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D. K. Solomon

University of Utah, kip.solomon@utah.edu

T. E. Gilmore

North Carolina State University, gilmore@unl.edu

B. Kimball

USGS

D. P. Genereux

North Carolina State University, genereux@ncsu.edu

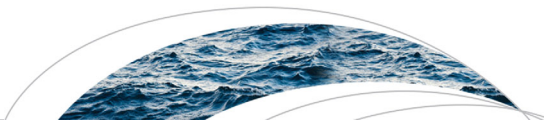
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RESEARCH ARTICLE

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Evaluating an unconfined aquifer by analysis of age-dating tracers in stream water

D. K. Solomon¹, T. E. Gilmore², J. E. Solder¹, B. Kimball³, and D. P. Genereux²

¹Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah, USA, ²Department of Marine, Earth, and Atmospheric Sciences North Carolina State University, Raleigh, North Carolina, USA, ³U.S. Geological Survey Utah Water Science Center, Salt Lake City, Utah, USA.

Key Points:

- Stream sampling can yield flow-weighted mean concentration in groundwater, C_{gw}
- C_{gw} was obtained from stream water for two age-dating tracers, SF₆ and CFC-11
- C_{gw} for SF₆, 0.55 fmol/L, suggests a groundwater mean transit time of 30 ± 5 years

Correspondence to:

D. K. Solomon,
kip.solomon@utah.edu

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Abstract The mean transit time (MTT) is a fundamental property of a groundwater flow system that is strongly related to the ratio of recharge rate to storage volume. However, obtaining samples for estimating the MTT using environmental tracers is problematic as flow-weighted samples over the full spectrum of transit times are needed. Samples collected from the base flow of a gaining stream in the North Carolina Coastal Plain (West Bear Creek) that were corrected for exchange with the atmosphere yielded environmental tracer concentrations (SF₆ and CFC-11) very similar to flow-weighted values from nine or ten streambed piezometers that directly sampled groundwater during low streamflow. At higher streamflow on the falling limb of the hydrograph, stream tracer concentrations (after correction for gas exchange) were significantly higher than the flow-weighted mean from piezometers, consistent with dominance of the stream tracer signal by transient influx of surface water and/or younger subsurface water. The apparent MTT derived from SF₆ in low flow stream water samples was 26 years, suggesting a groundwater recharge rate of about 210 mm/yr, that is consistent with vertical profiles obtained by sampling nested piezometers in the aquifer. When sampled under low flow conditions when streamflow consists of a high component of groundwater discharge, West Bear Creek appears to act as a flow-weighted integrator of transit times and, streamflow samples can provide fundamental information regarding groundwater recharge rate and MTT. Our study suggests that watershed-scale evaluation of some groundwater flow systems is possible without utilizing monitoring wells.

1. Introduction

Groundwater residence time in aquifers is a basic hydrologic attribute relevant to water quality and quantity. For example, over a decade after full implementation of rules to reduce nitrogen (N) loading to the Neuse River estuary in North Carolina by 30%, total N loading has dropped somewhat but leveled off short of the targeted reduction [Lebo *et al.*, 2012], in spite of large estimated reductions in N output from point sources and agricultural land. Among the factors potentially contributing to this finding is continued N discharge from groundwater systems charged with pollutant N in recent decades (i.e., the lag time between the change in N management and the change in N discharge from groundwater to surface water) [Meals *et al.*, 2010]. For a steady state system, the average groundwater residence time is equal to the volume of groundwater in storage divided by the volumetric flow into or out of the aquifer (e.g., recharge rate). From a water-resources perspective, the flow and the storage volume are two fundamental parameters. For a highly transient system (e.g., streamflow during and after storm events), the relationship between transit times, flows, and storage is considerably more complex.

The total groundwater residence time from recharge at the water table to discharge at springs or streams is often referred to as transit time. Recent reviews [McGuire and McDonnell, 2006; Maloszewski and Zuber, 1996, 1993] discuss tracer-based approaches used to estimate mean residence time (MRT) in groundwater (generally based on groundwater sampling) and mean transit time (MTT) in catchments (where the transit is mainly through a groundwater system, with sampling generally in stream water). Recently, other approaches have emerged based on trace gases traditionally used for groundwater age-dating, but with sampling focused in/near streams:

1. the streambed point approach based on point-scale measurements of both streambed seepage rate and the concentrations of an age-dating trace gas (e.g., CFC-12) in groundwater in or just below the streambed [Kennedy *et al.*, 2009b],

2. the mass balance approach based on estimating, from conservation of tracer mass, the flow-weighted mean concentrations of age-dating tracers in the groundwater input to a stream reach [Stolp *et al.*, 2010; Cook, 2013].

The objective of our study is to evaluate the mass balance approach in a stream for quantifying the flow-weighted mean concentration of age-dating tracers in groundwater discharging from the surrounding aquifer. Part of our motivation for sampling in/near streams stems from several inherent difficulties in estimating flow-weighted (average) concentrations and ages from wells. First, scientific-quality wells are uncommon. Second, groundwater ages typically vary with depth and obtaining flow-weighted integrated samples is problematic. In concept, a fully screened well might be used to sample a spectrum of flow paths and ages [Maloszewski and Zuber, 1996, 1993], but unless the aquifer is completely homogeneous, samples are likely to be biased by local regions of high permeability that preferentially contribute water to the well. We hypothesize that streams act as natural integrators of a spectrum of groundwater transit times and that mean transit time in the aquifer can be obtained by sampling a relatively modest number of stream samples. However, stream samples may only integrate over a portion of the aquifer and a full aquifer characterization requires an analysis of all discharges including wells, evapotranspiration, etc.

In this paper, we report environmental tracer results for a gaining stream, West Bear Creek, in the coastal plain of North Carolina, USA. Nearly all environmental tracers that contain young (less than 75 years) groundwater transit time information utilize dissolved gases [Plummer, 2005]. Once groundwater discharges into a stream, these dissolved gases exchange with the atmosphere. Corrections for this exchange must be made in order to carry out groundwater age-dating with volatile environmental tracers measured in stream water. While we measured numerous environmental tracers, our emphasis in this paper is on SF₆ because (1) its large molecular weight gives rise to a lower gas exchange rate than for example ³He (thus, the groundwater age signal from SF₆ is lost more slowly upon groundwater discharge to a stream and equilibration with air), and (2) its concentration in the atmosphere has been increasing linearly with time since about 1975 which allows the mapping of concentration to transit time when a sample contains a range of transit times over this linear period [Park *et al.*, 2002]. Our results are broadly applicable to studies that seek to obtain flow-weighted concentrations and ages in groundwater without utilizing wells, but rather by obtaining stream samples during base flow.

2. Background

2.1. SF₆ as a Groundwater Age Tracer

Sulfur hexafluoride (SF₆) is a relatively inert gas that is widely used in electrical switches and to protect metals from oxidation during casting operations. Since about 1970 the atmospheric mixing ratio of SF₆ has been increasing by about 7% each year; its current value (2015) is 8.4 pptv [NOAA, 2015]. This monotonic increase in the atmospheric mixing ratio results in a unique SF₆ concentration in groundwater recharge each year and hence its application in groundwater dating [Busenberg and Plummer, 2000].

In concept, groundwater at the water table contains SF₆ from three sources: (1) equilibrium solubility with the atmosphere (2) excess air, and (3) subsurface production referred to as terrigenous SF₆. Equilibrium solubility with the atmosphere can be described by Henry's law and is a function of temperature and atmospheric pressure (elevation). Groundwater often contains more atmospheric gases than can be explained by equilibrium solubility, due to dissolution of "excess air" [Heaton and Vogel, 1981]. Excess air can form during transient recharge events when the water table rises and air bubbles trapped below the water table dissolve under the elevated (greater than atmospheric) pressure [Aeschbach-Hertig *et al.*, 1999]. Terrigenous SF₆ has been found in fluorite [Harnisch and Eisenhauer, 1998] and significant concentrations in groundwater have been measured in areas with volcanic activity and igneous intrusions [Busenberg and Plummer, 1997; Gooddy *et al.*, 2006; Koh *et al.*, 2007; Darling *et al.*, 2012; Friedrich *et al.*, 2013]. If estimates of the recharge temperature (e.g., from dissolved noble gases), recharge elevation, and excess air (e.g., from measurements of dissolved Ne) are available, and terrigenous SF₆ is not significant, dissolved concentrations of SF₆ in groundwater can be converted to an atmospheric mixing ratio that in turn can be compared to the observed atmospheric mixing ratio in recent decades to provide an estimate of the year in which the water was last in contact with the atmosphere, i.e., the recharge year [Busenberg and Plummer, 2000]. An advantage to using SF₆ as a transit time tracer is that its time history in the atmosphere has been relatively linear

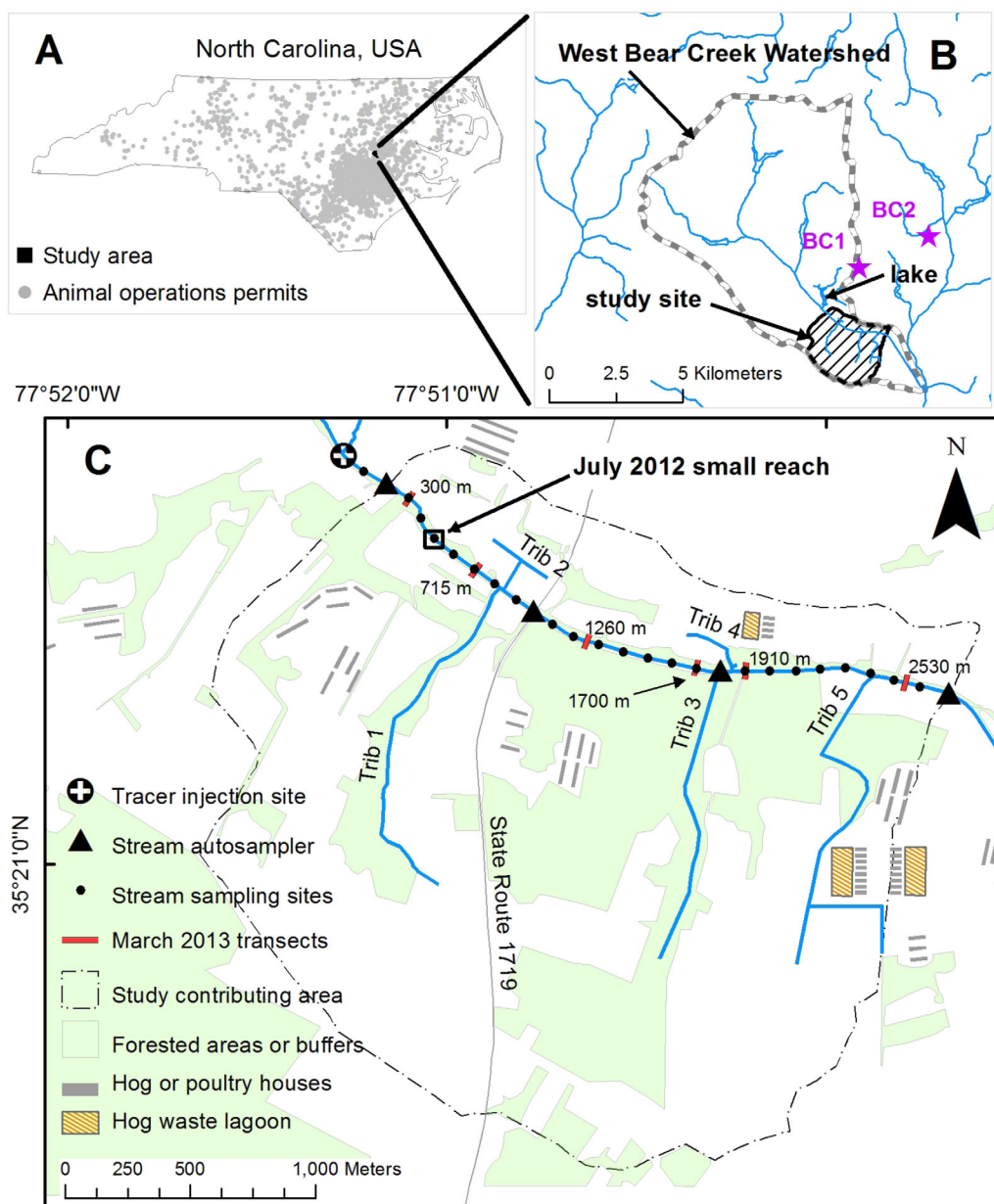


Figure 1. Location of field site in the North Carolina Coastal Plain. (b) The West Bear Creek watershed boundary and the location of monitoring well nests. (c) Details of the 2.7 km study reach including the locations of stream sampling sites during the bromide and noble gas tracer injections. Stream sites are named in meters downstream of the tracer injection site (defined as 0 m).

since about 1975. When the relationship between concentration and time is linear, a flow-weighted mixture of waters having different concentrations (because of different transit times) will map more closely to the true flow-weighted mean transit time than when the time-concentration relationship is nonlinear [Park *et al.*, 2002].

2.2. Site Hydrogeology and Previous Studies

We conducted two field campaigns (in July 2012 and March 2013) on a 2.7 km reach of West Bear Creek, located in the North Carolina Coastal Plain, near Goldsboro, NC (Figure 1). West Bear Creek drains a sandy aquifer that is part of the Black Creek Formation [Winner and Coble, 1996] and lies within the watershed of the Neuse River. The West Bear Creek watershed has about 50% agricultural land use, mainly cotton, soybean, and corn [Kennedy *et al.*, 2009b]. The Neuse River has experienced a degradation in water quality due

to excessive nitrogen loadings and in 1997 the North Carolina Environmental Management Commission adopted rules to reduce nitrogen loads [NCDWQ, 1999]. An overall objective of our study is to explore the lag time due to nitrogen transport in groundwater as a potential explanation for the persistent nitrogen concentrations in streams despite reduced loadings to the land surface. We plan to report details on nitrate contamination and transport along with groundwater age and transit time in future papers.

The nearest permanent stream gauging station to West Bear Creek was a USGS station (Mays Store) approximately 10 km downstream on Bear Creek. All stream locations are named by their distance in meters downstream of a tracer injection site defined as 0 m (Figure 1c), and most measurements were made at measurement stations from 200 to 2700 m.

The study site was previously investigated and is described in *Kennedy et al.* [2008, 2009a, 2009b] and *Genereux et al.* [2008]. These studies demonstrated the gaining nature of the stream reach, the distribution of nitrogen fluxes and apparent groundwater ages, and spatial patterns in streambed hydraulic conductivity.

3. Methods

3.1. Tracer Injections

In order to quantify stream discharge and groundwater discharge into the stream, we performed bromide tracer injections to West Bear Creek in July 2012 and March 2013. A concentrated solution of sodium bromide (NaBr) was prepared by dissolving 100 kg of salt in approximately 309 L of stream water. The Br injection concentration was monitored periodically and stayed very constant at $246,792 \pm 3.8$ mg/L, while the injection rate (62.71 mL/min) was monitored using a data logger [Kimball et al., 2002]. A total of 63.0 kg of Br was injected over 68 h in July 2012. The injection in March 2013 was similar, but the injection pump failed for about 8 h during the test. The tracer arrival, plateau, and departure (once the injection stopped) were monitored using ISCO automatic stream samplers at distances of approximately 200, 1000, 1700, and 2700 m downstream from the injection site.

Samples for Br analyses were filtered through 0.45 micron disposable filters and stored in polyethylene bottles. Samples were analyzed by ion chromatography along with extensive sample blanks, analytical standards, and a field QA/QC standard. The field standard was approximately 2 L of stream water collected during the tracer test, an aliquot of which was repeatedly analyzed to check for instrument drift. The Br tracer test is described in greater detail in *Gilmore* [2015].

Research grade Kr and Xe were also injected into West Bear Creek during the Br injections. Kr and Xe data were used to estimate the gas transfer velocity for the stream, which in turn was used in solving for the SF₆ concentration in groundwater discharging into the stream. The two gases were allowed to flow through silicone rubber tubing (6.4 mm OD × 3.2 mm ID, 18.6 m long for Kr and 11 m long for Xe in July 2012, and 23.5 m for Kr and 14.3 m for Xe in March 2013) that was submerged in the stream. Because Kr and Xe readily diffuse through silicone rubber, this system results in a bubble-less injection of gas into the stream. Because dissolved gases from the stream such as N₂ will also diffuse into the tubing, it is necessary to maintain a small flow of tracer gas through the tubing in order to maintain the gas purity inside the tubing. A back pressure of about 6 psi was maintained using needle valves.

The gas injection lasted for 20.5 h in July 2012 and 27 h in March 2013. The concurrent injection of NaBr showed that this was sufficient time for stream concentrations to reach steady state over the 2700 m long study reach. Stream water samples were collected at distances ranging from 200 to 2700 m downstream of the injection site. The NaBr injection also indicated that 200 m was sufficient distance to allow nearly complete mixing within the stream. Unfortunately, the Xe tank was depleted before stream sampling was complete in March 2013 and thus only Kr data were used in estimation of gas exchange rates in March 2013.

At 0.5 km downstream from the injection, the stream Kr concentration was 208 ccSTP/g (cubic centimeters of gas, at standard pressure and temperature, dissolved per gram of water) in July 2012 and 20.4 in March 2013, which are 34 and 2.3 times the atmospheric solubility values for the stream temperatures in July and March, respectively. Stream discharge was approximately 10 times higher in March 2013 than in July 2012, which is the primary reason for the larger concentration in July.

Stream samples for noble gas analyses were collected in 3/8" OD copper tubing by submersing the tube in the stream and using a small submersible pump (Whale pump) for purging. Metal pinch clamps were then

installed on the copper tubes for transport. In the laboratory, dissolved gases were extracted under high vacuum into 65 mL stainless steel flasks that were held at liquid N₂ temperature and equipped with a small capillary that functions as a water vapor diffusion pump [Bayer *et al.*, 1989]. The flasks were then installed onto a metal cleanup system that was pumped to high vacuum before sample inlet. The cleanup system removes reactive gases with a Ti-Zr getter, followed by cryogenic separation of the heavier noble gases (Xe, Kr, Ar) on a stainless steel trap [Lott, 2001]. The heavy noble gases were then measured using a quadrupole mass spectrometer (SRS, RGA300) under static (nonpumping) conditions.

3.2. SF₆ and CFC Sampling and Analysis

Stream water samples for SF₆ analyses were collected in 1 L glass bottles; each bottle was submerged in the stream and a submersible pump was used to flush the bottle with approximately three bottle volumes of stream water before capping the bottle under water. Stream water samples for CFC analysis were collected in a similar manner except that 125 mL bottles were used.

Groundwater seepage samples for SF₆ and CFC analyses were also collected from temporarily installed piezomanometers pushed into the sandy streambed [Gilmore, 2015]. Eight transects across the stream were sampled in July 2012 and six transects in March 2013, with SF₆ and CFC sampling on two of these transects in each campaign, at 481 and 516 m downstream of the injection site in July and 715 and 1260 m downstream of the injection site in March. Each transect consisted of 5 narrow (1.3 cm ID nominal) piezomanometers [Kennedy *et al.*, 2007, 2009a,b] with 5 cm long screens, approximately evenly distributed across the width of the stream. Groundwater seepage rate through the streambed was also determined at each sampling location, allowing measured groundwater SF₆ and CFC concentrations to be flow-weighted in terms of their contribution to concentrations in the stream. Details are given by Gilmore [2015].

SF₆ and CFC samples were analyzed by the Reston Groundwater Dating Laboratory of the U. S. Geological Survey (USGS) and at the University of Utah. The analyses were performed using custom-built purge and trap systems that utilize electron capture detectors. Details can be found in Busenberg and Plummer [2000] and Busenberg and Plummer [1992] for SF₆ and CFCs, respectively. Unfortunately, a number of the SF₆ samples broke in the laboratory while waiting for analysis. A total of eight samples were lost (one from July 2012 and seven from March 2013).

3.3. Gas Exchange Modeling

The steady state advective transport of a dissolved gas in a stream can be described by the following differential equation [Bencala, 1983; Genereux and Hemond, 1990; Runkel and Chapra, 1993; Cook, 2013], for gases without chemical or biological sources or sinks:

$$0 = -\frac{Q}{wb} \frac{dc_s}{dx} + \frac{q_L}{wb} (C_{gw} - C_s) + \frac{K}{b} (C_{atm} - C_s) \quad (1)$$

where, where C_s is stream concentration [M/L³], C_{gw} is groundwater concentration [M/L³], C_{atm} is concentration in equilibrium with the atmosphere [M/L³], Q is stream discharge [L³/T], q_L is groundwater discharge per unit length of stream [L²/T], w is stream width [L], b is stream depth [L], and K is gas transfer velocity [L/T].

Equation (1) assumes that streamflow, groundwater discharge, and groundwater concentration are constant in time, transport is dominated by advection, and that there is no net exchange of solutes with subsurface transient storage zones [Bencala, 1983]. When parameters such as Q or C_{atm} are not constant in time, dispersion can also influence the stream concentration but is not included in equation (1) [Knapp *et al.*, 2015]. The solution to equation (1) gives the concentration of a solute in the stream (C_s) at any distance (x) as a function of stream geometric parameters (w, b), groundwater discharge and the concentration of the solute in groundwater (q_L and C_{gw}), and (for a dissolved gas) the gas exchange between the stream and overlying air as described by the gas transfer velocity (K) and concentration in equilibrium with the atmosphere (C_{atm}).

Equation (1) was solved numerically using a spreadsheet (RADIN13) that was developed by Peter Cook (CSIRO Land and Water) with modification by the authors to optimize input parameters (e.g., the gas transfer velocity) by minimizing the residual between observed and computed stream concentrations. By performing simultaneous volatile (Kr and Xe) and nonvolatile (Br) injections and with groundwater concentrations that were well known, equation (1) was fit to observed tracer concentrations to provide

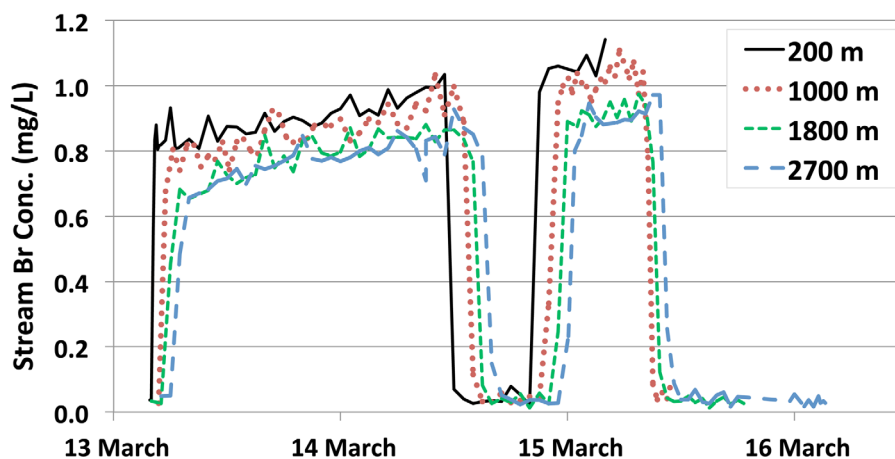


Figure 2. Bromide concentration versus time for four stream sites during the March 2013 tracer injection. Bromide was injected into the stream at a constant concentration and a time series of samples was collected downstream. The inadvertent failure of the injection pump around midnight on 14 March illustrates the lack of tailing in the Br concentration that would be expected if hyporheic flow were significant. The upward trend in the plateau Br concentrations is a result of decreasing streamflow, and the decrease in Br concentration downstream is due to groundwater discharge.

estimates of K and q_L . The model was then applied to measured stream concentrations of SF_6 and CFCs and optimized to provide best fit estimates of C_{gw} for these tracers.

4. Results

4.1. Stream Flow and Groundwater Seepage

During the Br injections, Br concentrations rose rapidly and reached a “quasi-plateau” (e.g., in March 2013, after about 1 h at 200 m from the injection and about 3 h at 2700 m; Figure 2). During both injections, records from the USGS gauging station on Bear Creek show that stream discharge was falling slowly, thus the slow upward drift in stream water Br concentration at plateau conditions (Figure 2). The minimal spreading of the observed tracer mass indicates that Br exchange into transient storage zones was a weak process in this system, consistent with other findings suggesting hyporheic zone thickness of 10 cm or less [Kennedy *et al.*, 2009a; Gilmore, 2015]. Br concentration generally decreased with increasing distance from the injection due to dilution by incoming groundwater, with some exceptions near 2000 m during March 2013 that suggest a transient loss of stream water from the channel in this area at high flow. The Br tracer injection pump inadvertently stopped on 14 March 2013, resulting in a rapid drop in Br concentration to essentially background in about 7 h at 2700 m. The lack of significant tailing in the Br concentration is further evidence that transient storage and hyporheic exchange are not strong processes in this system. Once the injection pump restarted, the Br concentration returned rapidly to the quasi-plateau trend from before the pump failure.

Once the Br had been injected at a constant rate for about 24 h, the stream was sampled every 100 m in order to obtain higher resolution in the patterns and magnitude of groundwater discharge (Figure 3). Velocity-area discharge measurements were also performed using a Sontek FlowTracker acoustic Doppler velocimeter (ADV). In July 2012, stream flow was about 50 L/s at the injection site and increased to more than 100 L/s at 2700 m. In March 2013, the flow increased from about 475 to 575 L/s over the study reach. While the absolute volume of groundwater in seepage along the study reach was greater in March, as a fraction of the total stream flow at 2700 m it was only 17%, compared to 50% in July. Seepage was relatively uniform along the study reach in July but more variable in March. In general, the Br-derived seepage rates agree well with the velocity-area (FlowTracker) measurements.

4.2. Gas Exchange

A modified version of the RADIN13 spreadsheet was used to evaluate the injected Kr and Xe in terms of the gas transfer velocity between the stream and the atmosphere. We utilized streamflow and

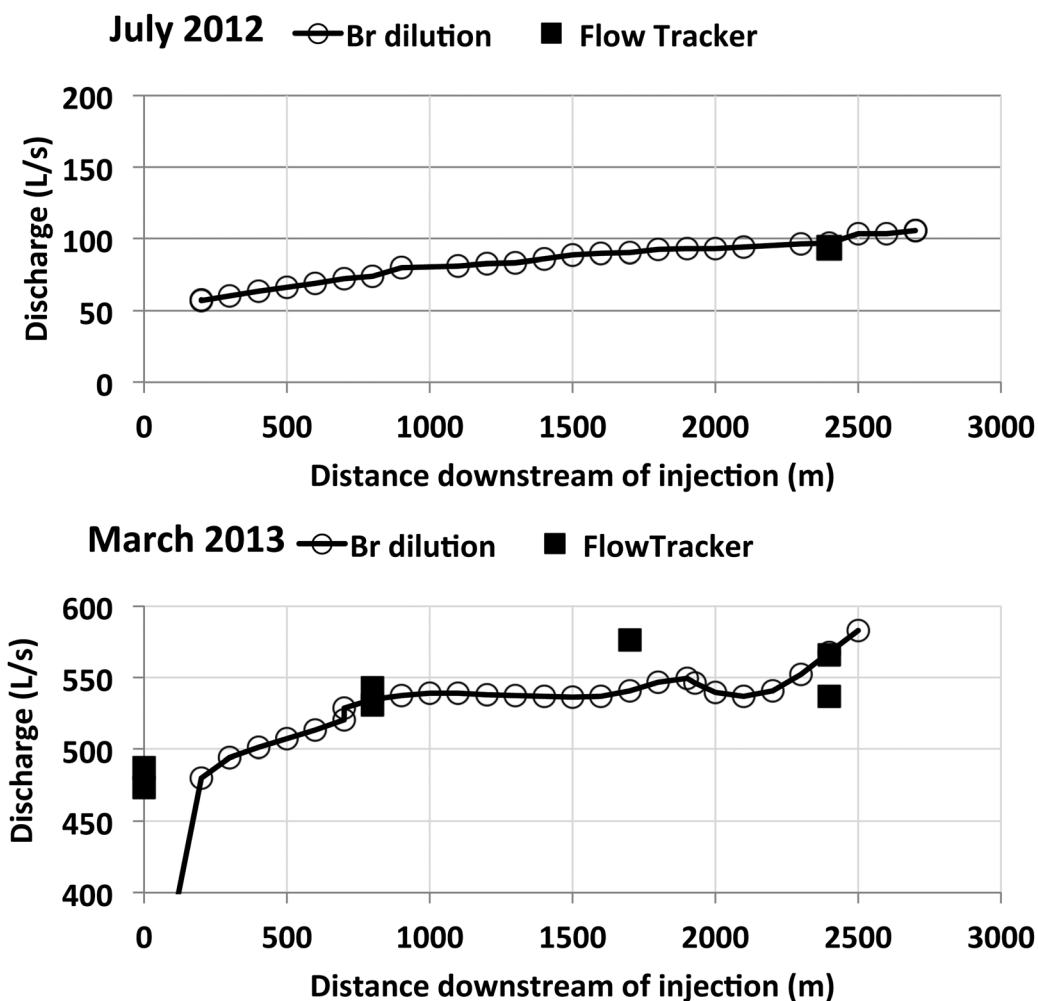


Figure 3. Streamflow versus distance along West Bear Creek during the tracer injections in July 2012 and March 2013. Streamflow was measured by the dilution of injected Br and by the standard velocity-area method. Although stream discharge was approximately ten times greater in March, the increase in stream discharge due to groundwater discharge was similar, with an average of $1.8 \text{ m}^3/\text{day per m}$ in July 2012 and $2.0 \text{ m}^3/\text{day per m}$ in March 2013. During March 2013 only, tributary inflows within the study contributed to the total increase.

groundwater seepage estimates from the Br tracer test along with measurements of the stream depth and width at the locations of velocity-area flow measurements (Figure 3) and groundwater sampling transects (Figure 1). We then minimized the root mean squared deviation (RMSD) between measured and simulated Kr and Xe stream water concentrations (with C_{gwr} , Q , q_L , w , and b held constant as independent measurements exist for these parameters) using the Solver® in Excel to obtain estimates of the gas transfer velocities for Kr and Xe that represent spatially averaged values between 200 and 2700 m. For the July 2012, test we obtained gas transfer velocities of 1.5 and 1.2 m/d for Kr and Xe and for March 2013 a value of 1.1 m/d for Kr (Figure 4). The Xe injection tank leaked and was depleted before sampling could be completed in March.

The simulated values are very sensitive to the gas transfer velocity. By randomly varying the stream discharge, groundwater discharge, stream width, stream depth, atmospheric concentration, and source concentration between $\pm 10\%$ (the approximate uncertainty associated with measured values) of the base values, a Monte-Carlo procedure resulted in an estimated uncertainty in the values of K of $\pm 0.15 \text{ m/d}$.

Jähne *et al.* [1987] showed that the relationship between gas transfer velocities (K) and aqueous diffusion coefficients (D) for two dissolved gases (subscripts 1 and 2) is:

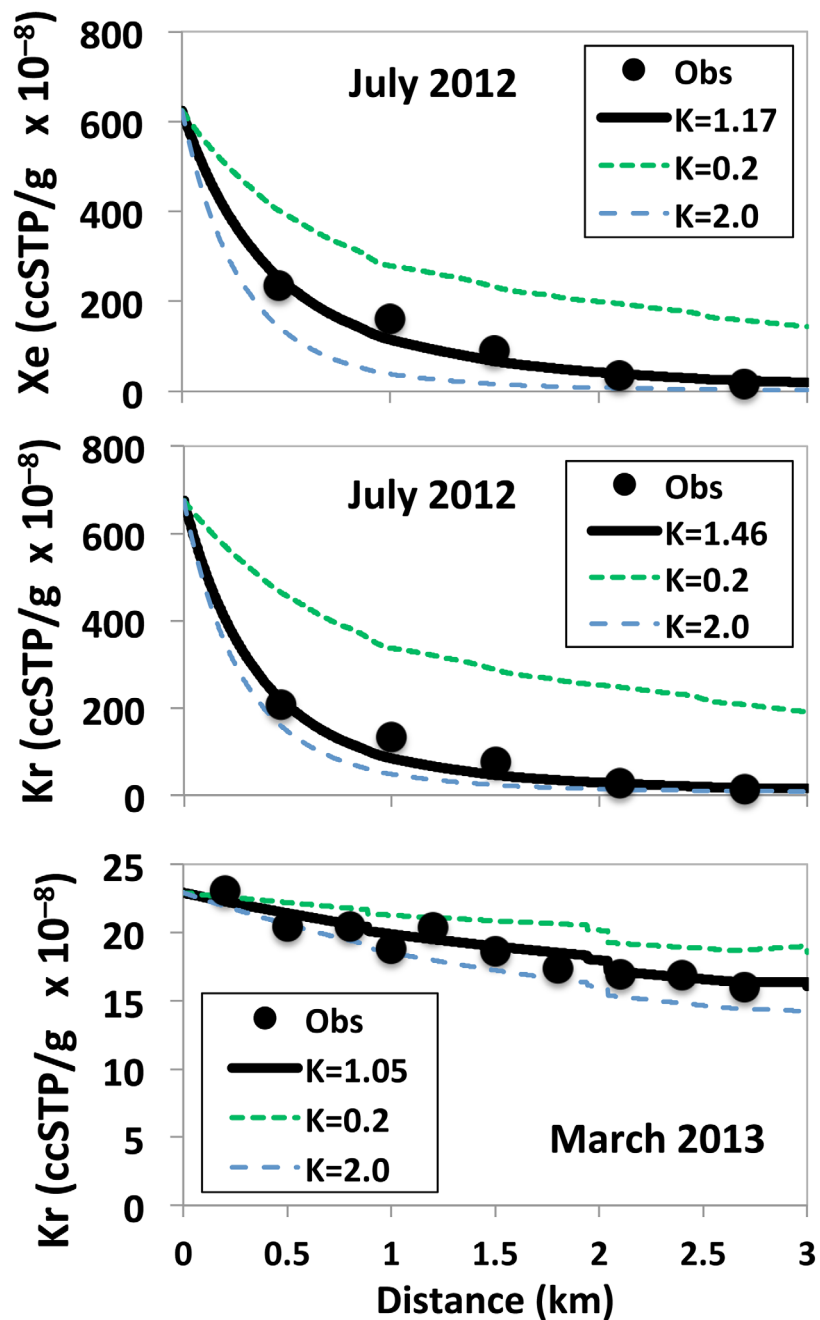


Figure 4. Stream water Kr and Xe concentrations versus distance downstream of the injection site for July 2012 and March 2013 with simulated curves based on different values for the gas transfer velocity (K) in m/day.

$$\frac{K_1}{K_2} = \left(\frac{D_1}{D_2}\right)^n \tag{2}$$

Using Kr and Xe data from July 2012 and published values of D (Table 1) equation (2) was solved for n, yielding a value of 0.92. Typically n is between 1/2 and 2/3 [Raymond *et al.*, 2012]. Because D_{Kr} and D_{Xe} only differ by a small amount, the uncertainty in n is more than 50%. Nevertheless this value of n, and aqueous diffusion coefficients (Table 1), were subsequently used in equation (2) to provide estimates of the gas transfer velocities of SF₆ and CFC-11. Because D_{SF_6} is also not significantly different than D_{Kr} , the uncertainty in n contributes very little to uncertainty in K_{SF_6} .

Table 1. Aqueous Diffusion Coefficients Used in Gas Exchange Model^a

Campaign	Temp (°C)	D _{Kr} (10 ⁻⁹ m ² /s)	D _{Xe} (10 ⁻⁹ m ² /s)	D _{CFC11} (10 ⁻⁹ m ² /s)	D _{SF6} (10 ⁻⁹ m ² /s)	K ₆₀₀ (m/d)
July 2012	25.2	1.9	1.5	1.0	1.2	1.1
March 2013	12.3	1.3	1.0	0.73	0.85	1.5

^aSource: Kr and Xe [Jähne et al., 1987], CFC11 [Zheng et al., 1998], and SF₆ [King and Saltzman, 1995].

For comparison with values from other sites, K₆₀₀ is often reported in which K is normalized to a Schmidt number (ratio of kinematic viscosity of water to the aqueous diffusion coefficient) of 600, which is for example the value of

Schmidt number for O₂ in freshwater at a temperature of 17.5°C. K₆₀₀ values for July 2012 and March 2013 are 1.1 and 1.5 m/d and were computed as:

$$K_{600} = K_{field\ temp.} \left(\frac{600}{Sc_{field\ temp.}} \right)^{0.92} \quad (3)$$

where Sc is the Schmidt number that was computed using the empirical temperature dependence summarized in Table 1 of Raymond et al. [2012]. Raymond et al. [2012] also summarized empirical scaling equations for estimating K₆₀₀ from stream parameters such as velocity, slope, depth, discharge, and Froude number. The K₆₀₀ value from West Bear Creek in March 2013 is within 10% of the values predicted by models 1 and 2 in Table 2 of Raymond et al. [2012], but differs by a factor of four to five from these same models for the July 2012 campaign. The width and depth of West Bear Creek in July with low streamflow was nearly the same as in March with approximately ten times more streamflow. The average stream velocity in July was significantly lower than the average stream velocity considered by Raymond et al. [2012] for streams having discharge similar to the July value. The low stream velocity in July 2012 may be the primary reason for the poor agreement of the July gas transfer velocity with the empirical equations in Raymond et al. [2012]. This suggests that factors not considered by the empirical equations (e.g., wind shear and microbubbles [Beaulieu et al., 2012]) were important for conditions in July 2012.

4.3. Simulations of SF₆ and CFC-11 Stream Concentrations

Using values of streamflow, groundwater discharge rate, and gas transfer velocity as previously described, RADIN13 was used to simulate the concentrations of SF₆ and CFC-11 in stream water for both the July 2012 and March 2013 data sets. The measured stream concentration at X = 0 was used as a boundary condition, and the values of C_{atm}, Q, q_L, w, b, and K were assigned as previously described, to then simulate the downstream concentrations of SF₆. CFC-12 and CFC-113 were also measured, and while it appears that CFC contamination or degradation complicate the use of CFCs for age dating in some areas of the system, CFC-11 is included in the analysis simply as an example of deriving groundwater dissolved gas concentrations from stream water samples.

The primary unknown parameter in these simulations is the flow-weighted mean concentration of SF₆ or CFC-11 in groundwater discharge to the stream, C_{gw} in equation (1). The Excel Solver® was used to minimize the RMSD between measured and simulated tracer concentrations in the stream, to arrive at 0.55 fmol/L as the best estimate of C_{gw} for SF₆ in July 2012 (Figure 5). A similar procedure was used for simulating CFC-11 with the optimal C_{gw} value being 1.28 pmol/L.

While the optimization procedure described above involves only a single unknown parameter (C_{gw}), the “measured” parameters (q_L, C_{atm}, Q, w, b, K) all have uncertainty. We evaluated the uncertainty in the optimized value of C_{gw} that results from uncertainty in the other input parameters using a Monte-Carlo approach. The measured values were randomly varied using the NORMINV(RAND(),Mean,Stdev) function in Excel. Standard deviations, as a percentage of mean values, were assigned as follows (as best estimates of the uncertainty): Q, q_L, C_{atm} 3%; w,b 5%; K 15%. For each realization of input parameter values, the Solver® was used to find the value of C_{gw} that best fit the observed values. This was repeated 500 times to produce 500 estimates of C_{gw} with a mean value of 0.55 fmol/L and a standard deviation of 0.21 fmol/L (38%). This translates to an uncertainty in the MTT (assuming piston flow) of about ±4 years. The same procedure with uncertainties of 10% for all parameters resulted in an uncertainty in C_{gw} of 74% (+11 – 6 years for MTT).

Plotting the RMSD versus C_{gw} (Figure 6) illustrates that reasonably unique discharge concentrations were obtained using this procedure (i.e., there are well-defined minima for both SF₆ and CFC-11).

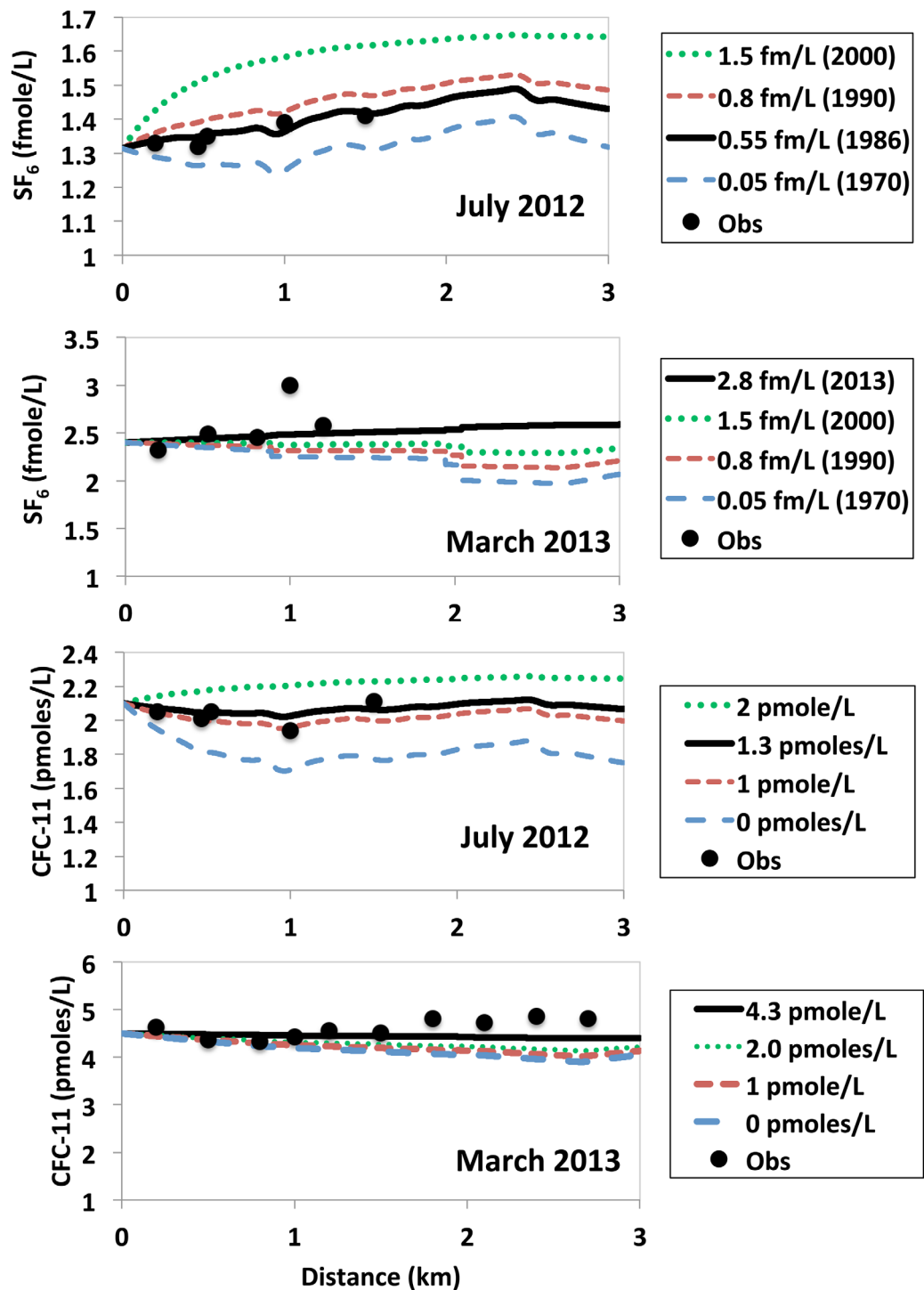


Figure 5. Stream water SF₆ and CFC-11 concentrations versus distance downstream of the injection site for July 2012 and March 2013, with simulated curves based on different mean groundwater concentrations for SF₆ and CFC-11. In July when stream flow consisted of a large fraction of groundwater discharge from within the study reach, the observed stream concentrations are uniquely fit with a mean groundwater concentration of 0.55 fmol/L for SF₆ and 1 pmol/L for CFC-11. In March the simulated stream concentrations were not very sensitive to the groundwater concentration due to much higher streamflows.

July 2012 C_{gw} values of 0.55 fmol/L for SF₆ and 1.28 pmol/L for CFC-11 correspond to apparent (piston-flow) recharge years of 1986 and 1971. The difference in apparent recharge years between SF₆ and CFC-11 is likely the result of some degradation of CFC-11 in the aquifer. Although in this system CFC-11 might not be an appropriate groundwater dating tool, our July 2012 results suggest that for both tracers it is possible to

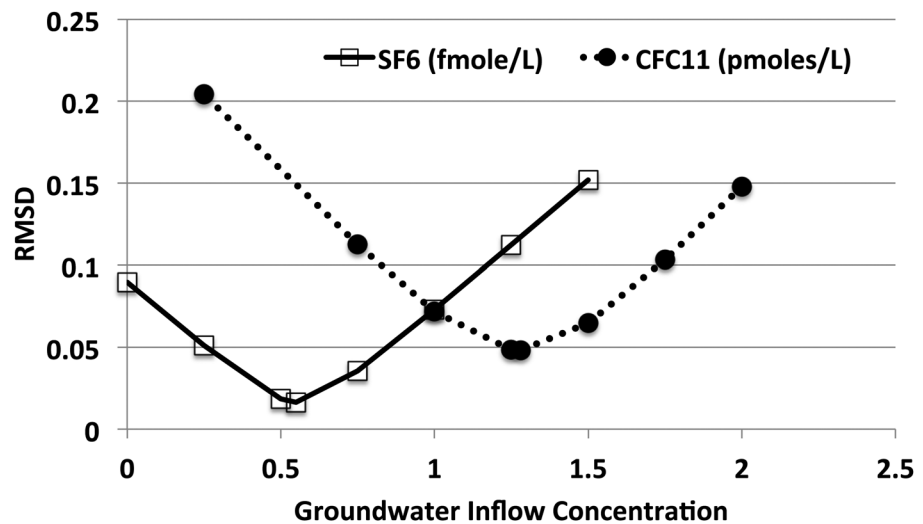


Figure 6. RMSD versus groundwater discharge concentration used in numerical model for SF₆ and CFC-11 in July 2012. Well-defined minima exist for both environmental tracers illustrating that unique values for the mean tracer concentration in groundwater can be derived from measurements in the stream. The total uncertainty in the groundwater inflow concentration is larger than illustrated as it also includes uncertainty in measured values (Q , q_L , C_{atm} , w , b , K) that were held constant while seeking the optimal value for C_{gw} .

estimate the mean concentration in groundwater discharge by measuring the concentration in stream water and correcting this (via a model such as RADIN13) for exchange with the atmosphere.

During March 2013, the observed stream water SF₆ seems consistent with an SF₆ C_{gw} value of about 2.8 fmol/L (Figure 5), reflecting a fundamentally different, wetter hydrologic regime during this campaign compared to July 2012. In July 2012 streamflow essentially doubled over the study reach (from 200 to 2700 m downstream of the injection site) due to groundwater seepage. Under the July 2012 flow conditions, the stream water concentration of SF₆ was sensitive to the C_{gw} value for SF₆ and less sensitive to exchange with the atmosphere. In March 2013, streamflow at the 200 m measurement station was 10 times larger than in July 2012 and the increase due to groundwater input between 200 and 2700 m was only about 18%, compared to 100% in July. The SF₆ stream water concentration is rather insensitive to the groundwater concentration (C_{gw}) and instead mostly reflects the input of very young water to the stream after a storm during the wettest time of year. A similar pattern is observed with CFC-11, with stream water concentrations being consistent with a C_{gw} of about 4.3 pmol/L for March 2013. The optimized values for the groundwater discharge concentrations of both SF₆ and CFC-11 for March 2013 are near the values that would be in equilibrium with the atmosphere at the temperature of the stream (2.8 fmol/L and 12 pmol/L, respectively). As discussed in the next section, groundwater samples collected directly from the streambed had similar SF₆ and CFC-11 values in July 2012 and March 2013 and these values are in good agreement with the optimized groundwater discharge values in our simulations for July 2012, but not for March 2013. We hypothesize that the inability of stream-based samples in March to reflect the value in groundwater discharge along the study reach was mostly an issue of dilution and loss of the groundwater signal when the total stream flow was 10 times higher and dominated by young stormflow or possibly bank storage.

5. Discussion

5.1. Comparison of Estimated SF₆ C_{gw} Values With Direct Measurements in Groundwater

SF₆ concentrations in streambed groundwater samples ($n = 10$) ranged from 0.17 to 2.14 fmol/L in July 2012, with lowest values (oldest water) occurring toward the center of the stream and highest values (youngest water) near the banks [Gilmore, 2015]. Seepage rates from the same 10 locations ranged from 0.06 to 144 cm/d with an average of 0.63 m/d [Gilmore, 2015]. However, the average seepage rate from all streambed measurements ($n = 39$) was 0.35 m/d, which is close to the groundwater discharge rate (0.36 m/d) determined by the Br injection described previously. At the ten streambed points at which both groundwater seepage rate and SF₆ concentration were measured in July 2012, the flow-weighted mean groundwater SF₆ concentration was 0.45 fmol/L [Gilmore, 2015], within about 20% (or about 3 years difference in

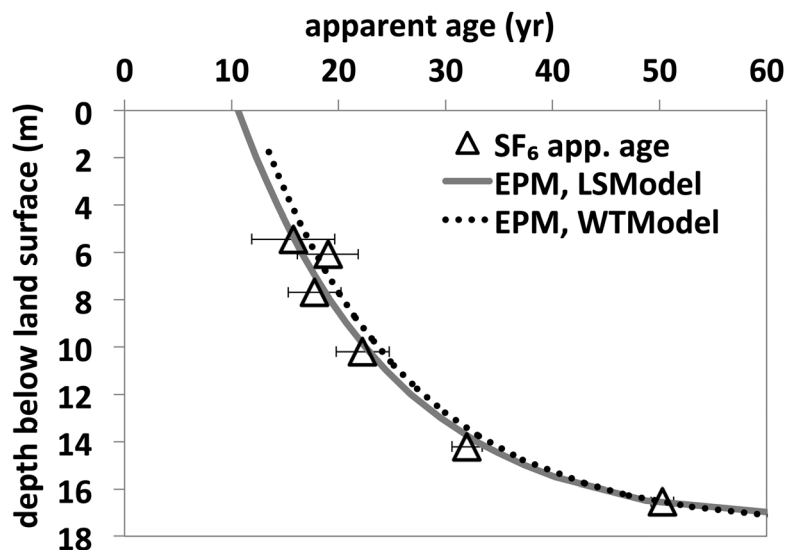


Figure 7. SF₆ apparent age versus depth (below land surface) from groundwater monitoring wells. Also shown are simulated curves for an exponential increase of age with depth assuming that the SF₆ “clock” starts at the water table (WTModel) and at land surface (LSModel). The associated recharge rates and mean transit times for these models are 200 mm/yr and 27 years for the WTModel, and 250 mm/yr and 25 years for the LSMModel.

apparent age) of the estimate of C_{gw} from stream water samples after correction for gas exchange (0.55 fmol/L). Streambed groundwater samples in March 2013 were from different transects but yielded a similar flow-weighted mean value of 0.51 fmol/L ($n = 9$).

In addition to groundwater samples from the streambed, in June 2013 we collected groundwater samples from nested wells near West Bear Creek (Figure 1) at depths below the water table ranging from about 3 to 15 m. Gilmore [2015] has details of the well installations and sampling. Noble gas concentrations in these groundwater samples suggested modest amounts of excess air ranging from 1.1 to 3.2 ccSTP/kg ($n = 6$, mean = 2.3, s.d. = 0.9 ccSTP/kg). The apparent SF₆ ages (corrected for excess air) are approximately consistent with an exponential increase of age with depth (Figure 7), assuming that the SF₆ “clock” starts at the water table (WTModel) or at the land surface (LSModel). However, apparent ages at the shallow wells were older than predicted by an exponential model based on uniform recharge to an unconfined aquifer of uniform thickness and porosity [Cook and Böhlke, 2000; Solomon et al., 2006]. The older ages at shallow depth could be related to shallow low-permeability layers restricting recharge near the wells [Gilmore, 2015]. The exponential-piston flow model (EPM) provides a better fit to the data (Figure 7); the EPM is based on recharge to an unconfined section of an aquifer lying upgradient of a confined section of the aquifer. The distribution of age with depth predicted by the EPM is an exponential in shape but with an offset in age at the upper boundary of the aquifer because no young groundwater (recharge) is replenishing the groundwater system during transport through the confined portion of the aquifer (Figure 7). Ages in the EPM are computed as:

$$\tau = \frac{L\theta}{R_{EPM}} \ln\left(\frac{L}{L-Z}\right) + \frac{L\theta}{R_{EPM}} \left(\frac{x^*}{x}\right) \quad (4)$$

where L is the saturated thickness, θ is porosity, z is depth in the aquifer, x is the length of the unconfined portion of the aquifer, x^* is distance downgradient (in the confined portion of the aquifer) from the edge of the confining layer, and R_{EPM} is the recharge rate in the unconfined portion of the aquifer.

Using a thickness of 18 m and a porosity of 0.35, the recharge rate (R_{EPM}) and x^*/x were adjusted in order to minimize the RMSD between observed and simulated ages. The recharge rates to the unconfined portion of the aquifer from the WTModel and LSMModel were 400 and 430 mm/yr, respectively. When averaged over the total length of the confined and unconfined portions of the aquifer ($R = R_{EPM}(1 + x^*/x)^{-1}$), the aerially averaged recharge rates R were 200 and 250 mm/yr, respectively. These recharge rates are close to the average value reported by McMahan et al. [2011] of 234 mm/yr for the northern Atlantic Coastal Plain. The

mean transit time was then computed as $MTT = (Ln/R_{EPM})(1 + x^*/x)$ [Solomon *et al.*, 2006]. This equation relates aquifer storage volume ($L\theta$), recharge rate (R_{EPM}), and the relative length of confined to unconfined portions of the aquifer (x^*/x) to the mean transit time from recharge to discharge from the aquifer (MTT). The MTT for the WTModel and the LSModel were 26.7 and 24.9 years.

The flow-weighted concentration of SF₆ in groundwater discharging into West Bear Creek in July 2012 was 0.55 fmol/L based on the stream water samples (corrected for exchange with the atmosphere) and 0.45 fmol/L based on the direct groundwater sampling in the streambed. The apparent piston-flow (PFM) SF₆ ages of these flow-weighted average concentrations are 26.5 and 28.5 years. Using the lumped parameter model TracerLPM [Jurgens *et al.*, 2012] with EPM ($x^*/x = 1.0$), we obtain MTTs of 34.5 and 37.5 for these same concentrations. These values are similar to the MTT estimates from the well samples, and indicate that flow-weighted mixtures of discrete groundwater flow paths can be mapped reasonably well to a mean value that is representative of the recharge rate and storage volume of the aquifer.

Similarity between the PFM and the EPM is expected when most of the individual transit times occur while the input function has been approximately increasing linearly with time (i.e., 1975 to present for SF₆). At the current point in time, differences in modeled concentrations of SF₆ between the PFM and the EPM ($x^*/x = 1$) are less than 5% when the MTT is less than 20 years, but rises to 38% and then 96% for MTTs of 30 and 40 years. These differences are even greater between the PFM and the EMM. Assuming that SF₆ continues to increase linearly in the atmosphere, the sensitivity of the modeled MTT to the TTD will decrease. For example, in 10 years from now the difference between the PFM and the EPM may be less than 5% for MTTs less than 30 years, and in 20 years from now the difference may be less than 5% for MTTs less than 40 years, and so on. While the insensitivity of the MTT estimates to the TTD is an advantage (when using SF₆ as a tracer) from a water resources perspective, a definition of the TTD is critical from a water quality perspective (i.e., when will a solute front arrive and how long will it take to transport all of it from the system?) Defining the TDD will require more than the approach outlined in this paper including the use of multiple tracers [Massoudieh and Ginn, 2011; Visser *et al.*, 2013], or direct sampling from the streambed [Gilmore, 2015].

5.2. Persistence of Groundwater Dissolved Gases in Streams

In the absence of significant gas exchange between the stream and the atmosphere (or for nonvolatile tracers), a gaining stream during base flow would have a tracer concentration that is similar to the flow-weighted average tracer concentration in groundwater. In contrast, when gas exchange is a strong process, a volatile tracer concentration in a stream will be controlled by atmospheric solubility and will bear little resemblance to the tracer concentration in groundwater. If we consider a stream that starts at a spring, maintains a constant width and depth, and receives only groundwater input, the concentration of a volatile tracer (e.g., SF₆) in the stream will depend on a balance between equilibration with the atmosphere and dilution (or loading for some gases) by discharging groundwater. In this model, the tracer concentration will be given by a simple solution to equation (1).

When the uptake of gas from the atmosphere is exactly balanced by dilution from groundwater, the concentration will be constant with distance [Solomon *et al.*, 1997, 2000] and the spatial derivative will be zero. Equation (1) then reduces to:

$$C_s = \frac{C_{gw} + C_{atm} \frac{Kw}{q_L}}{1 + \frac{Kw}{q_L}} \tag{5}$$

Equation (5) can be rewritten as:

$$\frac{C_{atm} - C_s}{C_{atm} - C_{gw}} = 1 - \frac{\alpha}{1 + \alpha} = \frac{\Delta_s}{\Delta_{gw}} \tag{6}$$

where $\alpha = \frac{Kw}{q_L}$ and Δ_i refers to the deviation from C_{atm} of the SF₆ concentration of water i (the stream water or groundwater).

We refer to equation (6) as the “uniform concentration model” because it shows the balance needed between groundwater input and gas exchange to achieve a uniform volatile tracer concentration in the stream water.

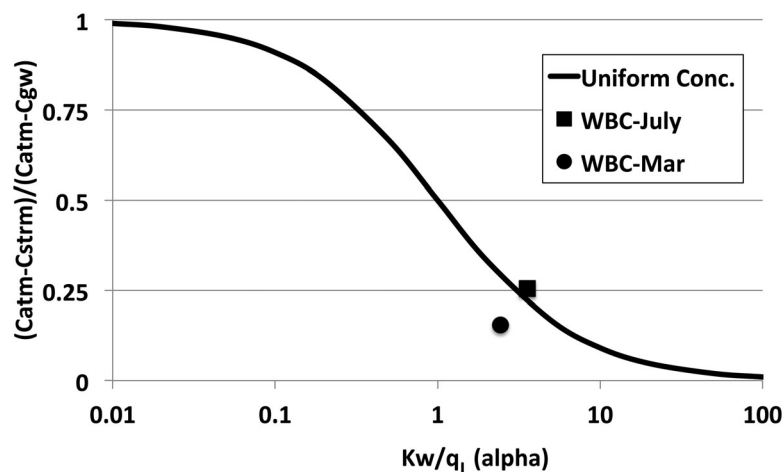


Figure 8. Semi-log plot of equation (6) (uniform concentration model), where points represent average conditions for the July 2012 and March 2013 field campaigns at West Bear Creek. Equation (6) can be used to estimate the extent to which gas exchange in the stream will alter the dissolved gas tracer signal (e.g., SF_6) of discharging groundwater. When Kw/q_L is greater than 10, less than 10% of the groundwater tracer signal will be retained in the stream.

The left-hand side of equation (6) is the ratio of the deviation of the stream concentration from the atmospheric solubility value to the deviation of the groundwater concentration from atmospheric solubility. The left-hand side of equation (6) can be thought of as the ratio of the apparent age in the stream to the apparent age of discharging groundwater. When α is large (gas exchange is strong), the ratio of the apparent age in the stream to the apparent age in groundwater will approach zero meaning that the stream will not contain a usable groundwater signal. When α is small, the apparent age ratio approaches unity and the tracer concentration in the stream will be similar to that of groundwater. When α equals 1, the uniform concentration model predicts that the deviation of the stream tracer concentration from C_{atm} will be 50% of the deviation of the groundwater tracer concentration C_{atm} . The uniform concentration model shows a sigmoidal dependence of $\Delta s/\Delta gw$ on $\log(\alpha)$ (Figure 8).

In July 2012, when streamflow was low and groundwater discharge over the 2.5 km study reach (200–2700 m) increased the total stream flow by 100%, $\Delta s/\Delta gw$ was about 27%. As previously discussed, correcting the July 2012 stream water concentration for gas exchange resulted in a reliable determination of the flow-weighted concentration in groundwater (i.e., the stream water contained usable information regarding the mean groundwater SF_6 concentration; Figure 6). Using the measured values of SF_6 in the stream water and groundwater along with gas transfer velocity (K), stream width (w), and groundwater discharge (q_L), $\Delta s/\Delta gw$ for July 2012 plots close to the theoretical value from the uniform concentration model (Figure 8). In contrast, during the March 2013 test with much higher total streamflow on the falling limb of the stream hydrograph, SF_6 concentrations in West Bear Creek were much higher than the flow weighted groundwater value from streambed piezometers, and as demonstrated in our previous modeling, C_s was not sensitive to the SF_6 concentration in groundwater. During March 2013, hydrologic conditions in West Bear Creek deviated substantially from the uniform concentration model because of the large and transient input of runoff, greater discharge from the small surface reservoirs feeding the stream, and shallow lateral subsurface flows [Gillmore, 2015]. Given the values for K , w , and q_L for the March 2013 test and the resultant computed value of α , the uniform concentration model suggests that the apparent age in the stream should have been about 30% of the groundwater value, rather than the observed 15% (Figure 8). This illustrates that in addition to considering gas exchange, one must consider whether or not water in a particular reach of stream during a particular sampling campaign consists mostly of groundwater discharge along the reach.

If a particular stream reach can be reasonably modeled using equation (5), then equation (6) and/or Figure 8 can be used to evaluate whether or not a volatile tracer signal might be preserved in streamflow.

Two criteria must be met. First, α must be less than about 10; at larger α values less than 10% of the groundwater signal will be retained by the stream due to gas exchange. For a typical stream gas transfer velocity of 1 m/d, the quantity q_L/w (which is the average-specific discharge through the streambed) would need to be greater than about 0.1 m/d in order to satisfy this first criterion. Second, the magnitude of the groundwater discharge and its associated tracer concentration must be large enough to make a measureable change in the tracer concentration in the stream. This criterion also applies to nonvolatile tracers [e.g., Cook, 2013].

The approach outlined in this paper involves simultaneous volatile and nonvolatile tracer tests in the stream, along with physical measurements of stream depth, width, and temperature, and then stream sampling for SF₆. These measurements provide input parameters to equation (1) and allow the flow-weighted mean groundwater inflow concentration (C_{gw}) to be obtained through an inversion procedure. An alternative approach is to estimate q_L using standard stream gauging methods (e.g., velocity area measurements at various distances along the reach) and to use the empirical equations summarized by Raymond *et al.* [2012] to estimate the gas transfer velocity. The success of this approach depends on the magnitude of α in equation (6). For WBC in July, 2012 with $\alpha = 3.6$ an uncertainty analysis in which q_L and K were varied randomly using the NORMINV(RAND(),Mean,Stdev) in Excel with Stdev = Mean \times 0.25, the optimized value for C_{gw} had a relative standard deviation of 46%. In other words, the uncertainty in C_{gw} from the optimization was about twice the uncertainty of q_L and K . So for WBC an uncertainty of less than 50% in C_{gw} could be obtained using standard stream gauging (typical uncertainty of 5%) instead of the Br tracer test, but would still require actual measurements of K rather than an estimate from empirical equations. However, at sites where α is smaller an empirically derived estimate of K might be sufficient.

6. Conclusions

When sampled under low flow conditions, we found that the stream concentration of SF₆ in West Bear Creek, NC USA was significantly lower than the concentration that would be in equilibrium with the modern atmosphere, due to discharging groundwater. By measuring the rate of groundwater discharge (from dilution of Br injected into the stream) and the gas transfer velocity (by injecting Kr and Xe), we calibrated a stream transport model to observed concentrations of SF₆ in the stream water. The resulting estimate of the mean SF₆ concentration in groundwater discharging into West Bear Creek (C_{gw} in equation (1)) is consistent with an apparent recharge year of 1986 (MTT of 26.5 years), similar to the estimate of 28.5 years from direct sampling of groundwater from the streambed (section 5.1). This is also similar to the MTT obtained from sampling groundwater monitoring wells (26–28 years) when an exponential-piston flow model is fit to the age versus depth data. When sampled under high flow conditions, the stream water SF₆ concentration was close to atmospheric equilibrium and was not sensitive to local groundwater seepage. At higher flow the MTT derived from the stream water concentrations was much younger than discharging groundwater and resulted from shallow, rapid flow associated with storm flow.

A simplified model of a gaining stream reach suggests that for a typical gas transfer velocity of 1 m/d, the groundwater seepage rate (specific discharge) into a gaining stream needs to be greater than 0.1 m/d in order for a stream to retain a dissolved gas tracer signal that allows determination of the mean dissolved gas tracer concentration in the groundwater discharging into the stream (C_{gw} in equation (1)). In addition, in order to evaluate recharge and MTT of a local groundwater flow system from C_{gw} , the total groundwater discharge within the study area must be sufficient to cause a measureable change in the age-dating tracer concentration in the stream.

When sampled under low flow conditions when stream flow consists of a high fraction of local groundwater discharge, West Bear Creek appears to act as a flow-weighted integrator of transit times, and stream water samples can provide recharge rates and MTT of groundwater in the surrounding aquifer. Our study suggests that it might be possible to obtain tracer-based field estimates of groundwater recharge rate and MTT at the watershed scale without utilizing monitoring wells.

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