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The suitability of using dissolved gases to determine groundwater discharge to high gradient streams

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ABSTRACT

Determining groundwater discharge to streams using dissolved gases is known to be useful over a wide range of streamflow rates but the suitability of dissolved gas methods to determine discharge rates in high gradient mountain streams has not been sufficiently tested, even though headwater streams are critical as ecological habitats and water resources. The aim of this study is to test the suitability of using dissolved gases to determine groundwater discharge rates to high gradient streams by field experiments in a well-characterized, high gradient mountain stream and a literature review. At a reach scale (550 m) we combined stream and groundwater radon activity measurements with an in-stream SF_6 tracer test. By means of numerical modeling we determined gas exchange velocities and derived very low groundwater discharge rates (~15% of streamflow). These groundwater discharge rates are below the uncertainty range of physical streamflow measurements and consistent with temperature, specific conductance and streamflow measured at multiple locations along the reach. At a watershed-scale (4 km), we measured CFC-12 and $\delta^{18}O$ concentrations and determined gas exchange velocities and groundwater discharge rates with the same numerical model. The groundwater discharge rates along the 4 km stream reach were highly variable, but were consistent with the values derived in the detailed study reach. Additionally, we synthesized literature values of gas exchange velocities for different stream gradients which show an empirical relationship that will be valuable in planning future dissolved gas studies on streams with various gradients. In sum, we show that multiple dissolved gas tracers can be used to determine groundwater discharge to high gradient mountain streams from reach to watershed scales.

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1. Introduction

Dissolved (noble) gas tracers in water have proven useful for identifying and quantifying groundwater discharge to streams and rivers (e.g., Wanninkhof et al., 1990; Cook et al., 2003; Gleeson et al., 2009). Dissolved (noble) gas tracers have several potential advantages over other methods including: (1) they are less costly and can provide a more detailed spatial resolution than stream gaging; (2) they are potentially more accurate than seepage studies (flow metering) (e.g., Cey et al., 1997; Cook et al., 2003); (3) they are generally not affected by in-stream (bio-)geochemical processes like some other natural chemical tracers (e.g., ion concentrations and specific conductance); (4) they do not necessarily require labor-intensive injection tests like salt tracer dilution tests; and (5) they do not require numerical modeling of river heat budgets as do studies utilizing temperature as tracer (Evans et al., 1998; Frei and Gilfedder, 2015). However, few published studies have used dissolved gas tracer methods to examine groundwater inputs to high gradient (>0.01) mountain streams (Rogers, 1958; Genereux et al., 1993; Wu et al., 2003). A complicating factor is that quantifying groundwater discharge with dissolved gas tracers requires an independent estimation of the gas transfer velocity (k) between the stream and the ambient air (Demars et al., 2015). Especially in high gradient streams, exchange velocities for a given gas can vary over orders of magnitude, and velocities derived using theoretical and empirical models are generally unreliable (St. John et al., 1994; Genereux and Hemond, 1992). Raymond et al., (2012) state three general types of models which predict k adequately, however they also mention that these models are not able to predict k for high gradient mountain streams. Relatively few experimentally-derived gas exchange velocities for mountain streams can be found in the peer-reviewed literature

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(Wanninkhof et al., 1990; Genereux and Hemond, 1992; Choi et al., 1998; Maprani et al., 2005; Benson et al., 2014). Thus, the potential utility of dissolved gas tracers for examining groundwater inputs to mountain streams remains uncertain. It is possible that high turbulence may cause gas exchange velocities to be too high to preserve groundwater dissolved gas signals in the stream for any appreciable flow distance, rendering the method useless or impractical.

In this study, we use the environmental tracers radon (^{222}Rn), delta-oxygen-18 (δ^{18}O) and chlorofluorocarbon-12 (CFC-12) to determine rates of groundwater discharge to a high gradient mountain stream. Additionally, we use artificially-injected sulfur hexafluoride (SF_6) data from an in-stream tracer test conducted at the same time as our field work (Benson et al., 2014) to determine a gas exchange velocity for a portion of the stream. ^{222}Rn is a radioactive noble gas that has been used in multiple prior studies to identify groundwater discharging to surface water bodies (Rogers, 1958; Ellins et al., 1990; Genereux et al., 1993; Cook et al., 2006; Charette et al., 2008; Cook et al., 2008; Stellato et al., 2008). Radon accumulates in groundwater due to the radioactive decay of radium, which is a decay product of uranium in aquifer materials. The activities in groundwater are typically 1–2 orders of magnitude larger than in surface water bodies, where radon is lost due to air–water exchange and radioactive decay. CFC-12 is a stable anthropogenic gas whose atmospheric concentration increased rapidly from 1950 to 1990. Therefore, groundwater older than about 25 years will have CFC-12 concentrations substantially lower than water in equilibrium with the atmosphere. CFC-12 is commonly used for groundwater age dating (Plummer and Busenberg, 2000), but has also been successfully used to quantify groundwater inputs to streams (Cook et al., 2003). δ^{18}O is the stable isotope ratio of oxygen (^{18}O/^{16}O) and an ideal tracer since it is an integral part of the water molecule. Surface water is usually subjected to evaporation, and is thus enriched in ^{18}O (higher δ^{18}O value) compared to groundwater (Coplen et al., 2000). CFC-12 and δ^{18}O were chosen as tracers because previous work suggests that their groundwater signature is substantially different from that of modern precipitation and stream water in the study area (Rademacher et al., 2001, 2002). Further, δ^{18}O is a conservative non-gas tracer that is unaffected by the gas exchange rate, meaning that the use of δ^{18}O together with CFC-12 increases the likelihood of successfully constraining both the gas exchange velocity and groundwater inputs. SF_6 is a non-reactive gas that is not degraded or retarded in natural systems and is detectable at very low concentrations (Wanninkhof et al., 1990; Wilson and Mackay, 1996; Hibbs et al., 1998; Clark et al., 2004). Using dissolved gases and stable isotopes as tracers is complementary to other methods used to characterize groundwater-surface water interactions (Kalbus et al., 2006; Brunner et al., 2017). Thus, we corroborate dissolved gas results by also measuring streamflows and stream geometries, and by conducting an in-stream survey of temperature and specific conductance (Lee, 1985; Harvey et al., 1997; Constantz, 1998; Becker et al., 2004; Cox et al., 2007).

Mountain headwater streams provide critical habitats for many species and are essential water resources, particularly in arid and semi-arid regions. A growing number of studies suggest that groundwater with residence times of months to years is a significant contributor to flow in mountain streams in addition to recent precipitation (e.g., Uhlenbrook et al., 2002; Liu et al., 2004; Blumstock et al., 2015). Groundwater contributions are most important during seasonal or drought-related periods of low precipitation when groundwater supports low flows which are critical for sustaining in-stream and riparian ecosystems (Manning et al., 2012). For example, cold groundwater inputs to mountain streams during summer maintain important salmonid spawning habitats (McDaniels et al., 2010; Douglas, 2006) as well as mountain wetland systems (Loheide et al., 2009; Lowry et al., 2011). The importance of examining low flow conditions could increase due to changing low flow and groundwater conditions (Jefferson et al., 2008; Rood et al., 2008; Singleton and Moran, 2010). For these reasons it is important to gain an improved understanding of the distribution, magnitude, and controlling processes of groundwater discharge to mountain streams, especially during low flow conditions.

2. Study objective, design and location

The objective of this study is to test the suitability of using dissolved gases to determine groundwater discharge rates to high gradient streams by field experiments in a well-characterized, high gradient mountain stream in combination with a literature review. The first component of the study is an examination of a ~550 m reach ("detailed study") in which we derive a gas exchange velocity described by Benson et al. (2014) and groundwater discharge using data from the SF_6 injection test, ^{222}Rn activities, and stream geometry measurements, in conjunction with a steady-state numerical model. Model results are also corroborated with measurements of temperature, specific conductance and streamflow. Our approach of experimentally deriving a reliable gas exchange velocity improves upon that of most previous similar studies, which rely on theoretical gas exchange velocities or weakly supported assumptions regarding inputs between measurement sites (Rogers, 1958; Wu et al., 2003). The second component is a study of a ~4 km reach ("watershed-scale study") in which we determine groundwater discharge using CFC-12 and δ^{18}O, along with the same steady-state numerical model used in the detailed study. The watershed-scale study tests the suitability of using environmental (not injected) tracers alone to obtain reasonable estimates of groundwater inputs to mountain streams over broad areas. This possibility is further examined by presenting a literature compilation of experimentally-derived gas exchange coefficients for streams of varying gradients. For clarity we use the term 'low flow' rather than 'baseflow' (Smakhtin, 2001; Burn et al., 2008), 'discharge' refers to groundwater discharge whereas 'streamflow' refers to the rate of water flow in the stream, and for all results 'X ± Y' implies $\mu \pm 1\sigma$.

Sagehen Creek is a first-order perennial stream in the northeastern Sierra Nevada Mountains, ~20 km north of Truckee, California, U.S. (Fig. 1). The ~27 km^2 Sagehen basin is a long term experimental watershed managed by the University of California, Berkeley and has a history of hydrologic, ecologic, geologic and geomorphic research (Needham and Jones, 1959; Johnson and Needham, 1966; Allen-Diaz, 1991; Kondolf et al., 1991; Andrews, 1994; Ashman, 1994; Rademacher et al., 2003, 2005; Blumhagen and Clark, 2008; Brumm et al., 2009). Much of the recent hydrologic and geochemical research in the Sagehen basin has focused on springs, which occur throughout the watershed (Rademacher et al., 2003, 2005; Brumm et al., 2009; Manning et al., 2012). The geology of the studied section of Sagehen Creek is dominated by Quaternary alluvium and lacustrine terraces in a U-shaped valley with underlying andesite and basalt/andesite flows (Sylvester et al., 2008). The area has a Mediterranean-type climate with cold, wet winters and warm, dry summers (mean temperatures of −3.8 °C and 14.2 °C, respectively). Mean annual precipitation is 840 mm with snowfall accounting for >80% of annual precipitation. Sagehen Creek is thus snowmelt dominated, with mean monthly flows that range broadly from 0.07 m^3/s in September to 1.22 m^3/s in May, and a mean annual flow of 0.34 m^3/s. The chemical evolution of springs and the creek suggests that low flow conditions are dominated by moderately old groundwater (mean age of ~28 years) (Rademacher et al., 2005). Therefore, constraining the spatial dis-

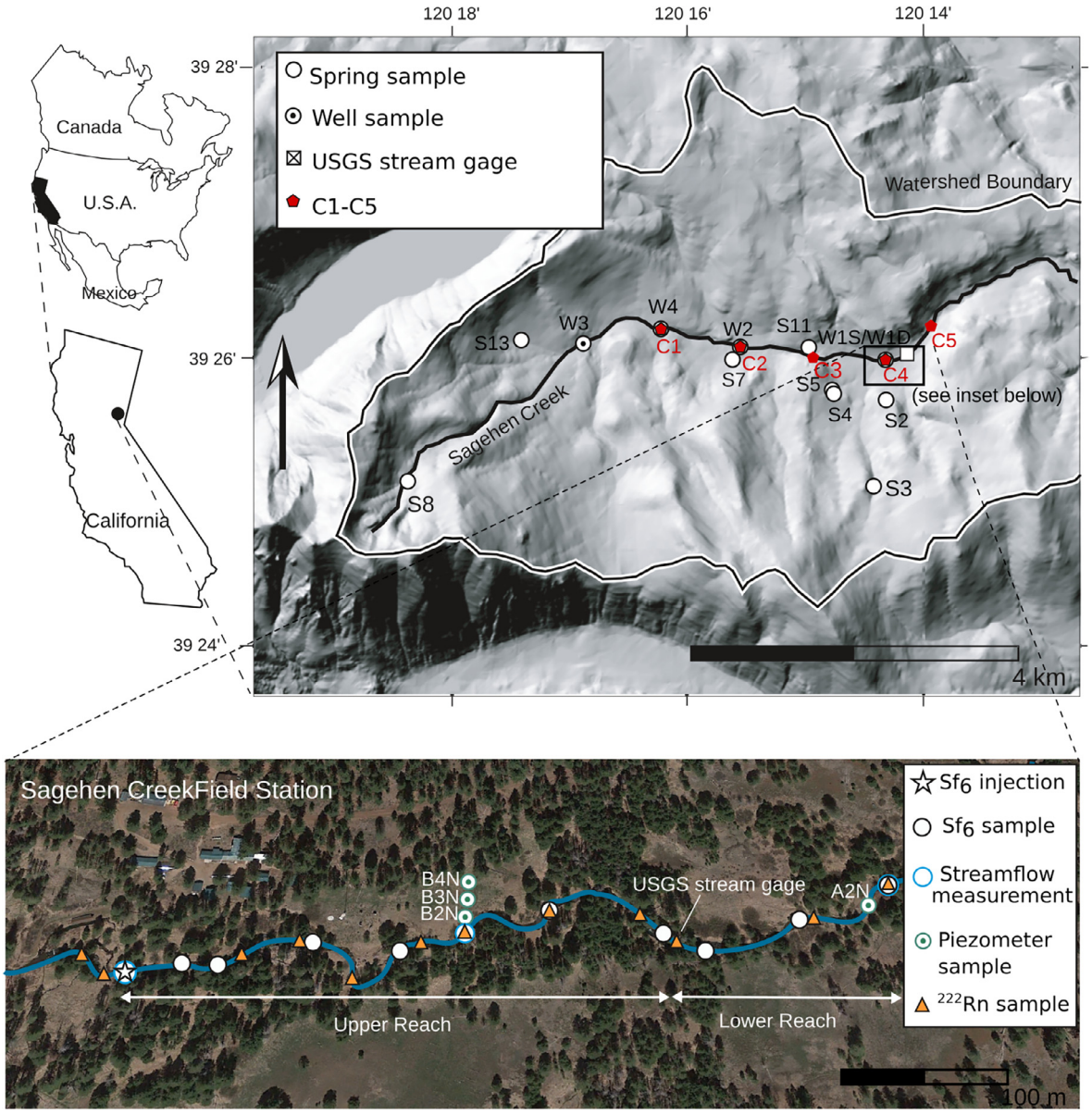

Fig. 1. Watershed and stream reach map. Upper map showing the watershed scale study location and its sampling points. Lower inset illustrating the detailed study reach with the partitioning in an upper and a lower reach and its sampling points.

tribution of groundwater inputs during low flow conditions is important for understanding the response of Sagehen Creek to potential decadal-scale changes in climate and to related changes in groundwater recharge (Manning et al., 2012).

The studied section of the creek flows alternately through fens where the valley bottom is broad and through rocky forest where the valley bottom is narrower. The stream is shallow with riffles, pools, and occasional minor falls, and the streambed consists of sand, rounded cobbles in the riffles or boulders in the falls. The watershed-scale reach is 4.04 km long and has a mean gradient of 0.022. The detailed study reach, located near the end of the watershed-scale study reach (Fig. 1) is 550 m long and has a lower mean gradient of 0.015. Here, the stream mainly meanders through fens and has a riffle and pool morphology (no falls). A USGS gage near the middle of the detailed study reach provides continuous streamflow data but also creates a localized turbulent section because of the structure of the stream gauge. A few, minor seeps are located in the fens but are not included in the calculations because their flow rate was too low to measure. Therefore, they are considered to be insignificant. In all tables and figures, distances are relative to the SF_6 injection site for the detailed study or relative to the uppermost sample site (C1) for the watershed-scale study (Fig. 1).

3. Theory and methodology

3.1. Theory and modeling methodology

Cook et al. (2006) developed a steady-state, numerical model that simulates longitudinal radon activities in a river as a function of groundwater inflow, evaporation, gas exchange with the atmosphere, radioactive decay, and hyporheic exchange. A brief overview of this model is presented here. Changes in radon activities in a gaining stream can be expressed by:

$$Q\frac{\partial c}{\partial x} = Ic_g - kwc - \lambda dwc - cL \pm F \quad (1)$$

where Q is the streamflow rate (m^3/day), c is the activity in the stream (Bq/L), c_g is the activity of groundwater inflow (Bq/L), I is the groundwater inflow rate per unit of stream length (m^3/m/day), L is the rate of water loss from the river per unit stream length from direct pumping or recharge to the underlying aquifer (m^3/m/day), F is the flux of radon in or out of the hyporheic zone (Bq/L), k is the gas exchange velocity across the water surface (m/day), λ is the radioactive decay constant for radon (per day), w is the width of the stream surface (m), d is the mean stream depth (m) and x (m) is the distance in the direction of flow. This equation assumes that radon activity in the atmosphere, radon production in the river, and dispersion are all negligible. The hyporheic zone is represented as a single layer beneath the streambed with a constant radon activity, continuous connection to the stream and no horizontal flow. Given expressions for solute mass balance in the hyporheic zone and river mass balance (Cook et al., 2006), changes in activity as a function of distance is expressed by:

$$Q\frac{\partial c}{\partial x} = I(c_g - c) + Ewc - kwc - dw\lambda c + \frac{\gamma hw\theta}{1+\lambda t_h} - \frac{\lambda hw\theta}{1+\lambda t_h}c \quad (2)$$

where

$$Q = Q_0 + \int I - \int L - \int Ew \quad (3)$$

and where E is the evaporation rate (m/day), γ is the production rate with the hyporheic zone (Bq/L/day), h is the mean depth of the hyporheic zone (m), θ is the porosity of the hyporheic zone, t_h is the mean residence time of water in the hyporheic zone (days), and Q_0 is the initial stream flow rate at the start of the reach under consideration (m^3/s). The six terms on the right-hand side of Eq. (2) represent changes in activity due to groundwater inflow (diffusion of chemical activity across the groundwater-streambed interface), evaporation, gas exchange, radioactive decay within the stream, production in the hyporheic zone and radioactive decay within the hyporheic zone.

The EXCEL spreadsheet simulator developed by Cook et al. (2006) solves Eqs. (2) and (3) using an explicit finite difference approach with a spatial discretization of one 1000th of the modeled reach length and computes a longitudinal radon activity distribution in the river. The model can be used to compute activities or concentrations of any tracer in a river as long as those are controlled solely by processes included in Eq. (2), and concentrations of multiple tracers can be simulated simultaneously. In this study, the simulator is used in an inverse mode to derive k and the spatial distribution of I by matching measured and modeled concentrations of two different tracers simultaneously (radon and specific conductance for the detailed study; CFC-12 and $\delta^{18}O$ for the watershed-scale study). The spreadsheet program was modified to allow the use of the SOLVER inversion tool included in EXCEL to minimize the difference between measured and modeled data. The modeled tracer concentrations take the form:

$$c(x) = c_0 e^{\frac{-(kw+dw\lambda)x}{Q}} \quad (4)$$

And Eq. (4) is re-arranged to solve for the gas exchange velocity (k) as follows:

$$k = \frac{\frac{-Q}{x}\ln\left(\frac{c(x)}{c_0}\right) - dw\lambda}{w} \quad (5)$$

In order to weight different tracer observations equally in the inversion, the difference between measured and modeled stream-water tracer concentrations was normalized for each sample as follows:

$$c_{error} = \frac{c_{meas} - c_{mod}}{c_{meas}} \quad (6)$$

where c_{meas} is the measured concentration and c_{mod} is the modeled concentration.

3.2. Field methodology

3.2.1. Detailed study

Field work was conducted during low flow conditions on September 10–12, 2009 along a 550 m study reach. The geometry of the creek was measured in detail using a tape measure at 27 transects completed at regular intervals as well as at every sampling location. At each transect, stream depth was measured every 0.2 m across the width of the stream. The cross-sectional area of each transect was calculated assuming each transect was trapezoidal. The mean depth of the stream was calculated by dividing the cross-sectional area by the stream width rather than averaging the depths of the transect so that the mean was not biased by boulders which locally cause large variations in depth.

A temperature and specific conductance probe (YSI 556) was manually dragged along the bottom of the upper and lower reaches to identify anomalies in temperature and specific conductance. Values were recorded every 15 m and at potentially anomalous locations where temperature or specific conductance changed. The probe is considered accurate to ±0.15 °C and ±1 μs/cm for temperature and specific conductance, respectively. Additionally, three detailed streamflow measurements using a pygmy flow meter were conducted simultaneously on September 11, 2010 (Fig. 1). The streamflow rate did not significantly change during field work, being 0.042 ± 0.0002 m^3/s during the detailed study and 0.045 ± 0.0001 m^3/s during the watershed-scale study. Therefore, the mean flow rates are used in all calculations. However, uncertainties in streamflow measurements accrue due to several factors including the number of verticals the cross-section is divided into, the length of measurement time, and the flow velocity. (Hinton, 2005).

For radon measurements we collected stream samples (2 L) and groundwater samples (0.25 L) in the upper and lower reaches of Sagehen Creek (Fig. 1). We collected stream samples directly from the middle of the stream (at depths of 5–10 cm) and groundwater samples from springs, monitoring wells (W1S, W1D, W2, and W4), and shallow piezometers (A2N, B2N, B3N, B4N) so that both shallow and deep groundwater were sampled (Fig. 1). Monitoring wells are located near the stream and are screened within unconsolidated material at depths of 5–20 m, with the exception of W1S, which is screened from 1 to 3 m. Shallow piezometers are also located near the stream and are less than 2 m deep. Springs (n = 9) were sampled directly from the spring pool using a siphon to minimize air–water interactions. Well samples were collected using a small submersible pump (n = 4). Piezometer samples were collected using bailers (n = 4).

A commercial radon-in-air detector (RAD7) was outfitted with two different air–water exchangers and the activity of ^{222}Rn-in-air (which equilibrated with the surface water) was calculated by measurement of the α-emitting daughters ^{214}Po and ^{218}Po (Burnett et al., 2001, 2006). Surface water samples were pumped continuously into a separate air–water exchanger (RAD-AQUA) and radon activities were measured over six 10-minute intervals with a detection limit of ~0.01 Bq/L using a method from Kluge et al. (2007) modified by Dugan et al. (2011). Radon-in-water activities were calculated from radon-in-air activities using the temperature dependence of the air–water phase equilibrium of radon (Burnett et al., 2001). Groundwater samples were aerated in the sample bottle (RAD-H_2O) with a detection limit of ~0.01 Bq/L. Corrections were made for the radioactive decay that occurred between time of sampling and analysis although this was generally insignificant because analysis was completed at the study site.

The tracer injection experiment using SF_6 was carried out from September 11–12, 2009 to quantify the gas exchange velocity. A

1:10 SF_6:N_2 mixture was released semi-continuously using a switcher valve and a timer allowing the mixture to bubble into the stream through a diffusion stone. We refer to Benson et al. (2014) for a detailed description of the injection and sampling of SF_6. SF_6 concentrations were measured on a gas chromatograph equipped with an electron capture detector using a head space method following Clark et al. (2004). Gas exchange velocities were calculated from SF_6 measurements using the one-dimensional advection–diffusion equation (Eq. (5)) assuming first order decay of a continuously released gas tracer in a river.

3.2.2. Watershed-scale study

Stream-water samples were collected from five locations (C1 – C5) over a distance of 4 km during low flow conditions on August 28, 2010 (Fig. 1), and analyzed for CFC-12 and $\delta^{18}O$. Samples collected for the watershed-scale study could not be analyzed for ^{222}Rn because the analytical equipment was not available during this phase of field work. Samples were collected from near the middle of the stream using a 12-volt submersible pump. Chlorofluorocarbon samples were collected in duplicate and were analyzed for CFC-11, CFC-12, and CFC-113 at the U.S. Geological Survey Dissolved Gas Laboratory in Reston, Virginia using techniques described in Busenberg and Plummer (1992). Only CFC-12 data are utilized in this study because of concerns regarding potential degradation of the other two CFCs (Hinsby et al., 2007). Replicate sample CFC-12 concentrations generally agreed within 2%, and concentrations presented here (Section 4.2.1) are averages of the replicate pairs. Oxygen isotope samples were analyzed using cavity ring-down spectroscopy at the Colorado Plateau Stable Isotope Laboratory in Flagstaff, Arizona. All $\delta^{18}O$ values are relative to VSMOW standard. Groundwater samples were collected on the same day as the stream-water samples from three of the monitoring wells (W1S, W1D, and W2 in Fig. 1). Samples from these three wells were believed to best represent CFC-12 and $\delta^{18}O$ values in the groundwater entering stream given their location immediately adjacent to the stream (within 3 m).

3.3. Literature compilation

For the literature compilation of published gas exchange velocities, we standardized velocities to their respective velocities with a Schmidt number of 600 in order to compare velocities derived using different gases. The Schmidt number of a gas (Sc_{gas}) is the ratio of kinematic viscosity of water divided by the diffusion coefficient of the gas and corrects for the temperature and species dependence of the diffusion coefficient of the gases (Jaehne et al., 1987). Commonly, gas exchange coefficients are transformed to the Schmidt number of 600 (Sc_{600}), which corresponds to CO_2 in freshwater at 20 °C. We used the empirical relations developed by Raymond et al. (2012) to calculate the Schmidt number for the different gases. With the following equation, the gas exchange velocity of any gas can then be normalized to the gas exchange velocity with a Schmidt number of 600:

$$k_{600} = k_{gas}\left(\frac{600}{Sc_{gas}}\right)^{-n} \quad (7)$$

where k_{600} is the gas exchange velocity in freshwater for a gas with a Schmidt number of 600, k_{gas} is the gas exchange velocity of a particular gas, Sc_{gas} is the Schmidt number of a gas for a particular temperature and n is the Schmidt number exponent, which is defined by Jaehne et al. (1987) to be 0.5 for classical surface models (Bade, 2009; Raymond et al., 2012). Stream gradients were derived either from the literature source or Google Earth.

4. Results

4.1. Detailed-study

4.1.1. Field data

The stream geometry is consistent with a width and depth of 3.6 ± 1.2 m and 0.13 ± 0.10 m, respectively. The only location where the creek is consistently deeper than 0.25 m is the pool directly above the USGS stream gage (Figs. 1 and 2). Downstream streamflow measurements are highly variable, although this is attributed primarily to the significant uncertainty in manual streamflow measurements (Table S1). Radon activities in groundwater were greater in samples derived from springs (19.5 ± 14.2 Bq/L) than wells (5.5 ± 8.3 Bq/L) suggesting the springs may be derived primarily from bedrock whereas both deep and shallow wells are drilled in the unconsolidated materials (Table S2). Both springs and wells have significantly higher radon activities than the creek (Fig. 3, Table S2) indicating that radon is a useful tracer of groundwater discharge. Fig. 4 illustrates SF_6 concentrations, radon activities, temperature and specific conductance measured in Sagehen Creek. SF_6 concentrations decrease systematically except around the USGS stream gage (Fig. 4A). Directly above the stream gage, the stream slope decreases, likely due to the increased depth (Fig. 2) and lack of turbulence in this ~10 m section. At the gage, SF_6 concentrations decrease systematically in a step-wise fashion, consistent with the significant turbulence at the gage (Fig. 4A). For these reasons, the SF_6 profile is divided into upper and lower reaches for calculating the gas exchange velocities (Figs. 1 and 4A). The simulated gas exchange velocity in the upper and lower reach were consistent during the four different sampling sessions at 4.1 ± 0.4 m/day and 5.4 ± 0.5 m/day, respectively (Table S3). Below (Section 5.3) we compare these gas exchange velocities to observations in other streams with various gradients.

The ^{222}Rn data show a drop at the gage, which does not have much influence on the overall trend of the ^{222}Rn data (Fig. 4B). Hence, the overall trend of the ^{222}Rn data seems little affected by the turbulence at the gage. Radon activities generally increased downstream suggesting groundwater is discharging in this reach. The consistency in SF_6 concentrations for samples taken at different times suggests that steady-state conditions are a reasonable approximation. Detailed temperature data do not indicate any point anomalies or trends whereas specific conductance marginally increases downstream (Fig. 4C).

4.1.2. Numerical modeling

Model parameters for the base case used to determine values of I are either measured mean values or values estimated from the literature (Table 1). The river width, depth and flow rate are derived

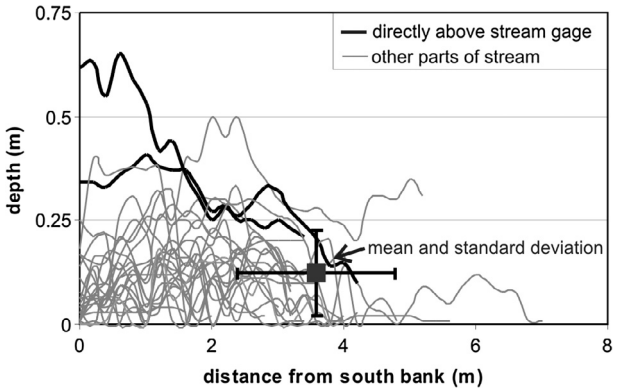

Fig. 2. Stream geometry measured at 27 cross sections. The stream depth is generally consistent except in the area directly above the stream gage.

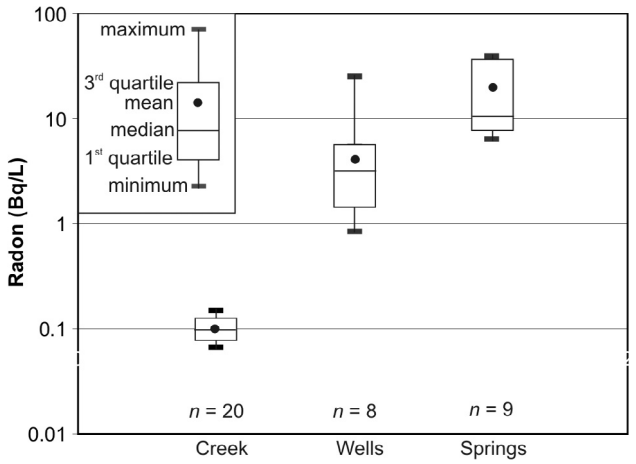

Fig. 3. Radon activities in the creek, wells/piezometer and springs. The radon detection limit is 0.01 Bq/L.

directly from measurements. The gas exchange velocity was derived from SF_6 data using a one-dimensional advection–diffusion equation (Eq. (5)). Radon and SF_6 gas exchange velocities are herein considered equivalent (Cook et al., 2006). The mean radon activity for the wells was used as the constant groundwater radon activity in a base case because groundwater discharging to the creek is assumed to be derived from the Quaternary sediments rather than the underlying bedrock. The sensitivity to the assumption of groundwater radon activity as well as parameter uncertainty is explored below. Since no streambed piezometers were available, hyporheic zone values are derived from Cook et al. (2006) although this study was conducted in a different environment. For trial-and-error calibration, only the stream radon activities measured during the SF_6 tracer experiment (11.09.2009) were used.

The most parsimonious model fit for all simulations is a groundwater discharge rate that linearly increases downstream – other, non-linear model fits are possible but are less parsimonious and such additional complexity is not demanded by the data. For the base case, the simulated groundwater inflow at the start and the end of the stream reach was 0.3 m^3/day/m and 0.4 m^3/day/m, respectively, which results in a groundwater discharge rate of 400 m^3/day (~15% of streamflow). The sensitivity of the model-derived groundwater inflow rate to all parameter values was evaluated by varying measured and estimated parameters in the base case model and observing the resulting change in modeled groundwater inflow. Each parameter was varied individually. Measured parameters were varied by 1σ and estimated parameters were varied by 50% of the parameter value (Fig. 5 and Table 1). In the sensitivity analysis, the groundwater inflow (I_g) is normalized to Q and thus expressed as a percentage of Q. The groundwater discharge is 15% in the base case model, and the minimum and maximum modeled groundwater discharge computed in the sensitivity test are 2% and 22%, respectively (Fig. 5). Modelled groundwater discharge is most sensitive to the measured parameters river width (w), and groundwater radon activity ($c_{g(wells)}$ or $c_{g(springs)}$). The model is less sensitive to estimated parameters derived from the literature.

4.2. Watershed-scale study

4.2.1. Field data

Measured CFC-12 concentrations and $\delta^{18}O$ values differ markedly in groundwater versus stream water, making them useful tracers for determining groundwater inputs to the stream (Fig. 6). CFC-12 concentrations range from 229 to 274 pg/kg in stream-water samples (mean of 254 pg/kg) and from 19 to 43 pg/kg in groundwater samples (mean of 29 pg/kg). CFC-12 concentrations in groundwater are lower because recharge occurred in the past when atmospheric CFC-12 concentrations were lower. Apparent ages of the groundwater samples computed from the CFC-12 concentrations are 47–53 years. Stream water fully equilibrated with air should have a CFC-12 concentration of about 274 pg/kg. Stream-water concentrations are as much as 45 pg/kg below air-equilibrated water, indicating that groundwater input rates are sufficiently high, relative to the gas exchange velocity for the stream water to preserve some of the groundwater's depleted CFC-12 signal. Measured $\delta^{18}O$ values range from −14.8‰ to −13.9‰ in stream water samples (mean of −14.5‰) and from −15.1‰ to −14.9‰ in groundwater samples (mean of −15.0‰).

Longitudinal profiles of measured stream CFC-12 concentrations (Fig. 7A) and $\delta^{18}O$ values (Fig. 7B) both show substantial variation, suggesting a substantial variation in groundwater input rates

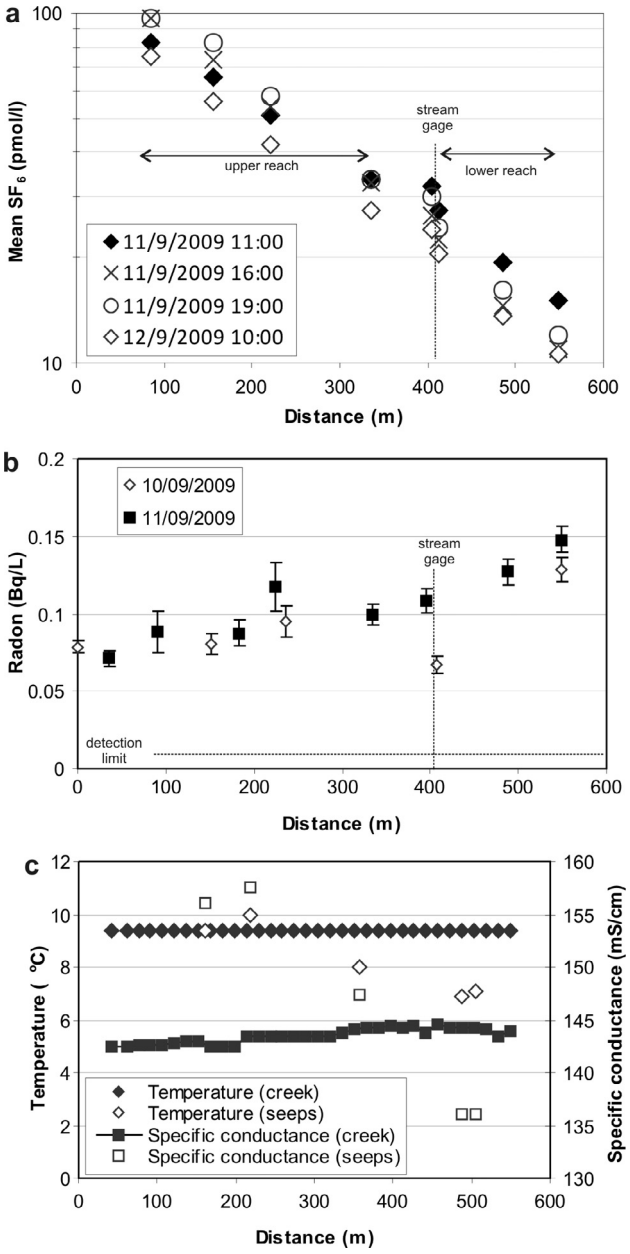

Fig. 4. A) mean SF_6 concentrations from 4 or 5 samples collected across each section. B) radon activities plotted with 1σ counting errors. C) temperature and specific conductance. All parameters are plotted against distance downstream from SF_6 injection point.

Table 1
Model parameters for simulation of ^{222}Rn.

Symbol	Description			Units	Reference
Measured parameters		μ	σ		
$k_{(upper)}$	gas exchange velocity for upper reach	4.1	0.4	m/day	Table S3
$k_{(lower)}$	gas exchange velocity for lower reach	5.4	0.5	m/day	Table S3
w	river width	3.6	1.2	m	Fig. 2
d	river depth	0.13	0.10	m	Fig. 2
$c_{g(wells)}$	radon activity in groundwater (wells)	5.5	8.3	Bq/L	Fig. 3
$c_{g(springs)}$	radon activity in groundwater (springs)	19.5	14.2	Bq/L	Fig. 3
c_0	initial radon activity in creek	0.07	0.005	Bq/L	Fig. 3
Q_0	initial streamflow	0.03	0.016	m^3/s	Table S1
Estimated parameters		Value			
E	Evaporation rate	0.002		m/day	WRCC (2005)*
h	hyporheic zone thickness	0.1		m	Cook et al. (2006)
q	hyporheic zone porosity	0.4			Cook et al. (2006)
t_h	hyporheic zone residence time	0.25		days	Cook et al. (2006)
g	radon production within hyporheic zone	3		Bq/L/d	Cook et al. (2006)

* In the 550-m long detailed study. Mean evaporation value from Tahoe station which is closest to the field site.

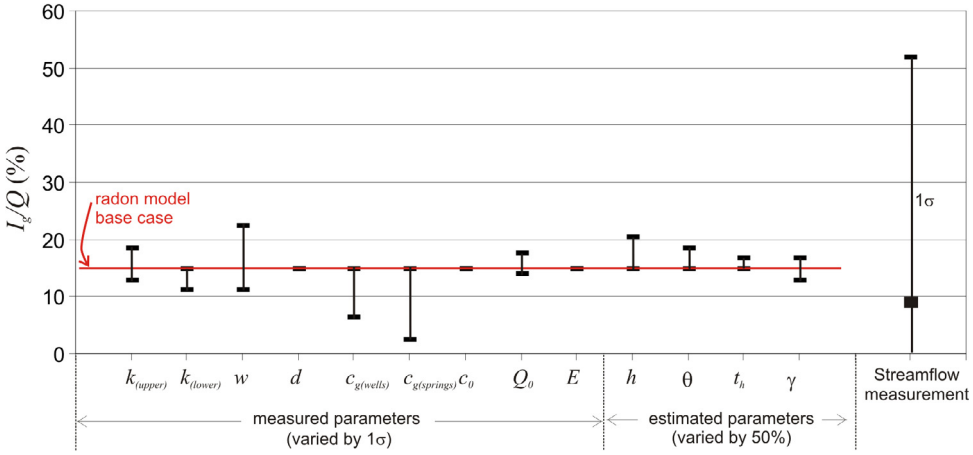

Fig. 5. Sensitivity to measured and estimated parameters, expressed as groundwater inflow (I_g) normalized to mean streamflow (Q). The black square represents the difference in measured streamflow in the studied stream reach with the error bars representing the standard deviation (1σ) of the measurement at the beginning of the stream reach.

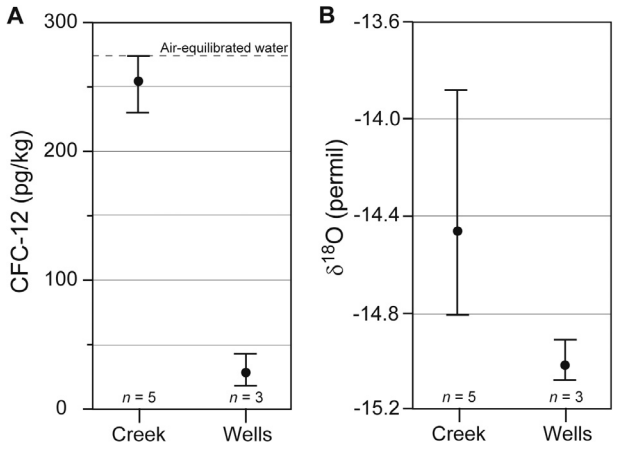

Fig. 6. Measured A) CFC-12 concentrations and B) $\delta^{18}O$ values in Sagehen Creek and groundwater. Error bars indicate range of measured concentrations for each sample type.

along the watershed-scale study reach. The CFC-12 profile shows a distinct low point at site C3 located about 2 km downstream, suggesting that groundwater inputs may be highest in this vicinity. The greatest drop in stream $\delta^{18}O$ occurs between sites C2 and C3, consistent with the stream CFC-12 data and with the highest groundwater input rates occurring near site C3.

4.2.2. Numerical modeling

Stream-water CFC-12 concentrations and $\delta^{18}O$ values were simulated simultaneously using the numerical model described in Section 3.1 and input parameters listed in Table 2. The stream dimensions at the watershed-scale are the same as in the model for the detailed study, except the stream width at the top of the watershed-scale reach is narrower (1.5 m). The groundwater CFC-12 concentration and $\delta^{18}O$ value are the means of the three collected groundwater samples. The CFC-12 concentration of air-equilibrated stream water was computed assuming a stream-water temperature of 10 °C (mean of the afternoon samples) and an elevation of 1950 m.a.s.L. (mean elevation of the watershed-scale study reach). The streamflow at the downstream end of the reach was estimated based on the flow measured at the nearby USGS gage on the day samples were collected. The gage is located 684 m upstream from the end of the reach (Fig. 1). A flow increase of 0.0045 m^3/s was estimated for this 684 m section assuming a uniform groundwater inflow rate of 0.57 $m^3/day/m$ as computed in the detailed study for the downstream end of the detailed study reach. This was added to the flow rate of 0.0453 m^3/s measured at the gage to produce an estimated rate of 0.050 m^3/s at site C5.

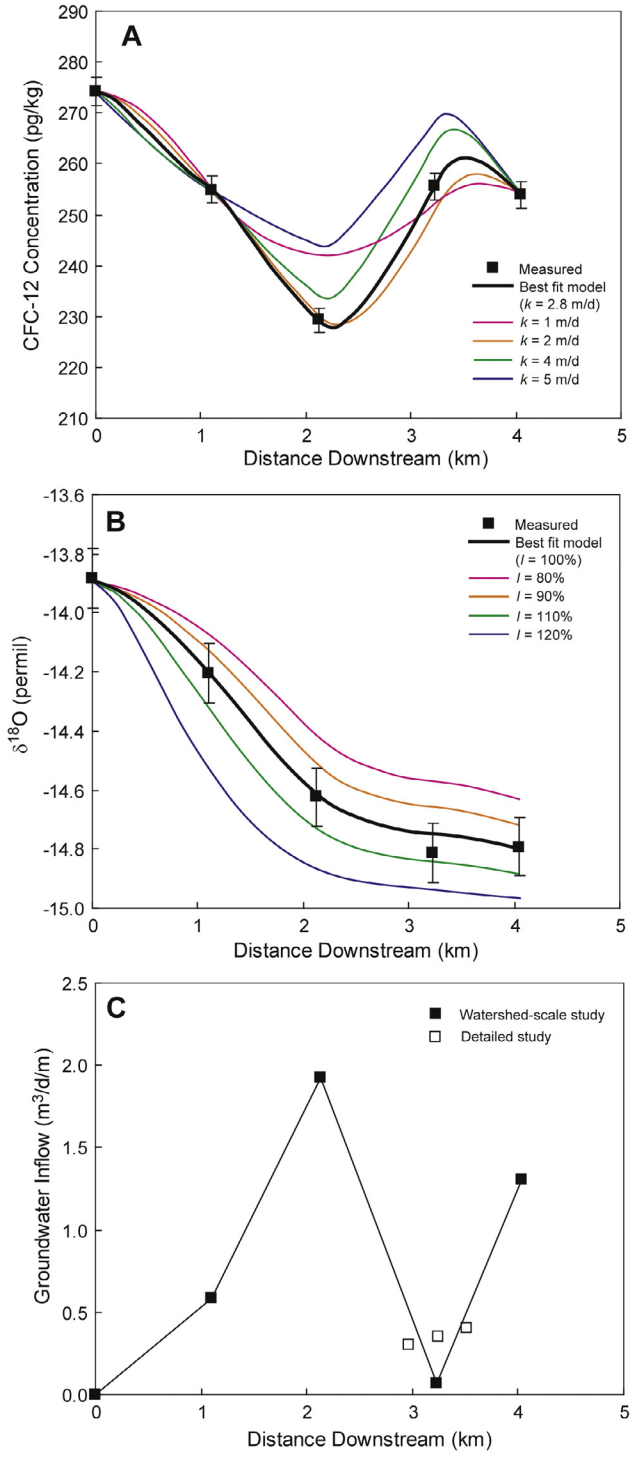

Fig. 7. Longitudinal profiles of measured and simulated A) stream CFC-12 concentrations, B) $\delta^{18}O$ values and C) groundwater inflow rates. Error bars indicate uncertainty (1σ) in measured values.

Five groundwater input nodes were assigned in the model collocated with the five sample locations. Any number of input nodes could have been assigned, but assigning fewer than five resulted in poor fits between measured and modeled values. Groundwater input rates at each of the five nodes, along with k and Q_0, were varied until the sum of all individual CFC-12 and $\delta^{18}O$ error terms (Eq. (6)) was minimized using the EXCEL SOLVER tool. Constraints applied in the inversion included: (1) modeled streamflow at the downstream end of the reach had to equal the estimated total streamflow (0.050 m^3/s); and (2) modeled Q_0 had to exceed 10% of flow at the downstream end of the reach, a minimum based on the stream width at C1 being approximately half that at C5, and the apparent flow rate being generally similar at both sites.

The modeled best-fit stream-water tracer concentrations are shown in Fig. 7. Modeled values closely match measured values for both CFC-12 and $\delta^{18}O$. The goodness of fit for both tracers (on the order of 1e-5) suggests that the solution is robust given that the two different tracers serve as independent constraints on the groundwater input rates. Total groundwater input through the reach is 0.0378 m^3/s, or 76% of total flow at the downstream end. Groundwater input rates vary significantly through the reach (Fig. 7C). Input rates are relatively high near site C3 as expected based on visual inspection of the measured tracer concentrations. The low input rates near site C4 are consistent with input rates derived in the detailed study. The derived value of k in the best-fit model is 2.8 m/day, which is lower than the 4.3 m/day derived in the detailed study, but still reasonably close given that k can vary over several orders of magnitude.

The potential utility of using CFC-12 alone to derive groundwater inputs to the stream was explored by performing a series of inversions in which only the sum of the CFC-12 error was minimized. To demonstrate the uniqueness of a solution based solely on CFC-12, inversions were run where k was fixed at either 1, 2, 4, or 5 m/day and groundwater inputs and Q_0 were varied. Resulting modeled stream CFC-12 concentration profiles shown in Fig. 7A indicate that only k values between roughly 2 and 4 m/day produce modeled concentrations that generally match measured concentrations. Associated total groundwater inflows are 0.0292 and 0.0448 m^3/s, respectively, or 77% and 118% of the inflow in the best-fit model. This CFC-12 dataset therefore constrains the total groundwater inflow rate reasonably well, ruling out total inflow rates that deviate from the best-fit model by more than about 20%.

The uniqueness of a solution derived solely from $\delta^{18}O$ data was similarly tested by performing inversions in which only the sum of the $\delta^{18}O$ misfits was minimized. Because stream-water $\delta^{18}O$ values are independent of k, groundwater inflows were fixed at either 80%, 90%, 110%, or 120% of best-fit model values and Q_0 alone was varied. Resulting modeled stream $\delta^{18}O$ profiles shown in Fig. 7B indicate that only total inflows between roughly 90% and 110% produce reasonably good fits between measured and modeled values. The $\delta^{18}O$ dataset therefore also provides a good constraint on groundwater inflow rates, ruling out total inflow rates that deviate from the best-fit model by more than about 10%.

5. Discussion

5.1. Detailed study

The detailed study provides experimentally derived k values for high gradient mountain streams. The gas exchange velocity is consistent with other reported values (Table 3) and falls close to the regression line through the data on Fig. 8. The detailed study successfully determines groundwater input rates to the stream in the detailed study reach, and supports the application of dissolved gas tracers as useful tools for studying groundwater inputs to high gradient mountain streams.

Numerical simulations quantify a relatively low groundwater discharge rate, which is consistent with the measured downstream increase in radon activities and specific conductance. The groundwater discharge rate is relatively well constrained to be between 2% and 22% of streamflow, especially when compared to the uncertainty of measured streamflow data under low flow conditions (Fig. 5). Uncertainty in physical streamflow measurements is

Table 2
Model input parameters for simulation of CFC-12 and $\delta^{18}O$ in the 4-km long watershed-scale study.

Symbol	Description	Value	Units	Source
w_t	river width at top	1.5	m	field estimate
w_b	river width at bottom	3.6	m	Fig. 2
d	river depth	0.13	m	Fig. 2
$c_{g\ CFC\text{-}12}$	CFC-12 concentration in groundwater	29.0	pg/kg	Fig. 6A
$c_{g\ \delta 18O}$	$\delta^{18}O$ value in groundwater	−15.0	permil	Fig. 6B
$c_{0\ CFC\text{-}12}$	initial CFC-12 concentration in creek	274	pg/kg	Fig. 7A
$c_{0\ \delta 18O}$	initial $\delta^{18}O$ value in creek	-13.9	permil	Fig. 7B
c_a	CFC-12 concentration in air-equilibrated water	274	pg/kg	see Section 4.2.2
Q_f	final streamflow	0.050	m^3/s	see Section 4.2.2

Table 3
Literature compilation of gas exchange velocities for this and other studies.

Tracer	k_{600} (m/d)	Temp. (°C)	Stream gradient	Location	Reference
SF_6	6.97	9.5	0.0146	Sagehen Creek, CA, USA	This study (upper reach)
SF_6	9.18	9.5	0.0146	Sagehen Creek, CA, USA	This study (lower reach)
SF_6	2.15	17.6	0.0026	Cockburn River, Australia	Cook et al. (2006)
SF_6	10.50	13.5	0.0380	West Fork Walker Branch, TN, USA	Wanninkhof et al. (1990)
SF_6	1.50	21.1	0.0010	Sugar Creek, IN, USA	Tobias et al. (2009)
SF_6	2.45	15.0	0.0004	Nemadji River, WI, USA	Hibbs et al. (1998)
^{222}Rn	48.39	4.2	0.1781	Pinecrest, Emigration Creek, UT, USA	Rogers (1958)*
^{222}Rn	73.63	4.2	0.1121	Red Butte Creek, UT, USA	Rogers (1958)
^{222}Rn	49.99	4.2	0.0784	Red Butte Creek, UT, USA	Rogers (1958)
^{222}Rn	31.39	4.2	0.0534	Mill Creek, UT, USA	Rogers (1958)
^{222}Rn	24.02	4.2	0.0165	Weber River, UT, USA	Rogers (1958)
^{222}Rn	0.99	28.3	0.0003	Daly River, Australia	Cook et al., (2003)
CFC-12	5.11	9.5	0.0215	Sagehen Creek, CA, USA	This study**
^{84}Kr	8.25	11.2	0.0050	Fischa-Dagnitz, Austria	Stolp et al. (2010)
^{84}Kr	1.40	24.9	0.0030	West Bear Creek, NC	Solomon (written comm. 2/6/2013)
CH_4	5.00	16.5	0.0070	Nine Mile Creek, UT, USA	Heilweil et al. (2013)
^4He	13.10	11.2	0.0050	Fischa, Austria	Stolp et al. (2010)
C_3H_8	3.10	20.0	0.0070	Panther Creek, TN, USA	Jin et al. (2012)
C_3H_8	3.20	20.0	0.0070	Panther Creek, TN, USA	Jin et al. (2012)
C_3H_8	0.70	20.0	0.0060	Ledbetter Creek, TN, USA	Jin et al. (2012)
C_3H_8	1.10	20.0	0.0060	Ledbetter Creek, TN, USA	Jin et al. (2012)
C_3H_8	0.90	20.0	0.0070	Little Panther Creek, TN, USA	Jin et al. (2012)
C_3H_8	3.00	20.0	0.0130	Little Bear Creek, TN, USA	Jin et al. (2012)
C_3H_8	25.50	5.3	0.0680	Krycklan Catchment 1, Sweden	Wallin et al. (2011)
C_3H_8	12.50	1.1	0.0380	Krycklan Catchment 2, Sweden	Wallin et al. (2011)
C_3H_8	8.80	2.7	0.0210	Krycklan Catchment 4, Sweden	Wallin et al. (2011)
C_3H_8	27.30	4.8	0.0370	Krycklan Catchment 5, Sweden	Wallin et al. (2011)
C_3H_8	5.90	3.4	0.0020	Krycklan Catchment 6, Sweden	Wallin et al. (2011)
C_3H_8	14.30	5.7	0.0440	Krycklan Catchment 7, Sweden	Wallin et al. (2011)
C_3H_8	6.50	8.0	0.0180	Krycklan Catchment 8, Sweden	Wallin et al. (2011)
C_3H_8	18.30	5.8	0.0120	Krycklan Catchment 9, Sweden	Wallin et al. (2011)
C_3H_8	15.90	7.6	0.0330	Krycklan Catchment 10, Sweden	Wallin et al. (2011)
C_3H_8	7.50	5.5	0.0000	Krycklan Catchment 12, Sweden	Wallin et al. (2011)
C_3H_8	53.90	5.3	0.0150	Krycklan Catchment 14, Sweden	Wallin et al. (2011)
C_3H_8	44.20	10.5	0.0580	Krycklan Catchment 15, Sweden	Wallin et al. (2011)
C_3H_8	7.10	11.9	0.0250	Krycklan Catchment 71, Sweden	Wallin et al. (2011)
C_3H_8	6.70	15.2	0.0050	Krycklan Catchment 78, Sweden	Wallin et al. (2011)
C_3H_8	13.90	16.9	0.0380	West Fork Walker Branch, TN, USA	Genereux and Hemond (1992)
C_3H_8	2.50	25.0	0.0026	Bonner Reach, WI, USA	Grant and Skavroneck (1980)

* Stream depth assumed for all streams of Rogers (1958); stream temperature only known of Weber River and assumed to be the same for all other streams from Rogers (1958).
** Schmidt number for CFC-12 estimated from Zheng et al. (1998).

significant 30–50% (Table S1) as reported in previous studies (e.g., Cey et al., 1997; Parra et al., 2016).

5.2. Watershed-Scale study

The apparent CFC-12 groundwater ages computed for the well samples in this study (47–53 years) are slightly older than the oldest apparent CFC-12 ages reported by Rademacher et al. (2001) for springs in the watershed (about 40 years). This is expected given that the wells are located closer to the creek than the springs, meaning that some well water has likely traveled farther (longer residence time) than the spring water. Rademacher et al. (2002) observed a clear positive correlation between $\delta^{18}O$ and CFC-12 values based on the apparent groundwater age for samples collected from springs in the watershed. Older samples displayed more negative $\delta^{18}O$ values, a trend they attributed to changes in climate and atmospheric circulation since the 1950s. Our groundwater $\delta^{18}O$ values are similar to the oldest and isotopically lightest samples presented by Rademacher et al. (2002) recharged around 1960 (−15.0‰ to −14.8‰), as expected given the apparent CFC-12 ages of our samples. The relationship observed by Rademacher et al. (2002) and the measured longitudinal stream $\delta^{18}O$ profile in Fig. 7B together suggest that stream water above the watershed-scale study reach is fed by relatively young and isotopically heavier

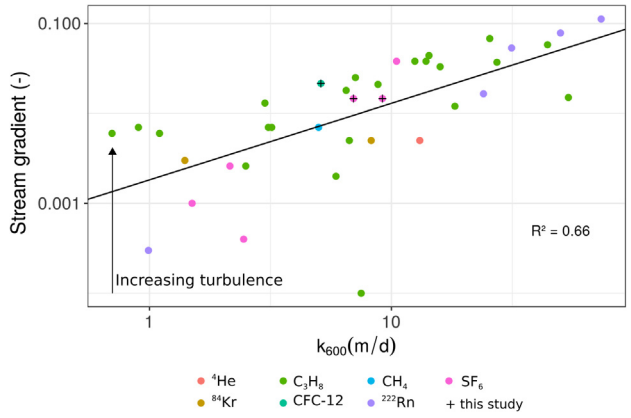

Fig. 8. k_{600} compilation for various gases with different stream gradients.

groundwater, then becomes progressively lighter isotopically as older groundwater enters the stream through the study reach. This hypothesis is consistent with the generally younger apparent groundwater ages (<20 years) observed by Rademacher et al. (2001) for springs located higher in the watershed.

The watershed-scale study provides a *k* value that is less well constrained than the detailed study, but useful nonetheless given the fact that there are only a few reliable *k* values for mountain streams. Using numerical simulations, groundwater inputs to the stream were successfully derived using CFC-12 and $\delta^{18}O$ in tandem. These input rates are relatively well constrained, and the derived inputs near site C4 agree well with derived input from the detailed study.

The watershed-scale study suggests that dissolved gas tracers are potentially useful when used alone to derive at least qualitative information over longer (km-scale) mountain stream reaches. Stream inputs derived using CFC-12 concentrations alone were relatively well-constrained (to within about 20%) and independently corroborated by the $\delta^{18}O$ data. However, the groundwater input regime for the watershed-scale reach is highly non-uniform, having very high inputs at site C3 followed by near-zero inputs at site C4, then rising back to high inputs at site C5. In this highly variable groundwater input regime, dissolved gas concentrations essentially are alternately controlled by either the groundwater input rate alone (high input reaches) or *k* alone (near-zero input reaches), which allows for a unique solution in which both *I* and *k* are constrained. On the other side of the spectrum of groundwater input regimes is a uniform groundwater input rate in which gas concentrations are simultaneously controlled by both *I* and *k* throughout. Under this regime, *I* and *k* values derived using dissolved gas concentrations will be completely non-unique, constrained only by the fact that *I* cannot exceed the total stream flow at the bottom of the reach. In this case, an independent knowledge of *k* would be required to successfully derive *I*. However, it should be noted that other studies quantifying groundwater input rates in mountainous streams under low flow conditions using different methodical approaches (e.g., Ward et al., 2013) or using similar approaches in different environments (Cook et al., 2003, 2006) have observed highly variable groundwater input rates like those observed in Sagehen Creek, suggesting that this scenario may be more common.

5.3. Compilation of gas exchange velocities for different stream gradients

To further explore the expected range of variation in *k* for high gradient mountain streams and the potential for the dissolved gas methodology, we conducted a literature review of peer-reviewed studies using different gases to quantify gas exchange velocities for different stream gradients. Heilweil et al. (2013) compiled gas exchange data including propane, SF6, methane, helium and krypton. Here, we expand to this compilation including radon and CFC-12 so that the present compilation comprises an empirical relationship between gas exchange velocities and stream gradients for various gases in different hydrologic environments (Table 3).

Fig. 8 indicates that there is a reasonable relationship with an R^2 of 0.66 (with a p-value of 6.9×10^{-10}) between reported gas exchange velocities and stream gradients. This compilation shows that stream gradients are a reasonable predictor for gas exchange velocities likely because of the relationship between stream gradient and turbulence (Bade, 2009). This information is especially useful for planning future field experiments in high gradient mountain streams and also suggests that the dissolved gas methodology for quantifying groundwater discharge can be applied in a variety of hydrologic settings.

6. Conclusion

In this paper we investigated groundwater discharge to a mountain headwater stream during low flow conditions on multiple scales using dissolved gas tracers. In a detailed study at reach scale (550 m) we used radon and artificially injected sulfur hexafluoride. The tracer data was complemented with measurements of stream discharge, stream geometry, temperature and specific conductance. By combining this data with a steady-state numerical model, we were able to determine the groundwater discharge rates at the detailed-study reach to be between 2% and 22% of streamflow. Groundwater inflows computed from streamflow measurements alone were considerably more uncertain (0–52% of streamflow).

In the larger watershed-scale study, we used chlorofluorocarbon-12 and $\delta^{18}O$ as tracers and also combined the field data with the same numerical model. The results of the watershed-scale study showed that reconnaissance-type estimates of the groundwater inputs to mountain streams over broad areas can be derived by using both environmental tracers together or each tracer alone. Groundwater input rates on a watershed-scale are highly non-uniform. To obtain well constrained results on a watershed scale it is necessary to know the type of groundwater input regime, which can be determined based on the type of controlling factors for dissolved gas concentrations. However, the derived groundwater input rates from the watershed-scale study agree well with the groundwater inputs rates derived in the detailed study proving that groundwater inputs derived from multiple tracers measured on two different scales show general agreement.

The detailed study, watershed-scale study and literature review demonstrate that dissolved gas tracers are valuable tools for determining groundwater inputs to mountain streams on multiple scales, and *k* values do not prelude their use in high gradient streams (>0.01).

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vic and E. Mundy and three anonymous reviewers provided useful suggestions. All the data used are listed in the references, tables and supplementary information. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jhydrol.2017.12.022.

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