference between total annual precipitation and total stream discharge during AMJJ represents groundwater recharge, evapotranspiration (ET), and runoff outside of the AMJJ season.

TABLE 6 Summary of well elevation and screen depth for MVGB wells.

Well ID	Well type	Elevation (m asl)	Top (m bgs)	Bottom (m bgs)
A	Production	1,753	82	274
B	Irrigation	1,796	76	274
C	Production	1,820	140	415
D	Production	1,783	85	338
E	Production	1,823	38	183
F	Production	1,791	27	122
G	Production	1,770	87	283
H	Production	1,796	30	313
I	Irrigation	1,797	15	61
J	Cistern	2,073	-	-
K	Production	1,783	66	244
N	Production	1,832	46	274
O	Production	1,830	43	274

Note. m bgs = meters below ground surface; m asl = meters above sea level; MVGB = Martis Valley Groundwater Basin.

TABLE 7 Sulfate concentrations, $^{35}\text{SO}_4^{2-}$ activity, and calculated PNS for MVGB groundwater surface water

Site ID	Date collected	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-}$ (mBq/L)	PNS (%)
Wells				
A	Jun. 19, 2012	6.6	1.2 ± 0.2	10.2 ± 2.2
B	Jun. 19, 2012	15	1.2 ± 0.2	10.7 ± 2.6
C	Jan. 19, 2012	0.5	1.3 ± 0.2	12.1 ± 2.7 ^d
C	Jun. 19, 2012	2.3	1.8 ± 0.2	15.2 ± 3.1
C	Sep. 5, 2012	2.8 ^a	ND	<9 ^b
D	Jan. 19, 2012	0.4	1.3 ± 0.2	11.4 ± 2.5 ^d
D	Jun. 19, 2012	1.5	1.7 ± 0.3	14.9 ± 3.2
D	05-sep-2012	1.4 ^a	ND	<11 ^b
E	Jan. 19, 2012	14	1.8 ± 0.2	16.6 ± 3.4 ^d
E	Jun. 19, 2012	14	1.0 ± 0.2	8.4 ± 2.2
F	Jun. 19, 2012	0.9	2.0 ± 0.3	17.3 ± 3.5
F	Sep. 5, 2012	1 ^a	ND	<11 ^b
G	Jan. 19, 2012	4	1.2 ± 0.2	11.0 ± 2.5 ^d
G	Jun. 19, 2012	3.9	1.7 ± 0.2	14.2 ± 2.7
G	Sep. 5, 2012	3.2 ^a	ND	<8 ^b
H	Dec. 20, 2011	3	1.5 ± 0.2	13.8 ± 3.1 ^d
H	Jun. 19, 2012	3.4	1.9 ± 0.2	16.3 ± 3.0
H	Sep. 5, 2012	5 ^a	ND	<11 ^b
I	Jun. 20, 2012	2.7	1.9 ± 0.2	16.3 ± 3.2
I	Sep. 5, 2012	2.4 ^a	0.7 ± 0.2	10.8 ± 3.7
J	Dec. 20, 2011	0.4	1.7 ± 0.3	15.1 ± 3.4 ^d
J	Jun. 20, 2012	<1	2.2 ± 0.3	19.2 ± 3.6
J	Sep. 6, 2012	0.6 ^a	ND	<8 ^b
K	Dec. 20, 2011	19	1.8 ± 0.3	15.9 ± 3.5 ^d
K	Jun. 20, 2012	15	1.5 ± 0.3	13.2 ± 3.4
N	Dec. 19, 2011	0.6	2.5 ± 0.3	22.5 ± 4.4 ^d
N	Jun. 20, 2012	0.9	3.2 ± 0.3	28.1 ± 5.2
N	Sep. 6, 2012	1.0 ^a	0.3 ± 0.3	5.0 ± 4.1

(Continues)

TABLE 7 (Continued)

Site ID	Date collected	SO_4^{2-} (mg/L)	$^{35}\text{SO}_4^{2-}$ (mBq/L)	PNS (%)
Wells				
O	Dec. 19, 2011	0.6	1.9 ± 0.3	17.2 ± 3.7 ^d
O	Jun. 20, 2012	1.1	2.2 ± 0.2	19.4 ± 3.5
O	Sep. 6, 2012	1.2 ^a	ND	<8 ^b
Springs				
X	Oct. 29, 2012	0.5	0.4 ± 0.2	2.8 ± 1.3 ^c
Y	Oct. 29, 2012	1.3	0.6 ± 0.3	3.7 ± 2.0 ^c
Z	Oct. 29, 2012	0.5	0.4 ± 0.2	2.5 ± 1.2 ^c
Surface water				
MC01	Jan. 25, 2012	6.6	2.4 ± 0.2	21.5 ± 4.1
MC01	Feb. 24, 2012	5.3	ND	<14 ^b
MC01	04-Apr-2012	3.5	1.6 ± 0.4	9.8 ± 3.3
MC01	02-may-2012	1.3	0.5 ± 0.3	2.8 ± 1.9
MC01	Jun. 21, 2012	1.0	1.8 ± 0.2	15.3 ± 3.1
WMC02	Jan. 19, 2012	1.2	1.6 ± 0.2	14.3 ± 2.9 ^d
MMC03	Feb. 24, 2012	6.8	0.6 ± 0.6	5.5 ± 6.1
MMC03	May 02, 2012	5.3	0.5 ± 0.3	3.2 ± 2.0
MMC03	Jul. 9, 2012	5.1	2.7 ± 0.4	27.6 ± 5.5
MMC04	Jul. 9, 2012	<1.0	0.9 ± 0.2	8.7 ± 2.7
MC05	Aug. 16, 2012	0.8 ^a	1.2 ± 0.2	16.7 ± 3.4
MC06	Jun. 21, 2012	0.8	2.0 ± 0.2	17.6 ± 3.3
MC07	Jul. 9, 2012	<1.0	0.9 ± 0.2	8.9 ± 2.5
MC08	Aug. 16, 2012	0.7 ^a	0.8 ± 0.2	10.3 ± 3.2
ML	Aug. 16, 2012	1.2 ^a	1.2 ± 0.3	16.5 ± 3.8
DC	Jun. 21, 2012	<1.0	2.5 ± 0.2	22.0 ± 3.9
DC	Jul. 9, 2012	1.2	0.9 ± 0.3	8.6 ± 2.9
TR	Dec. 20, 2011	1.4	2.2 ± 0.3	19.9 ± 4.3 ^d
TR	Jun. 21, 2012	1.2	2.4 ± 0.2	20.9 ± 3.7
TR	Jul. 9, 2012	1.8	0.9 ± 0.2	9.2 ± 2.8
TR	Aug. 16, 2012	1.5 ^a	1.1 ± 0.2	15.4 ± 2.9

Note. PNS = Percent of new snowmelt; MVGB = Martis Valley Groundwater Basin; ND = Not Detectable; ML = Martis Lake; DC = Donner Creek; TR = Truckee River. Errors are propagated $\pm 1\sigma$ counting errors.

^aSulfate concentration measured on Lawrence Livermore National Laboratory ion chromatograph.

^bReported PNS value is based on the minimal detectable activity (MDA) for samples that had $^{35}\text{SO}_4^{2-}$ activities at or below background. MDA values varied between 0.5 and 0.6 mBq/L because of variations in counting efficiencies.

^cCalculated PNS is based on the depth-weighted mean activity for MVGB snowpack decay corrected to the onset of snowmelt for WY 2012, April 8, 2012 (15.7 ± 3.2 mBq/L).

^dCalculated PNS is based on the average snowpack activity for January 25, 2012.

Based on the 27-km² area of SCB, SNOTEL #539 precipitation data, average daily ET of 1.4–1.8 mm/day (Markstrom et al., 2008; Tague & Peng, 2013), and the calculated new snowmelt discharged in streamflow during AMJJ, the annual precipitation recharged to the groundwater system was between 0% and 21% in WY 2010 and 41% in WY 2011. These recharge values should be interpreted as maximum values because new snowmelt was observed in stream discharge outside of the AMJJ period. Assuming a specific yield of 0.08–0.15 and ET rate of 1.8 mm/day for SCB (Markstrom et al., 2008), the equivalent

change in groundwater storage would be between 0 m for WY 2010 and 3.4–6.3 m for WY 2011 (Table 5). Based on the linear relationship between actual ET and precipitation in SCB reported in Tague and Peng (2013), ET rates were estimated to be 1.4 mm/day for WY 2010 and 1.8 mm/day for WY 2011, resulting in a change in groundwater storage of 1.0–1.8 m for WY 2010 and 3.4–6.3 m for WY 2011 (Table 5).

Groundwater discharge collected from Spring #11 provides further insight into storage of new snowmelt in the aquifer. The $^{35}\text{SO}_4^{2-}$ activity did not vary significantly between the three sampling events, which covered both baseflow and high-flow conditions. Based on $^{35}\text{SO}_4^{2-}$ activity of 0.1 ± 0.3 – 0.2 ± 0.3 mBq/L during low flow and 0.2 ± 0.2 mBq/L during high flow, the PNS in groundwater was between $0.8 \pm 3.5\%$ and $6.2 \pm 9.9\%$ (Table 3, Figure 5). The presence of new snowmelt in SCB groundwater is supported by a recent integrated groundwater tracer and modeling study, which concluded that groundwater discharge from springs is best characterized by a bimodal mixture of <1-year-old water and water recharged after 1950 (Manning et al., 2012).

The minimal PNS in both surface waters and groundwater throughout this study period indicates that there is substantial recharge of new snowmelt that is occurring in SCB on an annual basis and SCB has a relatively large groundwater storage capacity.

4.3 | MVGB: new snowmelt contribution in surface water and groundwater

In MVGB, tritium concentrations measured during WY 2012 from the same wells sampled in this study suggest a pervasive component of young recharge (<50 years old) in most groundwater samples collected in multiple seasons (Segal et al., 2014). The $^{35}\text{SO}_4^{2-}$ activity in groundwater collected from 12 wells screened at a wide range of flow depths (Figure 2B, Table 6), one cistern, and three springs provides a more complete understanding of new snowmelt contribution to groundwater recharge in MVGB basin.

For the December 2011 – January 2012 and June 2012 sampling events, all groundwater samples had measureable $^{35}\text{SO}_4^{2-}$ between 1.0 ± 0.2 mBq/L (well E, June 2012) and 3.2 ± 0.3 mBq/L (well N, June 2012) resulting in PNS ranging of $8.4 \pm 2.2\%$ and $28.1 \pm 5.2\%$, respectively (Table 7, Figure 7). These results indicate that there is a component of new snowmelt contributing to the groundwater system throughout the winter and spring seasons, which was also observed for groundwater sampled in SCB. The generally low PNS in both shallow and deep wells in June 2012 suggests that immediately following the primary snowmelt period of April to May, the majority of the groundwater (>60%) is derived from snowmelt that was recharged during previous winters.

In September 2012, only wells I and N had detectable $^{35}\text{SO}_4^{2-}$ activities (Table 7), with wells C, D, F, G, H, J, and O having $^{35}\text{SO}_4^{2-}$ activities at or below background levels. The largest activity of 0.7 ± 0.2 mBq/L was observed for well I, which is the shallowest well that is likely receiving a component of water from nearby DC. Segal et al. (2014) reported an anomalously high noble gas recharge temperature calculated for well I in September 2012, which the authors concluded was the result of mixing of local groundwater with water from

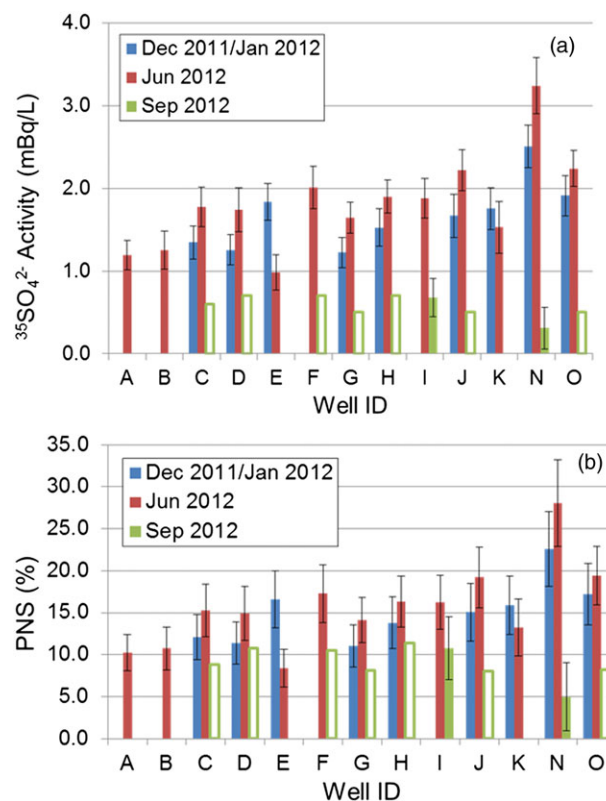


FIGURE 7 (a) $^{35}\text{SO}_4^{2-}$ activities for 12 Martis Valley Groundwater Basin wells and one cistern (well J) sampled in December 2011–January 2012, June 2012, and September 2012. Open bars for September 2012 represent minimal detectable activities for samples that are at or below detection limits. (b) Percent of new snowmelt (PNS) for groundwater sampled in December 2011–January 2012, June 2012, and September 2012. Error bars are propagated one sigma counting errors

DC during this period. Groundwater sampled from springs in October 2012 also had measurable $^{35}\text{SO}_4^{2-}$ activities, indicating that groundwater derived from new snowmelt is a component of the shallow aquifer system in the fall.

For the nine wells sampled in both June and September 2012, groundwater $^{35}\text{SO}_4^{2-}$ activity and subsequent PNS was significantly lower in September compared to June (Figure 7b). The apparent depletion of the new snowmelt fraction from spring to summer could be due to pumping from an age-stratified aquifer, natural discharge of new snowmelt via shallow flowpaths to streams and rivers, or mixing within the aquifer with groundwater derived from previous winters. Younger $^3\text{H}/^3\text{He}$ groundwater ages in June 2012 relative to September 2012 provide additional evidence for the depletion of a young groundwater component from spring to summer (Segal et al., 2014). Seasonal variability in the young (<50 years old) groundwater source (Segal et al., 2014) and a general shift to older $^3\text{H}/^3\text{He}$ groundwater ages from June to September may be due to a decrease in the component of new snowmelt component that was identified in this study. The unique data set of $^{35}\text{SO}_4^{2-}$ activity from various depths in the groundwater aquifer and MVGB surface waters provides insight into recharge and transport of new snowmelt in the basin.

Time series measurements of $^{35}\text{SO}_4^{2-}$ activity along Martis Creek, Middle Martis Creek, and West Martis Creek reveal a similar trend as

that observed in SCB with an inverse correlation between PNS and stream discharge. Daily stream discharge is not available for these streams; however, a U.S. Geological Survey stream gauge at nearby DC indicates that for WY 2012, peak flows in the basin occurred from April to May 2012, and baseflow conditions were established by early August 2012. For the most robustly sampled sites MC01 and MMC03, the $^{35}\text{SO}_4^{2-}$ activity in the stream was <6% during the high-flow period of May 2012 (Table 7; Figure 8a). PNS increased significantly as stream discharge declined in late June and August; however, PNS was consistently <30% for the multiple sampling events. Surface water samples collected from June to August 2012 from ML, DC, and TR also indicate minimal contribution of new snowmelt in surface water (PNS <26%; Figure 8b).

To investigate spatial variability of new snowmelt being discharged to the stream, we plotted PNS values versus the distance upstream from ML in Figure 8a. In July 2012, the PNS for site MMC03 was $27.6 \pm 5.5\%$, which was significantly higher than the PNS at sites MMC04 ($8.7 \pm 2.7\%$) and MC07 ($8.9 \pm 2.5\%$; Figure 8a). In August 2012, the PNS determined for the furthest upstream site, MC08, was $10.3 \pm 3.2\%$, which is similar to the PNS measured in July at sites MMC04 and MC07. A study using radon-222 (^{222}Rn) activity to identify groundwater influx into streams in MVGB found minimal groundwater contribution to streamflow for downstream sites MC01, WMC02, MMC03, and MMC04 in July 2012 (DeRubeis, 2013), with

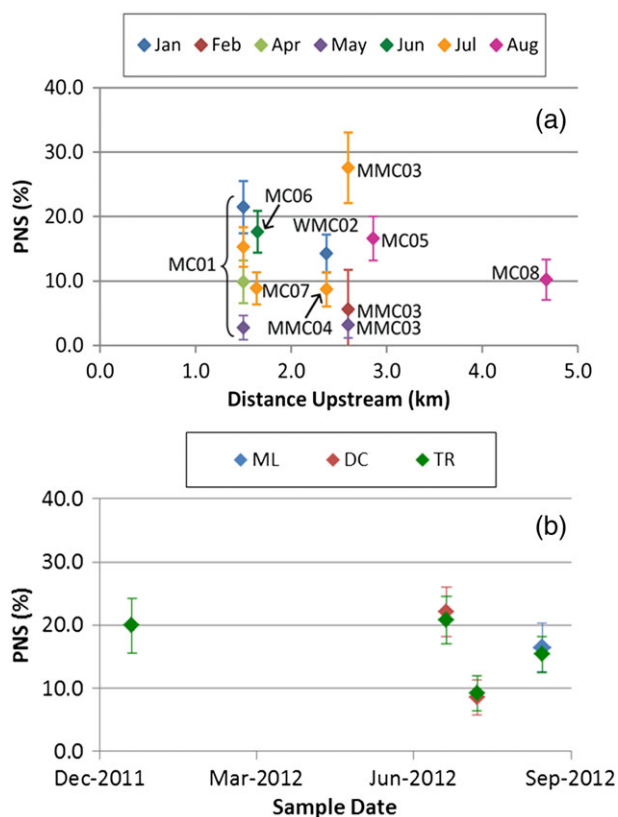


FIGURE 8 (a) Percent of new snowmelt (PNS) versus distance upstream from Martis Lake for surface water collected in WY 2012 from along Middle Martis Creek (MMC03 and MMC04) and Martis Creek (MC01 and MC05–MC08). (b) PNS for surface water sampled from Martis Lake (ML), Donner Creek (DC), and Truckee River (TR). Error bars represent propagated \pm one sigma counting errors

a secondary survey in August 2012 showing higher groundwater contribution at the MC08 upstream sampling site. Significantly higher PNS observed at site MMC03 also indicates that groundwater influx at this site is lower compared to site MC08. Although spatial variability in PNS is generally minimal along the 4-km reach, the significant increase over relatively short (<0.5 km) distances is useful in constraining groundwater discharge derived from old and new meltwater over a short study reach.

5 | SUMMARY AND CONCLUSIONS

$^{35}\text{SO}_4^{2-}$ is a useful environmental tracer that can answer questions regarding the recharge, storage, and transport of precipitation on <1-year timescales. In snow-dominated basins, the amount of snowmelt rapidly discharged from the basin during the primary snowmelt period provides insight into groundwater recharge and storage from seasonal snowmelt, which is useful for evaluating groundwater vulnerability to climate change and may lead to better surface or groundwater numerical models.

This study successfully utilized $^{35}\text{SO}_4^{2-}$ to quantify the PNS in groundwater and surface waters. The detection of $^{35}\text{SO}_4^{2-}$ reveals flow paths on annual timescales, which demonstrates the value of $^{35}\text{SO}_4^{2-}$ as a tracer tool. The calculated PNS values represent a minimum contribution of new snowmelt because the simplified model assumes no SO_4^{2-} attenuation during groundwater recharge or transport. A more accurate model could be developed with quantification of SO_4^{2-} -regulating mechanisms. Although sorption is expected to be minimal, biogeochemical processes in the subsurface may lower the ratio of ^{35}S activity to SO_4^{2-} concentration resulting in an artificially lower calculated PNS in groundwater and/or surface water.

A key finding was that despite large interannual variations in snowpack volume in SCB, new snowmelt had minimal direct contribution (PNS < 15%) to Sagehen Creek stream discharge. In both basins, the low PNS in surface flows (PNS < 30%) during the high-discharge period indicates that the majority of the seasonal snowmelt is either recharging the groundwater aquifer or being stored in the soil and lost via ET. Minimal PNS in groundwater sampled from springs or wells in both basins suggests that the groundwater reservoirs are relatively large in order to accommodate significant storage of annual snowmelt. Although significant annual recharge in MVGB is consistent with a large storage capacity that would be expected for a basin of this size, the significant annual recharge from snowmelt in the smaller SCB was not expected. The implications of these findings are the hydrogeologic system in SCB, and MVGB could respond to climate change in a two-phase manner: (a) rapid responses in stream and spring discharge because of annual variability in precipitation and (b) more gradual declines in discharge over decades because of reduced groundwater recharge resulting from declining snowpack. A test of this idea could be made now as a result of the prolonged drought that these basins are currently experiencing.

As precipitation patterns continue to shift in the Sierra Nevada, the underutilized $^{35}\text{SO}_4^{2-}$ tracer method will be a valuable tool for identifying how groundwater recharge processes may change under a

changing climate by identifying the storage and transport of new snowmelt on short (<1 year) timescales. In addition to providing information on the relative size and storage capacity of the groundwater reservoir of a given basin, $^{35}\text{SO}_4^{2-}$ may be a valuable scoping tool to identify which basins may be more vulnerable to the changing climate. Basins with shallow groundwater reservoirs are expected to have high contributions of new snowmelt in surface flows due to their limited storage capacities and therefore would likely be the most affected by climate change.

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APPENDIX

SULFATE MASS BALANCE FOR SAGEHEN CREEK BASIN

Previous studies in the southern Sierra Nevada reported terrestrial neutralization of acidity present in precipitation, with solute mass balances indicating that terrestrial processes uptake atmospherically derived N and S (Williams & Melack, 1997). To determine the potential extent of biogeochemical cycling of SO_4^{2-} in this region, we performed a simplified quantitative mass balance of SO_4^{2-} for Sagehen Creek Basin (SCB).

Monthly SO_4^{2-} concentrations in wet deposition were available beginning in Water Year (WY) 2002 from a National Atmospheric Deposition Program collection site CA 50 located near snow site S02 (see Figure 2a). Precipitation-weighted mean SO_4^{2-} concentrations for wet deposition varied between 0.01 and 1.59 mg/L, with a logarithmic curve being the best fit for the data (Figure A1). Although no correlation was observed between SO_4^{2-} concentration and total precipitation (Figure A2), the higher SO_4^{2-} concentrations (≥ 0.25 mg/L) occurred during months having monthly precipitation totals of < 20 cm, indicating a general dilution of SO_4^{2-} concentrations with increasing storm size.

Dry deposition has been identified as an important component of total S deposition in the Sierra Nevada and other high-elevation basins, supplying about 37% of the total S input (Williams & Melack, 1997; Likens et al., 1990). The average annual input of SO_4^{2-} derived from wet deposition was 1.86×10^2 kg, with the estimated bulk annual input of SO_4^{2-} being 2.55×10^2 kg when corrected for the contribution of dry deposition (Figure A3).

Sagehen Creek is the main tributary in SCB. Sulfate concentrations in Sagehen Creek water were measured by the US Geological Survey once or twice a month over a 9-year period (WY 2006–WY 2014) from a sampling location near the US Geological Survey stream gauge at the base of the basin (see Figure 2a). Stream SO_4^{2-} concentrations were between 0.03 and 0.30 mg/L (Figure A4), which is similar to the range of SO_4^{2-} concentrations for the majority of precipitation samples

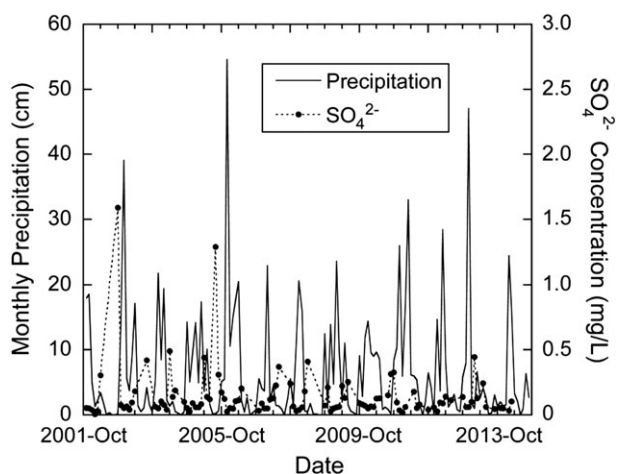


FIGURE A1 Monthly precipitation totals and depth-weighted mean SO_4^{2-} concentration in precipitation for Sagehen Creek Basin from WY 2002 to WY 2014. Data source: NADP

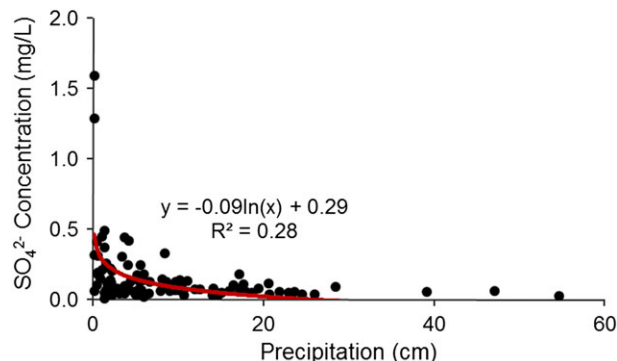


FIGURE A2 Precipitation-weighted mean SO_4^{2-} concentration versus precipitation totals

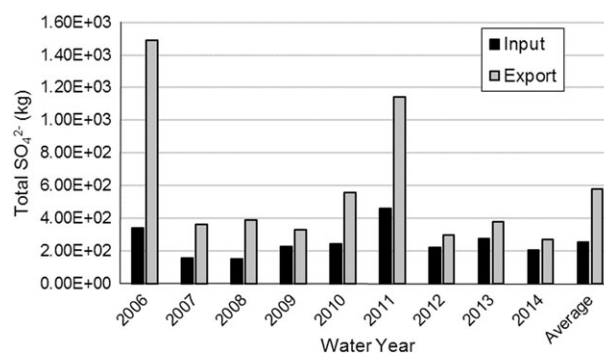


FIGURE A3 Annual input and export of SO_4^{2-} for WY 2006–2014. Input values are based on the bulk (wet + dry) deposition of SO_4^{2-}

collected during WY 2002–WY 2014. These results provide further evidence that minimum attenuation of SO_4^{2-} by adsorption-desorption is occurring in the basin and that weathering of SO_4^{2-} minerals is minimal. Monthly SO_4^{2-} concentrations were stable throughout the WY; however, small pulses of higher-concentration SO_4^{2-} water in the stream (≥ 0.2 mg/L) were observed during the early winter for WY 2009 and WY 2010, which may be due to solutes in snowpack becoming more concentrated during the melt season.

Average annual SO_4^{2-} output from the basin via Sagehen Creek was 5.80×10^2 kg (Figure A3), which suggests that more SO_4^{2-} is leaving SCB than is deposited on year-to-year basis. A possible explanation for the net export observed for WY 2006–WY 2014 is an increase in SO_4^{2-} deposition in previous decades that is not captured in the short, 12-year record examined in this simplified mass balance. For example, Heard et al. (2014) reported declining SO_4^{2-} concentrations in Sierra Nevada lakes beginning in the early 1980s, which the authors attributed to emission reductions and lower SO_4^{2-} loading resulting from air quality regulations. A record of SO_4^{2-} deposition from 1982 to 2015 at the central Sierra Nevada National Atmospheric Deposition Program site CA 99 located in Yosemite Valley also revealed generally higher SO_4^{2-} concentrations from 1982 to 2006 compared to 2007–2015 (Figure A5). In SCB, apparent groundwater ages of springs ranged from < 2 to 36 years (Rademacher et al., 2001; Manning et al., 2012), and the $^{35}\text{SO}_4^{2-}$ activities suggest that stream water is mainly derived from groundwater older than 1 year, indicating that groundwater flowpaths contributing to stream discharge may be derived from

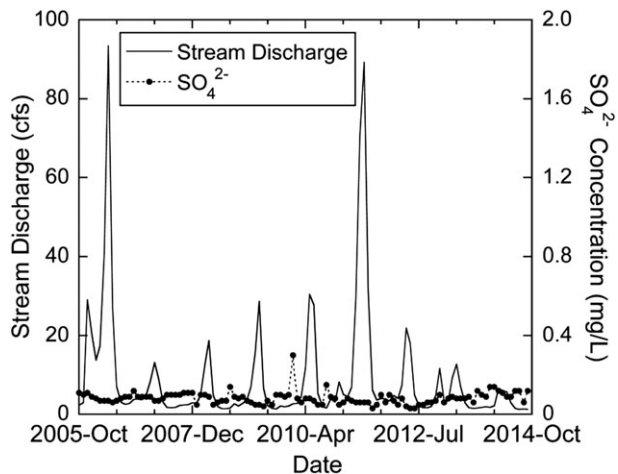


FIGURE A4 Time series of Sagehen Creek stream discharge and SO_4^{2-} concentration. Data source: US Geological Survey National Water Information System (http://waterdata.usgs.gov/ca/nwis/inventory/?site_no=10343500&agency_cd=USGS)

groundwater recharged prior to 2007. This older water with higher SO_4^{2-} loads could contribute to the overall net export of SO_4^{2-} from SCB.

In addition to net SO_4^{2-} export being potentially derived from SO_4^{2-} deposited in previous decades, organic matter mineralization may also contribute to the overall net export of SO_4^{2-} . Even after

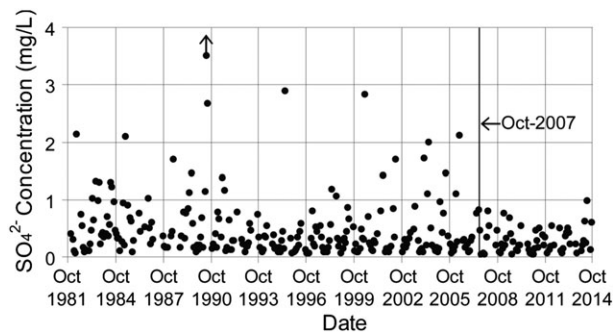


FIGURE A5 Monthly precipitation-weighted mean SO_4^{2-} concentration for NAPD site CA 99 in Yosemite Valley. The sample plotted with a vertical arrow is 14.1 mg/L. Data source: NADP (<http://nadp.sws.uiuc.edu/data/sites/siteDetails.aspx?net=NTN&id=CA99>).

correcting for dry deposition, the mean input due to deposition is less than 45% of the export by the creek indicating that there must be another source of SO_4^{2-} within SCB.

Although a net export of SO_4^{2-} may indicate minimal retention and immobilization of SO_4^{2-} , constraining the biogeochemical cycling of SO_4^{2-} requires additional data such as stable isotopic analysis of SO_4^{2-} ($^{34}\text{SO}_4^{2-}/^{32}\text{SO}_4^{2-}$). To accurately quantify the extent of SO_4^{2-} immobilization by microbial processes and vegetation, we find that stable isotopic composition of S in snowpack, groundwater, stream water, and vegetation would be valuable in future studies.