

A Stream-Based Methane Monitoring Approach for Evaluating Groundwater Impacts Associated with Unconventional Gas Development

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Abstract

Gaining streams can provide an integrated signal of relatively large groundwater capture areas. In contrast to the point-specific nature of monitoring wells, gaining streams coalesce multiple flow paths. Impacts on groundwater quality from unconventional gas development may be evaluated at the watershed scale by the sampling of dissolved methane (CH₄) along such streams. This paper describes a method for using stream CH₄ concentrations, along with measurements of groundwater inflow and gas transfer velocity interpreted by 1-D stream transport modeling, to determine groundwater methane fluxes. While dissolved ionic tracers remain in the stream for long distances, the persistence of methane is not well documented. To test this method and evaluate CH₄ persistence in a stream, a combined bromide (Br) and CH₄ tracer injection was conducted on Nine-Mile Creek, a gaining stream in a gas development area in central Utah. A 35% gain in streamflow was determined from dilution of the Br tracer. The injected CH₄ resulted in a fivefold increase in stream CH₄ immediately below the injection site. CH₄ and $\delta^{13}\text{C}_{\text{CH}_4}$ sampling showed it was not immediately lost to the atmosphere, but remained in the stream for more than 2000 m. A 1-D stream transport model simulating the decline in CH₄ yielded an apparent gas transfer velocity of 4.5 m/d, describing the rate of loss to the atmosphere (possibly including some microbial consumption). The transport model was then calibrated to background stream CH₄ in Nine-Mile Creek (prior to CH₄ injection) in order to evaluate groundwater CH₄ contributions. The total estimated CH₄ load discharging to the stream along the study reach was 190 g/d, although using geochemical fingerprinting to determine its source was beyond the scope of the current study. This demonstrates the utility of stream-gas sampling as a reconnaissance tool for evaluating both natural and anthropogenic CH₄ leakage from gas reservoirs into groundwater and surface water.

Introduction

Natural-gas production in the United States has increased rapidly because of technological advances allowing extraction from unconventional resources (Dammel et al. 2011; Nicot and Scanlon 2012; Schnoor 2012). Horizontal drilling and hydraulic fracturing, the

process by which target formations are fractured to increase permeability, have made natural gas reserves in new areas of the country more accessible and increased the productivity of existing well fields. The widespread application of hydraulic fracturing has resulted in significant public concern about the environmental effects of this unconventional gas development on watersheds and ecosystems, including both surface and groundwater resources (Pelly 2003; Mufson 2009; Kargbo et al. 2010; Kramer 2011). Groundwater contamination is possible if fluids and (or) stray gases mobilized during gas development migrate upwards along faults, fractures, or wells (Lustgarten 2009; Dammel et al. 2011). Recent studies have established a possible linkage between increased methane (CH₄) concentrations in overlying aquifers with

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either traditional vertical oil and gas wells that were improperly completed or unconventional gas horizontal drilling and hydraulic fracturing (Van Stempvoort et al. 2005; Renner 2009; Osborn et al. 2011).

Our conceptual model of CH₄ transport from an underlying natural gas reservoir into an overlying aquifer is shown in Figure 1. CH₄ transport can occur as a dissolved phase in upwardly migrating fluids through porous media, fractures, and improperly completed well bores (Lacombe et al. 1995). This migration may be driven by upward vertical gradients through naturally occurring fractures or induced (enhanced) by the increased hydrostatic pressure, fracture connectivity, and buoyancy effects associated with the injection of lower-density freshwater into higher density brines of shale-gas reservoirs during hydraulic fracturing (Myers 2012). Another potential transport mechanism is by gas phase (stray or fugitive CH₄) migration through pressurized well bores, part of which may dissolve into shallow groundwater (Van Stempvoort et al. 2005; Darrah et al. 2012). A recent study found higher thermogenic gas concentrations in groundwater wells closer to hydraulically fractured gas development sites (Osborn et al. 2011). Interpretive numerical modeling of groundwater flow through fractures in the Marcellus shale to the overlying aquifer has shown that advective transport of dissolved CH₄ and other contaminants from a 30-m thick shale through 1500 m of overburden (predominantly sandstone aquifers) could occur within ten years of hydraulic fracturing (Myers 2012). Much of this groundwater may eventually discharge to gaining stream reaches. This inflow to the stream from different groundwater flow paths would provide an integrated signal of groundwater quality such as dissolved CH₄ and other potential contaminants from gas development for a larger capture area than samples from monitoring wells.

Jones and Mulholland (1998) found that both shallow (riparian zone) and deeper (bedrock) groundwater are potential sources of dissolved CH₄ in streams. While they identified shallow subsurface flow through riparian soils as the primary source of stream CH₄ in their study site (Walker Branch, Tennessee), the relative importance of these two sources likely varies with climate and hydrogeology. CH₄ and other dissolved gases, once in the stream, will eventually dissipate to the atmosphere (De Angelis and Lilley 1987; Kling et al. 1992; Jones and Mulholland 1998; Billett and Moore 2007). To address this, our approach includes a combined CH₄/Br stream injection experiment and 1-D transport modeling to both assess the persistence of dissolved CH₄ and determine the apparent gas transfer velocity (k) describing the rate of loss of CH₄ to the atmosphere and/or microbial consumption. The steady-state gas tracer injection method (Rathbun 1979; Yotsukura et al. 1983; Kilpatrick et al. 1989) has been widely applied for determining gas transfer between surface-water bodies and the atmosphere. Previous injections of dissolved-gas tracers for determining gas transfer velocities include: ⁸⁵Kr, methyl chloride, and C₃H₈ for evaluating stream reaeration (Tsvoglou 1967; Tsvoglou and Neal 1976; Wilcock 1984; Jin et al. 2012); SF₆ and

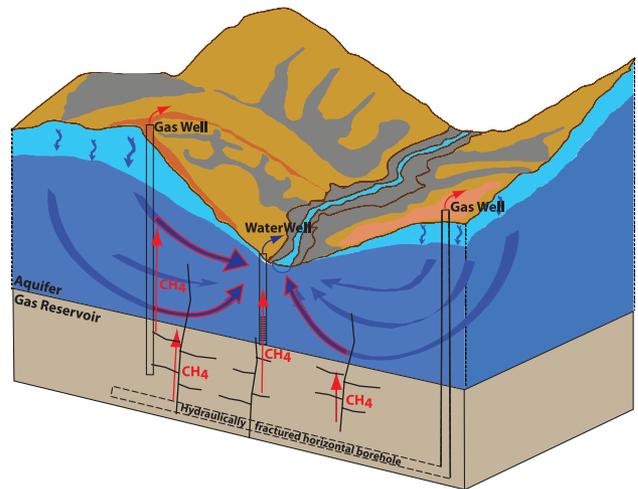


Figure 1. Conceptual model of methane transport from a hydraulically fractured gas reservoir to an overlying aquifer/stream system (vertical juxtaposition of aquifer directly overlying gas reservoir is a simplification—in many areas of natural gas development, these may be vertically separated by many thousands of meters).

C₃H₈ for investigating groundwater inflow/stream generation (Genereux and Hemond 1990, 1992; Wanninkhof et al. 1990; Cook et al. 2006); C₃H₈ for fluxes of CH₄ and CO₂ stream evasion to the atmosphere (Wallin et al. 2011); CFC-12 and ¹⁵N-enriched NO₃ for stream nitrogen fluxes (Duran and Hemond 1984; Bohlke et al. 2004); SF₆ for stream metabolism and denitrification estimates (Tobias et al. 2009), and He and Kr for groundwater dating (Stolp et al. 2010).

The objective of this study was to demonstrate the use of dissolved CH₄ in streams for assessing groundwater quality impacts associated with unconventional gas development. Invoking a conceptual model where groundwater ultimately discharges to gaining streams, this stream-based monitoring approach can provide a much broader evaluation than reported studies based on the sampling of monitoring wells (Breen et al. 2007; DiGiulio et al. 2011; Osborn et al. 2011). This work directly builds upon previous studies using gas injection to quantify groundwater CH₄ fluxes to streams (Jones and Mulholland 1998) and 1-D stream transport modeling to evaluate gas exchange (Cook et al. 2003, 2006) to develop a method for reconnaissance-scale evaluation of groundwater quality impacts from unconventional gas development. We report on the first direct determination of k_{CH_4} by CH₄ gas injection into a stream and combine this with other stream measurements in a transport model to quantify CH₄ fluxes from groundwater discharge.

Theory

The mass balance describing the change in CH₄ load with downstream distance (x) along a stream receiving groundwater inflow (modified from Cook et al. [2003,

2006]) is:

$$\frac{\partial QC}{\partial x} = IC_{\text{gw}} - \lambda_{\text{atm}}dw(C - C_{\text{eq}}) - \lambda_{\text{micr}}dWC + wEC \pm F \quad (1)$$

where Q is the stream discharge (L^3/T), C is the CH_4 concentration within the stream (M/L^3), I is the groundwater inflow rate per unit stream length ($L^3/L \times T$), C_{gw} is the CH_4 concentration of groundwater inflow including subsurface biogenic production in near-stream riparian zones (M/L), λ_{atm} is the gas transfer coefficient describing CH_4 loss to the atmosphere ($1/T$), d is the stream depth (L), w is the stream width (L), C_{eq} is the atmospherically equilibrated CH_4 concentration in the stream (M/L^3), λ_{micr} is a first order decay coefficient describing microbial consumption/oxidation ($1/T$), E is the evaporation rate (L/T), and F is the flux of CH_4 into or out of the hyporheic zone per unit stream length ($M/L \times T$). Wanninkhof et al. (1990) define the gas transfer velocity, k (L/T), as the product of the gas transfer coefficient, λ ($1/T$), and the stream depth, d (L).

Equation 1 can be reduced to a simpler CH_4 mass balance equation if the following assumptions can be made: (1) evaporative losses cause minimal stream CH_4 enrichment, (2) CH_4 fluxes into/out of the hyporheic zone are insignificant, and (3) an apparent gas transfer coefficient is used that combines atmospheric loss and microbial consumption. Regarding the third assumption, if C_{eq} is very small compared to C and treated as zero, then the λ_{atm} and λ_{micr} gas loss coefficients can be combined to a lumped ‘apparent gas loss coefficient, $*\lambda$ ($1/T$).’ Using the product rule, Q can be moved out of the derivative and the assumptions yield a simplified CH_4 mass balance (modified from Cook et al. [2003]):

$$Q \frac{\partial C}{\partial x} = I(C_{\text{gw}} - C) - *\lambda dwC \quad (2)$$

The CH_4 concentration of groundwater inflow to a stream (C_{gw}), therefore, can be evaluated by quantifying Q , I , C , d , w , and $*\lambda$. Q and I can be determined using tracer dilution techniques, C can be determined from gas chromatograph (GC) analysis of stream samples, d and w can be measured or determined during stream discharge measurements, and $*\lambda$ can be calculated by fitting dissolved-gas injection data using a 1-D transport model with gas transfer (Cook et al. 2003, 2006). Using this fitted value of $*\lambda$ with C measured prior to the tracer injection, C_{gw} (and CH_4 load) of groundwater discharging to the study reach can then be estimated in the transport model.

Site Description

Nine-Mile Creek is located in central Utah (Figure 2), about 60 km northeast of the town of Price. The study includes a 2300-m reach of the stream from the confluence of Daddy Canyon to the bridge just above the confluence with Unnamed Canyon. The geomorphic setting is an

upland wash within the Colorado Plateau Physiographic Province. Unconsolidated alluvium and fluvial deposits cover a small area along the narrow valley bottom and are presumed to be very thin. The exposed outcrop along the study reach of the stream is the Middle Member of the Eocene Green River Formation (Weiss et al. 1990). The Middle Member is characterized by light-gray and light-brown beds of mudstone, siltstone, and sandstone. Regionally this member of the Green River Formation ranges from 60 to 680 m thick. Aquifer testing in Piceance Creek Basin, Colorado, of the Parachute Creek Member (the Colorado equivalent of the Middle Member in central Utah; Self et al. 2010) yielded transmissivity values of 30–45 m^2/d (Ege et al. 1967).

The watershed of Nine-Mile Creek has a drainage area upstream of the lower end of the study reach (NMC-023) of 870 km^2 . The average stream gradient is 0.007 m/m. The tracer study was conducted during base-flow conditions (June 26–27, 2012), with an average depth (d) of 0.12 m, an average width (w) of 3.8 m, and an average stream velocity of 0.26 ± 0.09 m/s (1σ). Stream temperature varied from 12 to 21 °C. The estimated surface evaporation rate, based on studies in southern Utah (Marston and Heilweil 2013) is about 0.008 m/d, resulting in an evaporative loss of about 70 m^3/d for the study reach.

Methods

The conservative tracer dilution/synoptic sampling approach (Kilpatrick and Cobb 1985; Bencala and McKnight 1987; Kimball and Runkel 2009) was used to calculate Q and then determine I for each of 16 stream subsections along the Nine-Mile Creek study reach. Br was used as the conservative tracer, as it is generally found in very low concentrations in surface water. The Br-dilution method has been documented in previous applications to evaluate mass loading from mine drainage to streams (Kimball et al. 2002; Runkel et al. 2007). A NaBr solution was mixed using stream water from Nine-Mile Creek and pumped into the stream using a positive displacement piston pump (Fluid Metering, model QB), fitted with a sensor to allow control of revolutions with a Campbell CR10 data logger for providing a uniform and consistent quantity of Br to the stream. The injectate solution had a Br concentration of 230 g/L and was injected into the stream at a rate of 50 mL/min for a period of 24 h. During the synoptic sampling, stream water was collected at 25 sites along the 2300-m study reach downstream of the injection (Figure 2). This included three auto samplers (T1, T2, and T3) located 414, 1421, and 2030 m below the injection site, which collected hourly stream samples both prior to and during the injection to determine when the concentration plateau was reached. Water samples were collected in 125-ml polyethylene bottles rinsed with de-ionized water, filtered to 0.45 μm , and analyzed by ion chromatography using a Dionex DX-120.

Concurrent with the Br injection, CH_4 gas was injected into Nine-Mile Creek (as an analog to CH_4 -laden groundwater inflow) to evaluate its persistence in

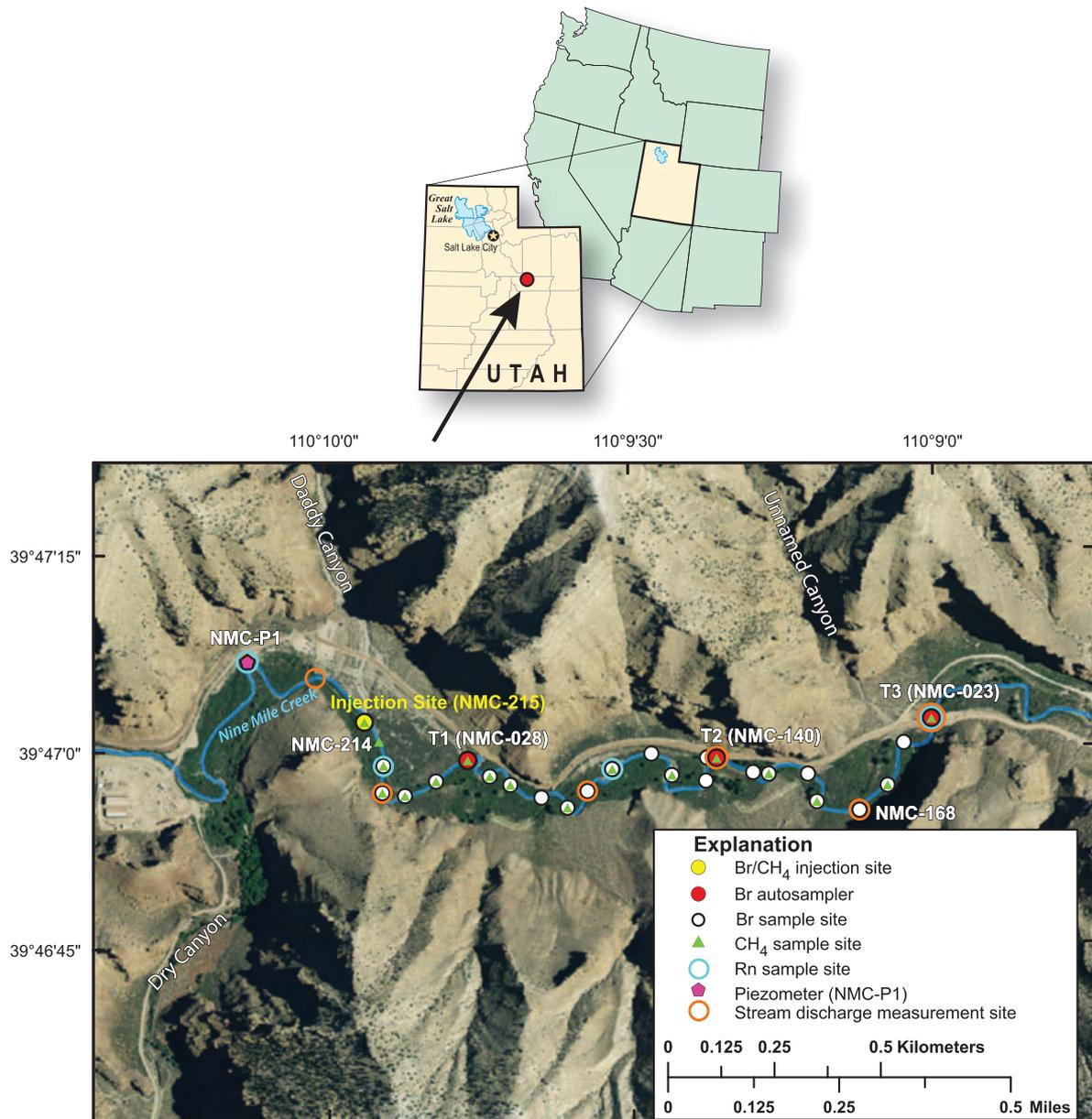


Figure 2. Site location map for the Nine-Mile Creek study area, Utah.

the stream and determine the gas transfer velocity (k). Following the gas-injection method described by Stolp et al. (2010), gas from a tank containing 99.5% pure CH_4 was discharged through 91.5 m of gas-permeable silicon tubing placed on the stream bottom for a 26-hour period. The average flow rate of CH_4 through the tubing was $370 \text{ cm}^3/\text{min}$; average line pressure was 88 kPa. The silicon tubing (peroxide-cured dimethyl silicon) has a 12.7-mm outside diameter and a 1.6-mm wall thickness. The approximate effective diffusion coefficient of the silicon tubing for CH_4 is $3.7 \times 10^{-5} \text{ cm}^2/\text{s}$ and was determined by tank experiments. This value was later confirmed by comparing theoretical to measured results in Nine-Mile Creek just below the injection site.

CH_4 samples were collected both prior to and during the injection at 17 stream sites along the 2300-m stream reach between Daddy Canyon and Unnamed Canyon

(Figure 2). Sampling during the injection began 0.69 d after a plateau in stream CH_4 was achieved at NMC-214 (50 m below the injection site). CH_4 samples were also collected (1) during a 24-h period at NMC-215, just above the injection site, to evaluate the background diurnal variation; and (2) in the NMC-P1 piezometer installed 0.5 m into the stream bed sediments along a gaining reach 400 m above the injection site to directly evaluate groundwater inflow chemistry. Unfortunately, attempts to install drive-point piezometers at three other downstream locations were not successful because of large cobbles in the stream bed.

Samples for CH_4 concentration and isotopic ($\delta^{13}\text{C}_{\text{CH}_4}$) analysis were collected in 250- and 125-mL glass bottles, respectively, using open-cap lids with silicone/Teflon septa. CH_4 concentration was analyzed with a field GC (PID Analyzer model HNU311). CH_4

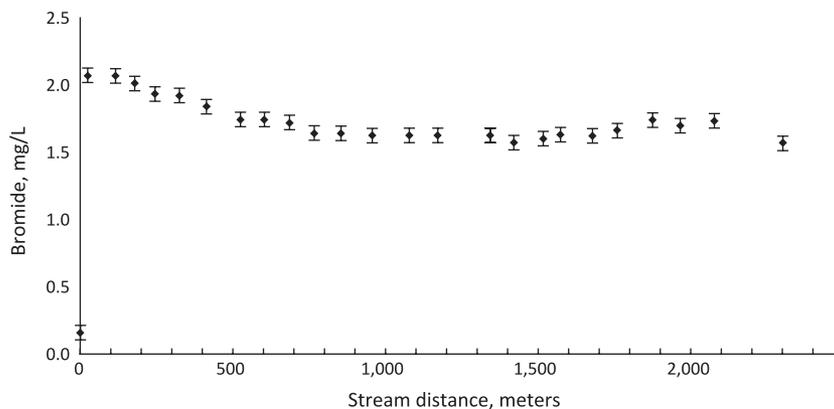


Figure 3. Bromide concentrations in Nine-Mile Creek during the tracer injection.

precision, based on calibration to CH_4 standards and replicate measurements, was about 60 nmol/L (1 ppb). A small number of these analyses were complicated by “coring” of the septum, which plugged up the syringe used to extract the head space and inject it into the gas chromatograph, and caused artificially low readings. Each water sample, therefore, was analyzed at least two times on the field GC and the highest CH_4 measurement from replicate samples was used. In addition, a subset of CH_4 samples was analyzed at the USGS Reston Chlorofluorocarbon Laboratory on a Hewlett Packard Model 5890 GC with a minimum reporting limit and precision of 30 nmol/L (0.5 ppb) for quality assurance. $\delta^{13}\text{C}_{\text{CH}_4}$ was analyzed by the University of Arkansas Stable Isotope Laboratory using a Picarro Instruments G2201-i.

Other supporting data included acoustic Doppler current profiler (SonTek YSI FlowTracker) stream discharge measurements conducted at seven locations along the study reach (Figure 2), field parameters (temperature, specific conductance, pH, dissolved oxygen, total dissolved-gas pressure), major/trace ion chemistry, and dissolved radon ($^{222}\text{Rn}_{\text{aq}}$). The $^{222}\text{Rn}_{\text{aq}}$ samples were collected in 250-mL glass bottles with polycone lids (to minimize head space) and analyzed within 4 d of collection with an electronic radon detector (DurrIDGE Rad7). $^{222}\text{Rn}_{\text{aq}}$ is a radioactive noble gas produced as the direct decay product of ^{226}Ra during uranium/thorium decay and has a half-life of 3.83 d. The groundwater concentration of $^{222}\text{Rn}_{\text{aq}}$ will increase until secular equilibrium, whereby the radioactive production rate is equal to the decay rate (Cook et al. 2003). Because of its near-zero atmospheric concentration and negligible production within the river (Cook et al. 2006), any elevated $^{222}\text{Rn}_{\text{aq}}$ values in the stream indicate a groundwater source.

Results

The background stream Br concentration at the injection site was 0.15 mg/L. During the injection, the highest stream Br concentration of 2.0 mg/L was measured at NMC-214, located 50 m below the injection site. Br

concentrations generally decreased to 1.57 mg/L at site NMC-140 (1420 m downstream), indicating an overall gaining stream reach (Figure 3). Groundwater inflow along this upper reach is assumed to have low Br, as indicated by a Br concentration of only 0.045 mg/L in a water sample collected from the NMC-P1 piezometer. Lower along the reach, five consecutive stream sites between 1420 and 1880 m (NMC-140 to NMC-168) showed a trend of increasing Br (1.57–1.74 mg/L). While this overall change is not much larger than the 0.1 mg/L analytical uncertainty, the consistency of the trend indicates a groundwater influx of Br to the stream (perhaps from Br-rich hydraulic fracturing fluids). Because the Br dilution method does not work if there are other sources of Br, stream Br was only used to quantify stream gain from groundwater inflow along the upper part of the study reach (0–1420 m). The combined uncertainty in stream Br and ion chromatograph analytical precision, was evaluated by determining the relative standard deviation (RSD) for the time series of bromide samples collected at T1, T2, and T3 during a 4-h synoptic sampling run on June 27, 2012. The RSDs at these sites were 1.2, 3.7, and 3.6%, respectively, with a mean RSD value of 2.4%, leading to an uncertainty of calculated stream discharge ranging from 2.4 to 3.4 L/s. Calculated discharge using the Br dilution method in the upper reach increased from 94 ± 2.4 L/s at the injection site to 127 ± 3.5 L/s at NMC-140, located 1420 m downstream (Figure 4). This increase in Q by 33 L/s indicates a 35% gain from groundwater inflow along the upper portion of the study reach.

Measured Q with a flow meter at seven sites along the study reach ranged from 79 to 117 L/s with estimated uncertainties of 1.4–7.8% (Figure 4). Estimated Q by both Br dilution and flowmeter measurements at the same five locations (0, 180, 410, 950, and 1420 m) differed by $10 \pm 8\%$ (1σ). The largest differences (16 and 20%, respectively) occurred along the upper part of the study reach (0 and 180 m). These discrepancies between the Br dilution and flowmeter measurements are greater than their combined uncertainties, indicating

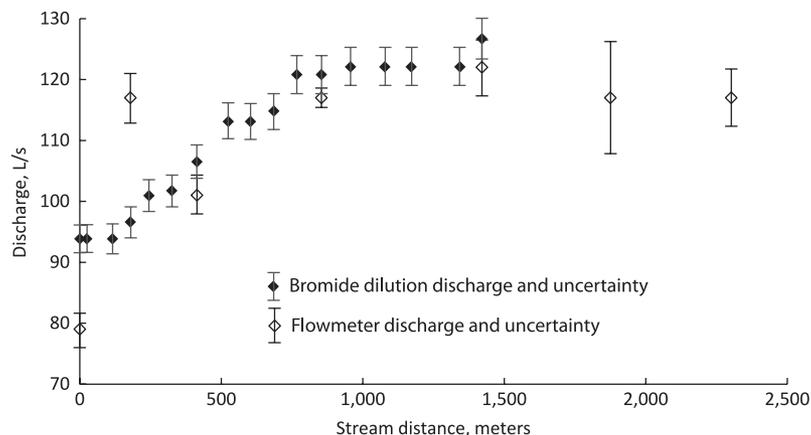


Figure 4. Nine-Mile Creek discharge determined from Br dilution and flow meter measurements.

that useful information regarding Q can be discerned from the contrasting results of these two methods. Unlike Br dilution, the flowmeter measurements can show both stream gain and loss. While the Br-based calculations show a gradual net gain along the upper 400 m of the study reach, the flowmeter measurements indicate both strongly gaining and losing sections along Nine-Mile Creek. The 35% Br-based gain in streamflow may be a minimum value; comparison of the upper and lower (NMC-214 and NMC-023) flowmeter measurements suggest the gain may be more than 40%. If groundwater inflow along the upper 400 m of the stream does contain Br (as proposed for the lower end of the study reach), this could also explain the discrepancy between the Br-dilution and flowmeter results. Flowmeter measurements for the NMC-140, -168, and -023 sites were used for evaluating Q from 1420 to 2300 m. Although these measurements show no net gain in Q , they have a relatively large uncertainty compared to the Br-dilution calculations for the upper part of the study reach. Increases in both stream Br (discussed above) and stream CH_4 (discussed below) indicate at least some groundwater inflow along the lower section of the study reach. The combined chemical and flowmeter data, therefore, support the interpretation that the lower part of the study reach contains both gaining and losing sections.

In summary, the Br-dilution and flowmeter measurements indicate that most of the gain in Q occurs in the upper part of the study reach (0–1420 m), with no net gain along the lower part. This is supported by stream $^{222}\text{Rn}_{\text{aq}}$, which decreased from 3.15 mBq/L at 50 m to 1.5 mBq/L at 960 m and 0.7 mBq/L at 2300 m. Higher $^{222}\text{Rn}_{\text{aq}}$ stream concentrations indicate the proximity of significant amounts of groundwater inflow since its source is predominantly in the subsurface; a concentration of 8.7 mBq/L from the NMC-P1 piezometer confirms that groundwater in the Nine-Mile watershed is elevated in $^{222}\text{Rn}_{\text{aq}}$. While only three stream $^{222}\text{Rn}_{\text{aq}}$ samples were analyzed during this study, it is a useful tracer of groundwater inflow that could be applied to a greater extent in future stream-based CH_4 studies.

The injected stream CH_4 was used to evaluate its persistence, the apparent gas transfer velocity ($*k$),

and the CH_4 load from groundwater inflow. Based on blanks, standards, and replicates, it was determined that field GC CH_4 measurements were not as accurate as the USGS Reston CFC Laboratory GC measurements. For quality assurance, a subset of four CH_4 samples was analyzed using both the field and USGS Reston CFC Laboratory GCs. The field GC measurements for these samples were generally about 15% higher than the laboratory GC values and were corrected using a linear least squares relation, although it is possible that there was some CH_4 loss from microbial consumption as the laboratory samples were run several days later and were not preserved. Corrected background CH_4 in the stream prior to the tracer injection ranged from 80 to 200 nmol/L (1.2 to 3.2 ppb; Figure 5). The highest background values occurred along the lower end of the study reach, with CH_4 more than doubling between 1760 and 2300 m. During the injection experiment, corrected CH_4 stream concentrations at NMC-214 (50 m) reached a plateau concentration of about 1000 nmol/L (16 ppb) about 5 h after the start of injection. Synoptic sampling began 16 h after plateau concentrations were achieved and held steady at NMC-214 to ensure tracer equilibrium along the entire study reach. Stream CH_4 generally declined downstream of the injection to NMC-140 (1420 m), at which point the analytical uncertainty of the background and injection concentrations overlapped. This decline in CH_4 is attributed to stream concentrations moving toward equilibrium with air-saturated water (C_{eq}) through gas transfer with the atmosphere. Stream CH_4 concentrations were also measured over a diurnal cycle just upstream of the injection site to evaluate natural fluctuations. Results show that background values varied from about 140–200 nmol/L (2.3–3.1 ppb), following an inverse relationship with stream temperature, which varied from 12 to 21 °C. This illustrates CH_4 's temperature-dependent Henry's Law solubility (Figure 6), although some of this change may also be caused by variability in CH_4 production/consumption or gas transfer velocity. Similar diurnal stream CH_4 fluctuations have been reported by Fedorov et al. (2003).

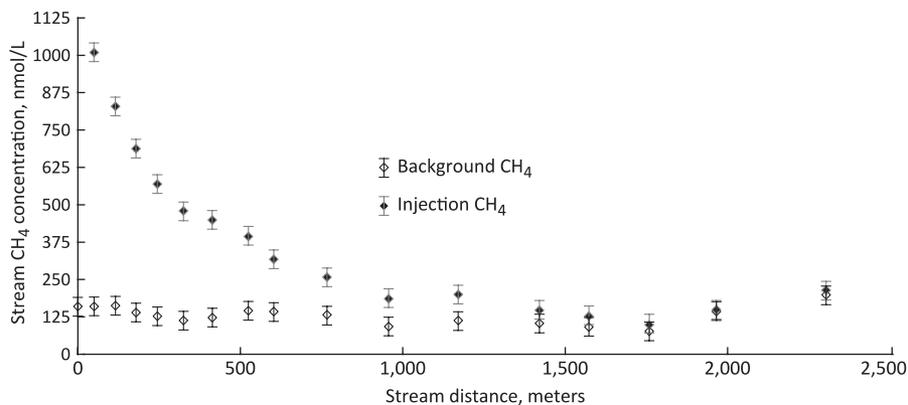


Figure 5. Background and injected methane concentrations along Nine-Mile Creek.

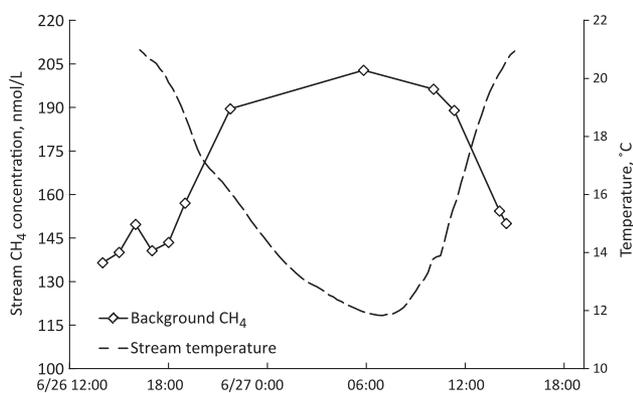


Figure 6. Nine-Mile Creek background methane concentration and water temperature.

Differences in background and injected $\delta^{13}\text{C}$ of the CH_4 molecule ($\delta^{13}\text{C}_{\text{CH}_4}$) were exploited to provide a more sensitive indicator of CH_4 persistence than was possible with total CH_4 measurements. $\delta^{13}\text{C}_{\text{CH}_4}$ has been previously used for examining the fate of stream CH_4 entering estuaries (Sansone et al. 1999). The tank $\delta^{13}\text{C}_{\text{CH}_4}$ was about -27‰ , whereas the background stream CH_4 varied between -49 and -54‰ (Figure 7). The $\delta^{13}\text{C}_{\text{CH}_4}$ results show the injected CH_4 traveled downstream to at least 1760 m and possibly as far as 2300 m, compared to more than 1500 m using total CH_4 . Because of the isotopic difference between the injected and natural CH_4 in Nine-Mile Creek, this experiment also illustrates the potential use of stream $\delta^{13}\text{C}_{\text{CH}_4}$ for evaluating groundwater sources of stream CH_4 .

Modeling

A 1-D stream transport model with gas exchange (Cook et al. 2003, 2006) was used to quantify CH_4 concentrations and load from groundwater discharge to Nine-Mile Creek. The measured stream CH_4 concentrations (C) during the tracer injection were compared to simulated values by solving the simplified version of the stream CH_4 mass balance (Equation 2) for each of 16 segments representing subreaches of Nine-Mile Creek. The

following are justifications for the simplifying assumptions needed to estimate groundwater CH_4 concentration and load with Equation 2: (1) Minimal evaporation loss: based on the estimated evaporative loss of about $70\text{ m}^3/\text{d}$ ($8 \times 10^{-7}\text{ L/s}$) from Nine-Mile Creek during the injection test, this loss represents less than 0.000001% of the stream discharge; (2) Insignificant CH_4 flux from/to the hyporheic zone: data from the three Br autosampler sites show a sharp bromide breakthrough, followed by a steady stream concentration over the duration of the Br injection, indicating piston flow; if there were significant hyporheic zone circulation in the streambed beneath Nine-Mile Creek, Br at these sites would have risen much more slowly due to hydrodynamic dispersion associated with these additional pathways; (3) C_{eq} is small and can be neglected: the CH_4 concentration of atmospherically equilibrated stream water (C_{eq}) was evaluated using the relation (modified from Aeshbach-Hertig et al. 2008) $C_{\text{eq}} = C_{\text{atm}}/H$, where C_{atm} is the atmospheric CH_4 mixing ratio (assumed to be 1700 nmol/mol based on a 2003–2008 Utah average reported by Frankenberg et al. 2011) and H is the Henry's Law CH_4 solubility (1.53×10^{-3} to $1.89 \times 10^{-3}\text{ mol/kg/atm}$ for the 12 – 21 °C stream water, based on $H = 1.42 \times 10^{-3}\text{ mol/kg/atm}$ at 25 °C with a temperature-dependent slope correction of 1600 °K ; Lide and Frederikse 1995). The resulting C_{eq} ranges from 2.4 to 3.0 nmol/L , or about 1.5 orders of magnitude lower than the highest stream CH_4 concentrations measured during the Nine-Mile Creek CH_4 injection experiment.

Using Equation 2, an apparent gas transfer velocity for CH_4 ($*k_{\text{CH}_4} = *\lambda d$) was determined numerically with a 1-D transport model using the specified stream parameters and atmospheric boundary conditions given in Table 1. While the simulated groundwater inflows maintain the same total stream gain of 33 L/s , the individual subsection rates were smoothed in the numerical simulation (Figure 8) because a large part of their variability is attributed to uncertainty in calculated inflows (2.3 – 3 L/s based on a RSD of 2.4% , similar in magnitude to the subsection inflow rates). Using a linear least-squares fit, the best-fit value for $*k_{\text{CH}_4}$ is $4.5 \pm 1\text{ m/d}$ (Figure 9). Based

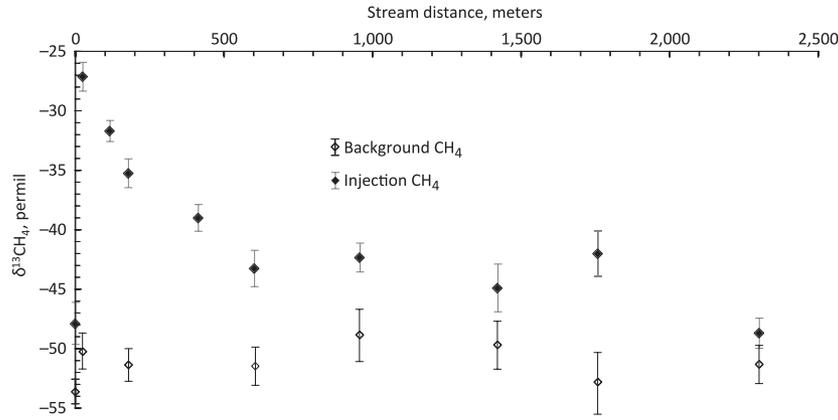


Figure 7. Background and injected $\delta^{13}\text{C}_{\text{CH}_4}$ concentrations along Nine-Mile Creek.

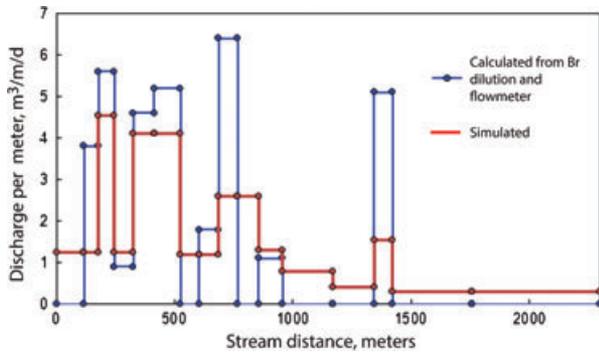


Figure 8. Groundwater inflow to Nine-Mile Creek calculated from Br-dilution and flowmeter data, compared with smoothed values used in the numerical simulation.

on an average stream depth of 0.12 m, the apparent gas transfer coefficient ($*\lambda$) is $38 \pm 8/\text{d}$.

Using a $*k_{\text{CH}_4}$ value of 4.5 m/d, the 1-D transport model was then calibrated to background stream CH_4 largely by varying C_{gw} (but also I_{gw} within the uncertainty of stream gain calculations) to evaluate natural CH_4 concentrations and loads (Figure 10). Using a linear least squares regression, simulated groundwater inflow CH_4 concentrations (c_{gw}) ranged from 0 to 14,000 nmol/L (0–230 ppb) for the 16 stream subsections. The upper end of this range is within the same order of magnitude as the CH_4 concentration of the NMC-P1 groundwater sample (45,000 nmol/L). CH_4 loads of 0 to 90 g/d were calculated for the stream subsections by multiplying these CH_4 concentrations by the groundwater inflow rate. The total simulated CH_4 load from groundwater inflow for the entire study reach was 190 g/d. The largest simulated CH_4 load was located along the lower end of the study reach (1760–2300 m). This coincides with the observed increase in background CH_4 from 70 to 200 nmol/L (1.2 to 3.2 ppb) along this section of the stream.

Discussion

The calculated $*k_{\text{CH}_4}$ of 4.5 ± 1 m/d ($*\lambda = 38 \pm 8/\text{d}$) was compared to other reported k values by conversion

Table 1
Specified Model Parameters for Simulation of Methane Concentrations Along Nine-Mile Creek, Utah

Parameter	Symbol	Value	Unit
Initial stream discharge	Q_{str}	8100	m^3/d
Subsection groundwater inflow rate per unit stream length ¹	I	0.0–5.6	$\text{m}^3/\text{m}/\text{d}$
Background stream CH_4 concentration	C_0	160	nmol/L
Injection initial stream CH_4 concentration	C_i	1000	nmol/L
Stream CH_4 concentration in equilibrium with the atmosphere	C_{eq}	2.7	nmol/L
Stream length	L	2300	m
Stream width	w	2.7 to 4.9	m
Stream depth	d	0.10 to 0.15	m
Apparent CH_4 gas transfer velocity ²	$*k_{\text{CH}_4}$	4.5 ± 1	m/d

¹Based on Br dilution for upper 1400 m and flowmeter measurements for lower reach.

²Determined by calibrating to injected methane; used for evaluating natural methane load of groundwater inflow.

to the k_{600} value (revised from Jahne et al. [1987, equation 2]):

$$k_{600} = k_{\text{gas}} \left(\frac{600}{SC_{\text{gas}}} \right)^{-n}$$

where k_{600} is the gas transfer velocity in freshwater for a gas having a Schmidt number of 600 (CO_2 at 20°C or O_2 at 17.5°C), k_{gas} is the gas transfer velocity for a particular injected gas, SC_{gas} is the Schmidt number (ratio of the kinematic viscosity of water divided by the diffusion coefficient of the gas) based on empirical relations defined by Raymond et al. (2012), and n is the Schmidt number exponent, which can range from 0.5 for the classic surface renewal model to 1.0 for the film model (Jahne et al.

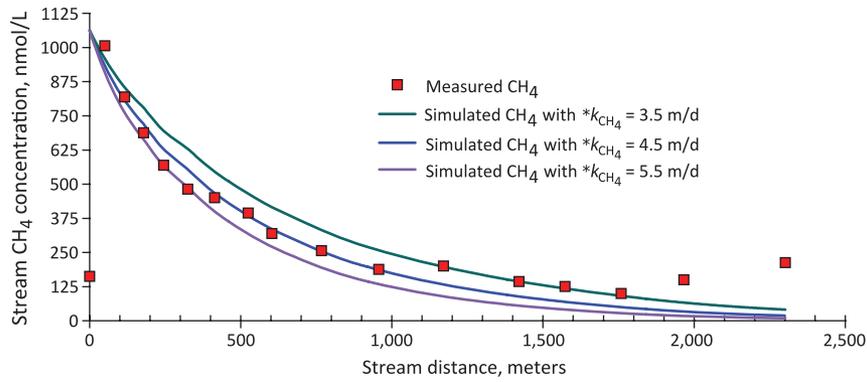


Figure 9. Simulated Nine-Mile Creek stream methane concentrations using a 1-D transport model with gas transfer.

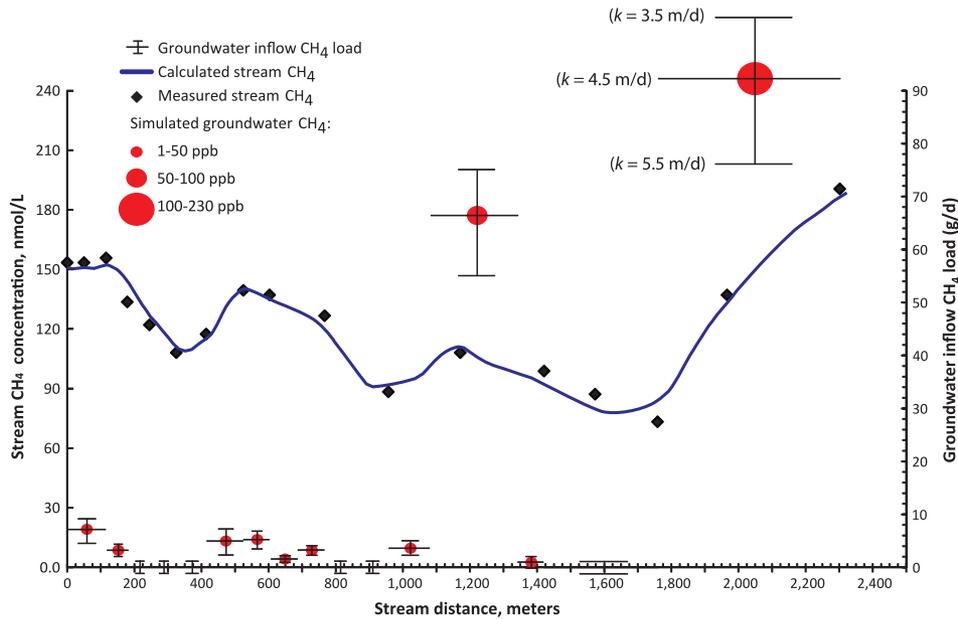


Figure 10. Background Nine-Mile Creek stream methane concentrations and simulated methane loads of groundwater inflow.

1987). Following Wanninkhof et al. (1990, equation 7) and Raymond et al. (2012, equation 3), an n value of 0.5 was used for all calculations; a sensitivity analysis showed that increasing the n value to 1.0 increases k_{600} values from 10 to 110%. The $*k_{600}$ value for Nine-Mile Creek of 5.0 m/d is within the range of previously reported stream gas tracer injection results of 0.6–54 m/d (Table 2). These k_{600} values are for streams with gradients (0.0004–0.068) and discharge values (0.02–0.68 m³/s) that bracket those of Nine-Mile Creek (0.007 and 0.12 m³/s).

The k_{600} values of streams can also be predicted with empirically derived equations. Predicted k_{600} values using average stream velocity, slope, and water depth (equation 1 of Table 2 in Raymond et al. 2012) range from 20 to 330% of the k_{600} values calculated from gas injection tests. This level of uncertainty may be sufficient for an initial modeling evaluation of whether significant amounts of groundwater CH₄ are discharging to the stream; it could be followed up by a field-based gas tracer injection to more precisely determine k for a quantitative assessment of groundwater CH₄ concentrations and loads.

While CH₄ consumption through anaerobic oxidation is an important process in high-sulfate marine sediments and other reducing conditions, the magnitude of such degradation may not be significant in freshwater environments including streams and estuaries (De Angelis and Lilley 1987). Bopp et al. (1981) reported relatively small biological consumption of 0.01–0.1/d for CH₄ in model estuarine ecosystems, several orders of magnitude lower than reported gas transfer coefficients for CH₄. Genereux and Hemond (1990) suggested that biological degradation of propane (C₃H₈) in small streams would be even slower and would not be a significant factor in the evaluation of k . While the Nine-Mile Creek $*k$ value determined by CH₄ injection may include some non-conservative loss of CH₄ in the stream through bacterial consumption, quantification of this loss was not within the scope of the current study; further work is in progress.

The uncertainty in calculated groundwater CH₄ concentrations and loads discharging to Nine-Mile Creek is primarily caused by both the range in calculated $*k_{CH_4}$ (3.5–5.5 m/d) and uncertainty in groundwater inflow

Table 2
Gas Transfer Velocity and Other Stream Parameters For This and Previous Studies

Location	Tracer Gas	Experiment k_{600} (m/d) ¹	Empirical k_{600} (m/d) ²	Difference Between Experimental and Empirical k_{600} (%)	Gas Transfer Velocity (m/d)	Gas Transfer Coefficient (1/d)	Stream Slope	Depth (m)	Temperature (°C)	Stream Velocity (m/s)	Stream Discharge (m ³ /s)	Reference
Nine-Mile Creek, UT	CH ₄	5.0	5.8	117	4.5	37.5	0.007	0.12	16.5	0.26	0.12	This study
Fischa, Austria	⁴ He	13.1	8.4	64	15.0	50.1	0.005	0.30	11.2	0.35	0.68	Stolp et al. (2010)
Fischa, Austria	⁸⁴ Kr	9.0	8.4	94	7.0	23.3	0.005	0.30	11.2	0.35	0.68	Stolp et al. (2010)
Cockburn River 0–10 km, Australia	SF ₆	2.1	3.4	157	1.6	6.4	0.003	0.25	17.6	0.24	0.41	Cook et al. (2006)
Cockburn River 10–33 km, Australia	SF ₆	2.1	7.1	331	1.6	2.1	0.003	0.75	17.6	0.29	0.58	Cook et al. (2006)
West Fork Walker Branch, TN	SF ₆	10.5	7.4	70	7.0	70.0	0.038	0.10	13.5	0.07	0.02	Wanninkhof et al. (1990)
West Bear Creek, NC	⁸⁴ Kr	1.4	0.8	58	1.6	5.3	0.003	0.3	24.9	0.05	0.10	D. Solomon, written comm. 2/6/2013
Panther Creek, TN 7/26/2006	C ₃ H ₈	3.1	1.9	61	2.4	24.4	0.007	0.1 ³	20.0	0.09	0.06	Jin et al. (2012)
Panther Creek, TN 8/30/2006	C ₃ H ₈	3.2	2.0	60	2.5	22.3	0.007	0.113 ³	20.0	0.09	0.06	Jin et al. (2012)
Ledbetter Creek, TN 7/26/2006	C ₃ H ₈	0.7	1.0	140	9.5	5.4	0.006	0.101 ³	20.0	0.05	0.03	Jin et al. (2012)
Ledbetter Creek, TN 9/1/2006	C ₃ H ₈	1.1	0.9	77	0.9	9.8	0.006	0.09 ³	20.0	0.04	0.03	Jin et al. (2012)
Little Panther Creek, TN 11/10/2006	C ₃ H ₈	0.9	0.6	68	0.7	8.8	0.007	0.081 ³	20.0	0.03	0.01	Jin et al. (2012)
Little Bear Creek, TN	C ₃ H ₈	3.0	1.1	37	2.4	28.2	0.013	0.084 ³	20.0	0.03	0.01	Jin et al. (2012)
Sugar Creek, IN September 2003	SF ₆	1.5	0.3	20	1.2	6.1	0.001	0.2	21.1	0.05	0.02	Tobias et al. (2009)
West Fork Walker Branch, TN	C ₃ H ₈	13.9	—	—	10.0	100	—	0.10	16.9	—	0.00	Geneux and Hemond (1992)
Krycklan Catchment 1, Sweden	C ₃ H ₈	25.5	—	—	13.5	150	0.068	0.09	5.3	—	—	Wallin et al. (2011)
Krycklan Catchment 2, Sweden	C ₃ H ₈	12.5	—	—	5.9	49.0	0.038	0.12	1.1	—	—	Wallin et al. (2011)
Krycklan Catchment 4, Sweden	C ₃ H ₈	8.8	—	—	4.3	43.2	0.021	0.10	2.7	—	—	Wallin et al. (2011)
Krycklan Catchment 5, Sweden	C ₃ H ₈	27.3	—	—	14.3	79.2	0.037	0.18	4.8	—	—	Wallin et al. (2011)
Krycklan Catchment 6, Sweden	C ₃ H ₈	5.9	—	—	3.0	13.0	0.002	0.23	3.4	—	—	Wallin et al. (2011)
Krycklan Catchment 7, Sweden	C ₃ H ₈	14.3	—	—	7.6	85.0	0.044	0.09	5.7	—	—	Wallin et al. (2011)
Krycklan Catchment 8, Sweden	C ₃ H ₈	6.5	—	—	3.7	23.0	0.018	0.16	8.0	—	—	Wallin et al. (2011)
Krycklan Catchment 9, Sweden	C ₃ H ₈	18.3	—	—	9.8	57.6	0.012	0.17	5.8	—	—	Wallin et al. (2011)
Krycklan Catchment 10, Sweden	C ₃ H ₈	15.9	—	—	8.9	38.9	0.033	0.23	7.6	—	—	Wallin et al. (2011)
Krycklan Catchment 12, Sweden	C ₃ H ₈	7.5	—	—	4.0	15.8	0.000	0.25	5.5	—	—	Wallin et al. (2011)
Krycklan Catchment 14, Sweden	C ₃ H ₈	53.9	—	—	28.5	47.5	0.015	0.60	5.3	—	—	Wallin et al. (2011)
Krycklan Catchment 15, Sweden	C ₃ H ₈	44.2	—	—	26.9	122	0.058	0.22	10.5	—	—	Wallin et al. (2011)
Krycklan Catchment 71, Sweden	C ₃ H ₈	7.1	—	—	4.5	44.6	0.025	0.10	11.9	—	—	Wallin et al. (2011)
Krycklan Catchment 78, Sweden	C ₃ H ₈	6.7	—	—	4.6	57.6	0.005	0.08	15.2	—	—	Wallin et al. (2011)
Bonner Reach, WI	C ₃ H ₈	2.5	—	—	2.2	7.3	—	0.3	25	—	0.048	Grant and Skavroncek (1980)
North River, MA	C ₃ H ₈	5.3	—	—	5.4	12.0	—	0.45	27	—	0.62	Kwasnik and Feng (1979)
Bickford Watershed, MA	C ₃ H ₈	0.6	—	—	0.4	37.4	—	0.01	12.3	—	—	Geneux and Hemond (1990)

¹Using a modified version of Jahne et al. (1987, equation 2) and assuming $n = 0.5$.

²Using equation 1 in Table 2 of Raymond et al. (2012).

³Stream depth is estimated based on area and width at location of discharge measurement.

derived from stream discharge calculations. The uncertainty in groundwater inflow quantities has the greatest impact along the lower end of the Nine-Mile Creek study reach (1760–2300 m) where Br dilution could not be used. The calculated CH₄ load along this reach (90 ± 20 g/d) is based on flowmeter measurements at 1875 and 2300 m with uncertainties of 4–8%. Although these two sites had the same calculated stream discharge of 117 L/s, their uncertainties (±9 and ±5 L/s at 1800 and 2300 m, respectively) allow for a small gain from groundwater inflow, as indicated by the observed increase in stream CH₄ along this part of the study reach. The simulated groundwater inflow of 1.9 L/s with 14,000 nmol/L (230 ppb) is equal to 1% of the total flow (half of the smaller flowmeter measurement uncertainty). Increasing this to 4% of the total flow (half of the larger flowmeter uncertainty), the same CH₄ load could alternatively have been simulated by quadrupling the amount of simulated groundwater inflow to 7.6 L/s, with a CH₄ concentration of 3500 nmol/L (56 ppb). While this illustrates the importance of accurate discharge measurements for quantifying groundwater CH₄ concentrations, the increase in CH₄ at the lower end of the study reach indicates the ability of a small amount of groundwater discharge to contribute a significant CH₄ load to a stream.

Previous studies have noted methanogenesis in organic-rich stream sediments as a potential source of CH₄ (De Angelis and Lilley 1987; Jones and Mulholland 1998), possibly causing the elevated background CH₄ in Nine-Mile Creek. Geochemical fingerprinting with CH₄ isotopes, hydrocarbon ratios, and noble-gas ratios was beyond the scope of the current work, but could be used in future studies to differentiate between biogenic and thermogenic subsurface sources (Revesz et al. 2010; Osborn et al. 2011; Hunt et al. 2012). Also, because baseline characterization was not conducted prior to gas development in the Nine-Mile Creek area, it cannot be determined if the groundwater inflow of CH₄ to the stream is naturally occurring or a result of stray gas associated with gas development. Ideally, stream-based monitoring for groundwater CH₄ would begin prior to the inception of gas development activities in order to establish baseline conditions.

This paper demonstrates the utility of stream-based CH₄ measurements for evaluating groundwater CH₄ discharge to a gaining reach of Nine-Mile Creek. The applicability of this method to other gaining streams depends on the amount of groundwater inflow relative to gas transfer to the atmosphere. As noted in previous studies (McCutchan et al. 2002; Cook et al. 2003; Solomon et al. 2006; and Stolp et al. 2010), when groundwater inflow is large relative to gas transfer, there is a high likelihood of success using stream-based gas measurements for deriving the groundwater dissolved-gas concentrations (c_{gw}). Figure 11 shows the location of Nine-Mile Creek near the upper end of k/q_{gw} ratios (q_{gw} is groundwater discharge divided by stream surface area). Using the uncertainty in simulated k of 3.5–5.5 m/d and a q of 0.32 m/d (2800 m³/d stream gain from groundwater inflow divided by the stream's surface area of 8700 m²),

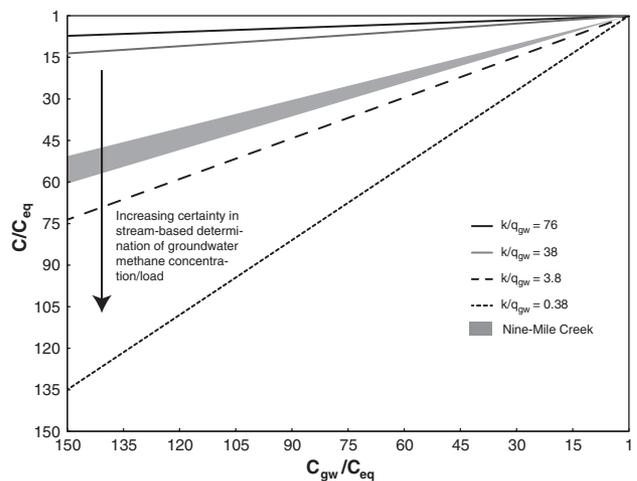


Figure 11. Location of Nine-Mile Creek within previously published range of gas transfer velocity (k)-to-groundwater inflow (q_{gw}) ratios (modified from Stolp et al. 2010). C , C_{eq} , and C_{gw} are the methane concentrations in the stream, air-equilibrated water, and groundwater, respectively.

the resulting k/q_{gw} values range from 11 to 17 (gray shaded area of Figure 11; note that these values are not related to axis labels). Using the average background C in Nine-Mile Creek of 150 nmol/L and C_{eq} of 2.7 nmol/L in Nine-Mile Creek, the stream C/C_{eq} ratio (vertical axis) is 55. This indicates that the C_{gw}/C_{eq} ratio (horizontal axis) would be 150, yielding a C_{gw} of about 400 nmol/L. Assuming an analytical detection limit for dissolved CH₄ of 60 nmol/L (1 ppb), groundwater concentrations of 160 nmol/L (2.6 ppb) or greater should be detectable in Nine-Mile Creek.

The intent of this paper is to describe a relatively low cost and simple approach for establishing baseline stream CH₄ conditions and conducting reconnaissance investigations of large areas for signs of impact from unconventional gas development. Additional hydrogeologic studies such as groundwater flow modeling, geochemical characterization, and groundwater dating may be necessary to evaluate particular flow paths and travel times for determining the timing and extent to which groundwater impacts from gas development activities reach the stream. For applying this stream-based CH₄ monitoring approach in other watersheds, it is important to recognize the large possible range of hydrogeologic variability between watersheds. With differences in geology, hydraulic properties, catchment size, topographic gradient, and climate, the size of groundwater capture areas for gaining stream reaches may vary greatly. As an example, if groundwater discharge to a stream is focused, such as preferential flow along a fracture, the capture area may be much smaller than for a stream that steadily gains throughout a watershed.

In designing a stream-based CH₄ monitoring program, the first step would be to identify gaining stream reaches during baseflow conditions (using flowmeter, tracer-dilution, or ²²²Rn measurements) and collect stream CH₄ samples to establish baseline conditions prior

to gas development. Kilometer-scale spacing may be appropriate for initial reconnaissance CH₄ sampling, but higher resolution could be necessary for evaluating point sources, especially in geologic settings with heterogeneous properties (e.g. bedrock fractures or lithologic variability). As gas development proceeds, additional seasonal or annual stream CH₄ sampling during baseflow conditions could be used for trend evaluation. If temporal increases in stream CH₄ are observed, groundwater CH₄ concentrations and loads to a stream can be determined by calculating the gas transfer velocity using a tracer gas-injection coupled with stream-transport/gas-exchange numerical modeling. Because of the spatial and temporal variability (daily, seasonal, interannual) of groundwater-stream interactions (including hyporheic flow and transient storage; Bencala et al. 2011), multiple measurement periods and detailed sampling may be required for a complete characterization of groundwater CH₄ loading to streams. To detect impacts from natural gas development, the method would require substantially larger CH₄ anomalies than the observed natural variability (noise) in background stream concentrations.

Conclusions

The development of stream-based CH₄ assessment methods for evaluating groundwater impacts from natural gas development could have a wide range of applications for both an initial regional reconnaissance and for detailed studies to locate and quantify fluxes of groundwater CH₄ entering gaining streams. The approach utilizes baseflow of a gaining stream as an integrated average of groundwater quality at a larger scale than obtained by sampling monitoring wells. As shown in the application at Nine-Mile Creek, these methods are cost-effective and relatively easy to implement, in comparison to the installation and sampling of monitoring-well networks. CH₄ injection into Nine-Mile Creek illustrates its persistence in streams at the km scale. The calculated apparent k_{600} gas transfer velocity of 5 m/d (k_{CH_4} of 4.5 m/d) determined with stream discharge measurements and 1-D transport modeling is consistent with other reported gas tracer experiments. Using this information, the background CH₄ load from groundwater inflow was estimated to be 190 g/d along the Nine-Mile Creek study reach. Because of its utility at Nine-Mile Creek, a relatively turbulent and shallow stream, it is likely that this method will be able to detect even lower CH₄ concentrations of groundwater discharging into more-placid and deeper streams receiving significant amounts of groundwater inflow (smaller k/q_{gw}).

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