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METHOD

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Key Points:

- Steady tracer gas injections are regularly used to measure the gas exchange velocity (v) between streams and the overlying air
- Temperature variation affects tracer gas solubility, which can lead to unsteady gas injection rate and error in measured v
- A zero-headspace tracer solution method was field tested and is proposed to measure v in the presence of large temperature variation

Supporting Information:

Supporting Information may be found in the online version of this article.

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Modified Tracer Gas Injection for Measuring Stream Gas Exchange Velocity in the Presence of Significant Temperature Variation

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Abstract Gas exchange between streams and overlying air is an important physical-chemical environmental process that is typically determined by injecting a tracer gas into a stream at a steady rate and sampling steady-state tracer gas concentrations in the stream water. Previous modes of tracer gas injection allow gas-water partitioning of the tracer gas, making the rate of gas injection and thus the measured gas transfer velocity potentially sensitive to temperature variation. Presented here is a modification to the tracer solution injection method in which a tracer gas solution was prepared in Tedlar® bags from which all headspace was removed before injecting the solution into the stream. Along with four other strategies to prevent a headspace from forming in the bags during tracer injection in the field, this zero-headspace tracer solution method prevents gas-water partitioning anywhere in the injection system, allowing a steady delivery of tracer gas to the stream even in the presence of variation in air and/or stream water temperature. A field test of the method in Nebraska yielded a gas transfer velocity of 4.1 m/day, within the range found in the literature for similarly-sized streams.

Plain Language Summary This paper reports on the development and testing of a method that allows injection of tracer gases into streams and rivers at a constant rate even if the temperature of the air or water is changing over time. The new method allows accurate estimation of gas transfer velocities from injected tracer gases at times and places with significant temporal variation in temperature.

1. Introduction

Gas exchange between streams and overlying air is an important physical-chemical environmental process, often closely linked to aquatic and terrestrial ecological processes. Quantifying gas exchange is critical to a range of research questions in ecology, geochemistry, and hydrology (Crawford et al., 2014; Hope et al., 2001; Jensen et al., 2022; Jones and Mulholland, 1998a, 1998b; Raymond et al., 2012; Solomon et al., 2015).

The "gold standard" for field determination of the gas exchange rate in streams is to inject a tracer gas into a stream and measure the decrease in aqueous concentration of the tracer gas as a function of distance downstream from the injection site (Choi et al., 1998; Genereux & Hemond, 1992; Kilpatrick et al., 1989; Natchimuthu et al., 2017; Parker & DeSimone, 1992; Wallin et al., 2011). Typically, the volatile tracer is injected either instantaneously or continuously at a constant rate, in conjunction with a conservative tracer to account for dilution by groundwater and tributary input to the stream (Chapra & Wilcock, 2000; Oviedo-Vargas et al., 2015; Rawitch et al., 2019). Propane, methyl chloride, SF_6, and the noble gases have been used as volatile tracers (Jin et al., 2012; Reid et al., 2007; Solomon et al., 2015; Tobias et al., 2009; Wilcock, 1988). For a continuous injection, it is critical that the tracer gas injection be steady in time so that each parcel of stream water passing the injection site receives the same rate of tracer gas input.

A methodological problem not previously overcome with the tracer gas method is the issue of ensuring a truly steady tracer gas injection in the presence of significant temporal variation (diurnal or otherwise) in temperature. Previously published applications of the tracer gas method have utilized tracer injection systems that involve gas-water partitioning during the injection, a process that is sensitive to temperature variation. Often, this partitioning is between the stream water and tracer gas bubbles released through fine-pore diffusers on the streambed

(Genereux & Hemond, 1992; Oviedo-Vargas et al., 2015; Reid et al., 2007). Since gas solubility decreases at higher temperatures, the rate of volatile tracer input to the stream could decrease if the stream warmed during these types of injections. Streams in North America have been shown to undergo diurnal temperature fluctuations as much as 2°C in winter months and 12°C in summer months (Abe et al., 2009; Chapin et al., 2014; Ferencz & Cardenas, 2017). For a stream initially at 10°C, an increase in stream temperature of 2–12°C would cause a decrease of 8%–35% in propane solubility (Hayduk, 1986).

Another approach to the tracer gas method is to inject a tracer solution from a carboy (Jin et al., 2012) or a Tedlar® bag (Tobias et al., 2009). By not bubbling the tracer gas into the stream, this method minimizes the potential disturbance of natural dissolved gas concentrations in the stream water (Tobias et al., 2009). It also allows for a relatively long tracer injection with a small quantity of tracer gas, compared to the bubbling mode of tracer gas injection, and the potential to observe temporal variation in gas exchange during the longer injection (Tobias et al., 2009).

However, previous applications of the tracer solution method allowed gas-water partitioning between the tracer solution and a gas headspace inside the container holding the solution. Under this condition, if an increase in air temperature warms the container, the result could be a decrease of tracer gas concentration in the solution and thus tracer gas input to the stream, even if the rate of injection of tracer solution is held steady. As an example, for a container holding water and pure tracer gas headspace at 10°C, and given the sensitivity of gas solubilities to temperature, a 5°C increase in the temperature of the container would reduce the aqueous concentration of the tracer gas by 18% for propane (Hayduk, 1986) and 17% for SF_6 (Clever et al., 2005), though only 2% for helium (Clever, 1979). Tobias et al. (2009) placed their Tedlar® bag in a large water bath, which could reduce the potential impact of temperature variation. We used several different steps to achieve this objective.

Presented here is a modified tracer solution injection method specifically designed for environments with significant temporal variation in stream and/or air temperature. First, a tracer gas solution was prepared in Tedlar® bags from which all headspace was removed before bringing the bags outdoors to the field. In this zero-headspace tracer solution method, we also used four additional strategies explained below to prevent a headspace from forming in the bags during tracer injection in the field. With the approach outlined here, there is no gas-water partitioning or equilibration anywhere in the injection system, allowing a steady delivery of tracer gas to the stream even in the presence of variation in air and/or stream water temperature. The method was field tested by using a precision metering pump to inject a propane tracer solution into a Nebraska stream, to measure the gas exchange rate constant and gas transfer velocity.

2. Materials and Methods

2.1. Overview

The zero-headspace tracer solution method was field tested in a Nebraska stream, using propane and NaCl as injected volatile and conservative tracers, respectively. The objective was to demonstrate the feasibility of the method by determining the first order gas exchange rate constant (k_{C3H8}) and the gas transfer velocity (v_{C3H8}) for propane in a reach of the stream, using Equations 1 and 2 below (Natchimuthu et al., 2017; Oviedo-Vargas et al., 2015; Wallin et al., 2011):

$$k_{\mathrm{C3H8}} = \frac{1}{\tau}\ln\left(\frac{[C_3H_8]_u Q_u}{[C_3H_8]_d Q_d}\right) \tag{1}$$

$$v_{\mathrm{C3H8}} = k_{\mathrm{C3H8}} d_{\mathrm{avg}} \tag{2}$$

where $[C_3H_8]$ is the steady-state stream water propane concentration caused by the injection, Q is the stream discharge (volume/time), τ is the solute travel time through the study reach, the u and d subscripts differentiate between the upstream and downstream ends of the reach, respectively, and d_{avg} is the average depth of the stream in the study reach.

2.2. Sampling Location

Work was carried out on 19 May 2019, at Gudmundsen Sandhills Laboratory, a cattle ranch owned and operated by the University of Nebraska-Lincoln (Figure 1). Propane and NaCl injections were performed in a channelized

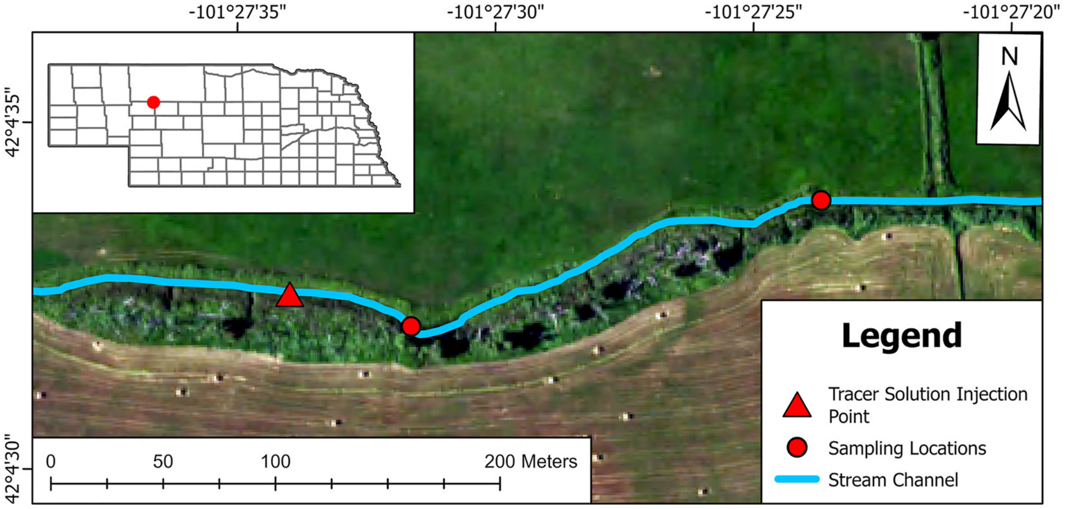

Figure 1. Study stream for gas exchange measurement at the Gudmundsen Sandhills Laboratory in Nebraska, USA. Stream flow is from west to east. The inset shows the study site and county boundaries in the state of Nebraska.

tributary to the South Branch Middle Loup River (N 42°04′32″, W 101°27′31″). The stream runs through a wide relatively flat grass-covered valley floor between vegetated sand dunes, typical of the Sand Hills region of Nebraska (Gosselin et al., 1999).

The upstream and downstream sampling stations defined the ends of the 200 m study reach. The tracer injection point was 50 m upstream of the upstream sampling station to facilitate transverse mixing of the injected tracers upstream of the study reach (Kilpatrick et al., 1989). Mean stream depth and width were 33.6 (±4.2) cm and 292.3 (±34.1) cm, respectively, in the study reach, based on 11 measurements of each, every 20 m along the reach.

2.3. Preparation and Injection of Propane Tracer Solution

Tap water was degassed via boiling in the laboratory and was allowed to completely cool in capped 1-gallon jugs with no headspace before being siphoned into three 25 L Tedlar® bags (Smith Air Sample Supply Co. in Mebane, NC). The same volume of water, 20 L, was placed into each bag. Any air headspace that remained in the bags (less than 50 mL) was removed via syringe and replaced with a bubble of high purity ≥99% propane (Airgas Inc.) of sufficient size (roughly 1,400 mL) to not fully dissolve in the water. The propane headspace was left in each bag overnight, with significant agitation in the evening after preparation and again the next morning, so that the propane gas would reach equilibrium with the water in the bag. The remaining propane headspace was removed via syringe the next morning, leaving zero-headspace water-filled bags (Figure 2a).

Four strategies were used to avoid exsolution of propane from the solution due to temperature increases while in the field. These four strategies focus on ensuring that the total dissolved gas concentration in the Tedlar® bag remains below saturation if the temperature increases. The first strategy, mentioned above, was to degas the solution water via boiling prior to the addition of propane gas, to minimize the presence of other dissolved gases in the solution. Second, the tracer solution was prepared in the lab where the temperature was roughly 12°C warmer than the maximum air temperature in the field (7.8°C). Third, the propane concentration in the solution was reduced further by diluting the 20 L of propane-saturated water in each Tedlar® bag with an additional 2 L of degassed water after the propane headspace had been removed from the bag. The combined effect of the second and third strategies was to ensure that the calculated propane concentration (1.6 mmol/kg, based on the solubility of propane (Hayduk, 1986) at the lab temperature of 20°C) was about 43% lower than the solubility of propane at the field temperature (2.8 mmol/kg). With these steps, propane would not exsolve from solution as long as the temperature of the tracer solution remained below 23°C. Air temperatures measured at a nearby weather station in Whitman, NE on the day of the injection ranged from 0.5 to 7.8°C (High Plains Regional Climate Center, 2019). Fourth, to avoid warming above the ambient temperature in the field, the bags were stored in covered boxes with white lids to minimize warming from direct sunlight (Figure 2b), though skies were overcast during the tracer release.

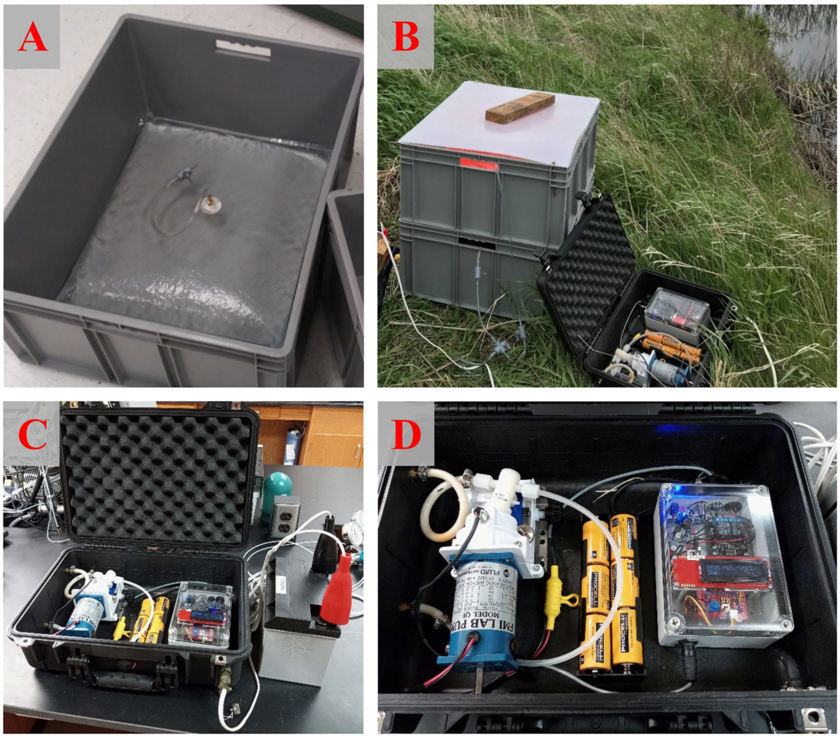

Figure 2. Propane tracer solutions were prepared in 25 L Tedlar® bags (a) and were injected into the stream using a metering pump (Model QB from Fluid Metering, Inc.) at a rate of 168 mL/min (b–d). A Lifeline GPL-U1T 12-V AGM battery (33 Ah) powered the pump which was controlled via a custom-built microprocessor-based control module (d).

For the injection, tracer solution was pumped from each Tedlar® bag into the stream, one bag at a time, using a metering pump (Model QB) from Fluid Metering, Inc. The end of the tubing carrying the tracer solution to the stream was placed below the top of the stream water, just above the streambed. The propane injection continued for 5.25 hr, and the pump rate was controlled at 168 ± 0.4 mL/min through a custom-built microprocessor-based control module (Figure 2). The metering pump delivers a precise volume of fluid with each rotation. The control module monitors the pump rotations such that during a 15 s injection cycle a constant (programable) number of rotations is achieved. This provides a highly constant injection rate (±0.23%) even though the time required to achieve a fixed number of rotations is variable due to battery voltage, head in the Tedlar® bag, and ambient temperature. The bags were custom made with hose-barbs which allowed them to be connected to the metering pump via 3/16″ ID tubing. Three-way valves were used to switch between bags so that a new bag could be easily brought inline when the previous bag was depleted.

Table 1
Results From the Zero-Headspace Tracer Solution Method

Parameter	Value ± (error)
Q_u: upstream flow (L/s)	46.6 ± (0.6)
Q_d: downstream flow (L/s)	42.7 ± (1.4)
C_u: upstream C_3H_8 concentration (nM)	75.3 ± (2.2)
C_d: downstream C_3H_8 concentration (nM)	10.6 ± (1.7)
τ: travel time between sampling points (min)	61.7 ± (0.3)
k_{C3H8}: gas exchange rate constant (day^{-1})	12.2 ± (2.8)
v_{C3H8}: gas exchange velocity (m/day)	4.1 ± (1.1)

Note. 1σ error was estimated for each parameter by Jensen et al. (2022). The instantaneous salt slug method used is not capable of determining water loss from a stream reach to its surroundings; thus while the Q_d value above is slightly less than Q_u, 95% confidence intervals for the two values overlap and we interpret the salt slug results as showing no significant groundwater gain in the study reach. $Q_u/Q_d = 1$ was used in Equation 1.

2.4. Analysis of Propane in Stream Water Samples

Five stream water samples were collected at each sampling station, in 50 and 150 mL glass syringes at the upstream and downstream stations respectively; samples were immediately put on ice in the field. Sample collection at the upstream and downstream stations occurred 2.08 and 5.25 hr after the start of the injection, respectively. Given the 62-min travel time through the 200 m reach (Table 1), the sampling times were long enough after the start of injection to ensure steady-state propane concentrations at the sampling stations (Kilpatrick et al., 1989). The next morning, the syringes were allowed to warm to room temperature in the laboratory, and about 10 mL of high purity N_2 gas was introduced into each syringe for headspace equilibration of the propane (Oviedo-Vargas et al., 2015). The equilibrated headspace was injected through a gas sampling valve (1.6 mL sample loop) into an SRI 8610C gas chromatograph equipped with a flame ionization detector (GC-FID) and a HayesSepD packed column (calibration data is in Supporting Information S1). In this method, lower aqueous propane concentrations can be measured by collecting larger sample volumes (Oviedo-Vargas et al., 2015), so larger sample volumes (150 mL syringes) were collected at the downstream sampling station than at the upstream sampling station (50 mL syringes).

2.5. Stream Discharge (Q) and Reach Travel Time (τ)

At the start of the propane injection, a slug of 2.01 kg NaCl dissolved in about 15 L of stream water was released into the stream to allow calculation of Q at each sampling station and τ for the reach. The slug was instantaneously released over the width of the stream channel at the injection site to facilitate full mixing across the stream cross-section. A HOBO© conductivity-temperature data logger monitored the salt breakthrough curve at each sampling station. The travel time between the upstream and downstream sampling stations was calculated as the difference in the peak times of the breakthrough curves at the two stations.

All conductivity data were temperature corrected to 25°C (U.S. Geological Survey, 2019) and were then converted to NaCl concentrations using a calibration curve generated in the lab. Q was calculated at each station as the mass of NaCl released in the slug divided by the area under the temperature-corrected NaCl concentration breakthrough curve (Kilpatrick et al., 1989; Oviedo-Vargas et al., 2015).

3. Results

The k_{C3H8} for the 200 m reach was 12.2 days^{-1}, and v_{C3H8} was 4.1 m/day (Table 1). Stream flow in the tributary was elevated above baseflow due to recent precipitation and snow melt and did not show significant groundwater inflow. Overall, the zero-headspace tracer solution method yielded plausible values of k_{C3H8} and v_{C3H8} within the range found in the literature for similarly sized streams (Hope et al., 2001; Jensen et al., 2022; Natchimuthu et al., 2017; Oviedo-Vargas et al., 2015; see Supporting Information S1).

4. Discussion

From the start of the propane injection to when the downstream samples were collected, the stream temperature increased from 8.38 to 10.34°C, though larger stream temperature changes have been recorded in this stream (e.g., a temperature increase of 9.99°C occurred from 7:30 a.m. to 5:16 p.m. on 30 May 2019, 11 days after the tracer injection). Even a relatively small 2°C increase during the tracer injection would be associated with a 7.9% drop in propane solubility which would decrease the rate of propane input to the stream by the same magnitude if the traditional bubbling method for propane release is used. Depending on the timing of stream water sampling, the effect of this temperature change on the propane injection rate could lead to the k measured in this field test being up to 15.7% lower than the actual k (if stream water sampled at the downstream and upstream stations had passed the propane injection site before and after the temperature increase, respectively). With the same assumption regarding sampling, the measured k could be up to 72.9% lower than the actual k following a 10°C increase in temperature (see in Supporting Information S1). The magnitude of stream temperature change was moderate on the day of our tracer injection, but the zero-headspace tracer solution method was designed to improve the determination of gas exchange rates in systems with larger temporal changes in temperature.

With the zero-headspace tracer solution method for tracer release, advance planning is required to estimate the minimum injection rate (Q_b) and the minimum volume of tracer solution (V_b) necessary to achieve a steady state concentration above the lower limit of quantification (LLQ) for the tracer gas in water at the downstream sampling station. Assuming the travel time between the injection site and the upstream measurement station is negligible compared to travel time through the study reach, a modified version of Equation 1 can be used to aid in planning:

$$Q_b = \frac{(\mathrm{LLQ})Q_d \exp(k\tau)}{[C_3H_8]_b} \tag{3}$$

where $[C_3H_8]_b$ is the concentration of propane in the tracer solution in the Tedlar® bag (about 1.6 mmol/kg in this work) and Q_b is the pumping rate of tracer solution from bag to stream. During the planning stage, estimates of

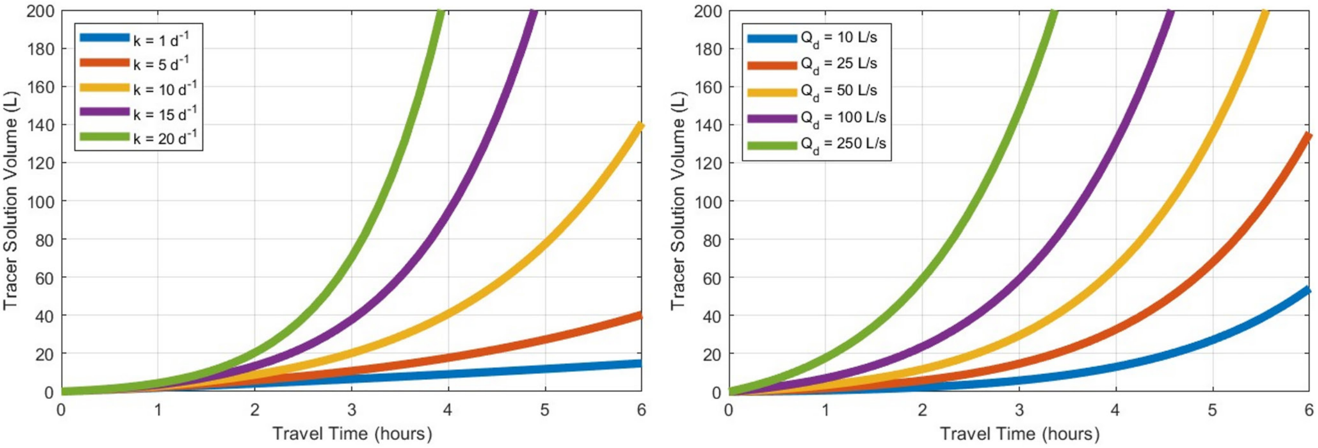

Figure 3. Tracer solution volume required to obtain a steady downstream propane concentration above the lower limit of quantification (LLQ) as a function of tracer travel time through a reach, for different values of gas exchange rate constant (left) and stream discharge at the downstream end of the reach (right), based on Equation 4. The graphs assume conditions from our field test in Nebraska: LLQ = 4.8 nM, C_b = 1.6 mmol/kg (propane solubility at 20°C diluted by 9%), Q_d = 45 L/s (left graph only), and k = 12.2 day^{-1} (right graph only).

the $[C_3H_8]_b$, k, τ_b, and Q_d expected during the injection can be used in Equation 3 to estimate Q_b. The Q_b attainable by the metering pump used in this field test ranged from 35 mL/min to about 550 mL/min. The minimum volume of tracer solution (V_b) required to maintain an injection at the required Q_b can be determined by multiplying Q_b by the duration of the injection. Assuming 4τ is a sufficient injection duration to achieve steady state (Kilpatrick et al., 1989):

$$V_b = \frac{4\tau(\text{LLQ})Q_d \exp(k\tau)}{[C_3H_8]_b} \tag{4}$$

LLQ for a tracer gas analyzed using the headspace equilibration method depends on the ratio of headspace to water volume in the equilibration container and the solubility of the gas tracer. For our tracer test, 10 mL of headspace at 20°C for a 140 mL stream water sample resulted in a LLQ of 4.8 nM for propane (see in Supporting Information S1). Additionally, Q_d and τ were estimated using a simple slug release of NaCl 2 days prior to the propane injection, which required beginning with at least an approximate idea of the length of reach to be studied for gas exchange (another planning variable in addition to Q_b and V_b). $[C_3H_8]_b$ was estimated from the known solubility of propane in water (Hayduk, 1986) at the temperature at which the tracer solution was prepared, and the dilution of the solution after the propane headspace was removed from the Tedlar® bags. Finally, planning with Equation 4 also involved using literature values of k in streams with similar stream discharge to bracket the range of likely k values for the study stream (Hope et al., 2001; Natchimuthu et al., 2017; Oviedo-Vargas et al., 2015).

According to Equation 4, the volume of tracer solution needed increases exponentially with τ (Figure 3), and τ is a function of both the reach length and the stream velocity. Consequently, V_b is linked to the length of the study reach.

Preparing the tracer solution in the lab at a higher temperature than expected in the field, degassing the water used in the tracer solution by boiling, and diluting the propane-saturated water by 9% ensured no degassing from the final tracer solution and a stable propane injection rate for field air temperatures up to 23°C. This was a conservative approach to preventing headspace formation in the Tedlar® bags. While it was probably not strictly necessary to include all three steps, it was prudent to demonstrate all three in this first full-scale test of the zero-headspace tracer solution method.

Another option would be to prepare the tracer gas solution in the field by pumping stream water into empty Tedlar® bags (Tobias et al., 2009) which would involve skipping two of the steps that were used in the lab (boiling water and preparing the solution at a temperature above the field air temperature) and possibly adding two new steps (pumping the stream water to the bag and filtering the stream water to avoid potential complications with suspended sediments in valves or the pump). Streamside preparation of the tracer solution has the advantage that a larger volume of tracer solution could be prepared, in one or more Tedlar® bags (bags up to 100 L are commercially available). In this case, dilution of the tracer solution after removal of the tracer gas headspace from the Tedlar® bag(s) would be critical for preventing propane from exsolving out of the solution. If multiple Tedlar® bags are used, having a steady tracer injection also requires that the volume of water used in each bag is carefully controlled both during equilibration with the tracer gas and subsequent dilution, to ensure the same tracer gas concentration in each bag.

An additional consideration is that the tracer solution volume responds linearly to the LLQ, meaning that lowering the LLQ can allow a tracer injection in longer reaches or in reaches with higher stream flow. For example, a headspace equilibration method allows lower aqueous tracer gas concentrations to be measured if a greater stream water sample volume is collected because more tracer mass can be injected into the GC. Larger sample volumes were collected at the downstream sampling station, where the lowest propane concentrations were expected, in order to lower the LLQ there and reduce the required volume of tracer solution. Alternatively, a tracer gas with a lower LLQ can be used. For instance, SF_6 can be measured to a precision of 3% at concentrations above 0.2 fmol/L (U.S. Geological Survey, 2019); this significantly lower LLQ requires far less tracer solution, and SF_6 has previously been used to measure gas exchange via a tracer solution injection (Tobias et al., 2009). However, there is the trade-off in that SF_6 is a very potent greenhouse gas compared to propane (Myhre et al., 2013). Also, SF_6 can be used as a groundwater dating tool and contamination of a riparian zone with injected SF_6 might last for many years.

While the zero-headspace Tedlar® bag method may improve measurement of gas exchange by achieving a steady tracer gas injection in the presence of temperature variation, it can't remove the sensitivity of gas exchange to temperature change when a tracer gas with non-negligible atmospheric concentrations is used (e.g., a noble gas instead of propane). In general, gas exchange flux between water and overlying air is proportional to $C–C_{eq}$, where C is the dissolved gas concentration in the water and C_{eq} is the dissolved gas concentration of water in equilibrium with the atmosphere (e.g., Liss & Slater, 1974; Whitman, 1923). Because C_{eq} is temperature-dependent, a change in temperature may change the gas exchange flux, unless $C_{eq} = 0$ (as expected for propane in almost all field sites). This is separate from the issue addressed by the zero-headspace tracer solution method.

Figure 3 suggests that the most straight-forward applications of the zero-headspace tracer solution method will be in small to medium size streams. However, larger streams and longer reaches can be studied if careful consideration is given to the expected field and experimental conditions. Such effort is warranted if significant temperature changes are expected. In these circumstances, the zero-headspace tracer solution method removes the effect of gas-water partitioning in the injection system, likely improving the measurement of the gas exchange rate constant and gas transfer velocity in the presence of temporal variation in temperature.

Data Availability Statement

All data used in the paper are listed in Table 1.

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