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Key Points:
- Gas transfer from steep streams was investigated using tracer tests, with 4 very steep streams compared to 4 moderately steep streams
- Gas transfer was higher during high flow events, and gas transfer coefficients could be predicted by the product of discharge and slope
- Most gas evaded within 100 to 400 m highlighting the importance of characterizing gas sources when estimating evasion

Supporting Information:
- Supporting Information S1
- Data Set S1

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The Influence of Flow and Bed Slope on Gas Transfer in Steep Streams and Their Implications for Evasion of CO_2

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Abstract The evasion of greenhouse gases (including CO_2, CH_4, and N_2O) from streams and rivers to the atmosphere is an important process in global biogeochemical cycles, but our understanding of gas transfer in steep (>10%) streams, and under varying flows, is limited. We investigated gas transfer using combined tracer injections of SF_6 and salt. We used a novel experimental design in which we compared four very steep (18.4–29.4%) and four moderately steep (3.7–7.6%) streams and conducted tests in each stream under low flow conditions and during a high-discharge event. Most dissolved gas evaded over short distances (~100 and ~200–400 m, respectively), so accurate estimates of evasion fluxes will require sampling of dissolved gases at these scales to account for local sources. We calculated CO_2 gas transfer coefficients (K_{CO2}) and found statistically significant differences between larger K_{CO2} values for steeper (mean 0.465 min^{-1}) streams compared to those with shallower slopes (mean 0.109 min^{-1}). Variations in flow had an even greater influence. K_{CO2} was substantially larger under high (mean 0.497 min^{-1}) compared to low flow conditions (mean 0.077 min^{-1}). We developed a statistical model to predict K_{CO2} using values of streambed slope × discharge which accounted for 94% of the variation. We show that two models using slope and velocity developed by Raymond et al. (2012) for streams and rivers with shallower slopes also provide reasonable estimates of our CO_2 gas transfer velocities (k_{CO2}; m d^{-1}). We developed a robust field protocol which could be applied in future studies.

1. Introduction

Streams and rivers contribute substantial amounts of greenhouse gases to the atmosphere including carbon dioxide (CO_2) (Butman & Raymond, 2011; Lauerwald et al., 2015; Rawlins et al., 2014; Raymond et al., 2013), nitrous oxide (N_2O) (Beaulieu et al., 2011), and methane (CH_4) (Stanley et al., 2016). Oxygen degassing and reaeration are also important in regulating stream metabolism (Dick et al., 2016; Marzolf et al., 1994).

Understanding gas transfer between streams and rivers and the atmosphere requires an accurate estimate of the gas transfer coefficient (K), which is reported in units of time; or the gas transfer velocity (k) which is the gas transfer coefficient multiplied by the stream depth, and is reported in units of distance/time. K varies substantially in both space and time (Kokic et al., 2015; Wallin et al., 2011). This is primarily due to variations in turbulence which is a major control on gas transfer rates (Moog & Jirka, 1999; Vachon et al., 2010; Zappa et al., 2007).

Direct measurements of gas transfer can be made using the floating chamber method (Alin et al., 2011; Crawford et al., 2013; Khadka et al., 2014). However, results from this approach may sometimes be inaccurate (Oviedo-Vargas et al., 2016; Vachon et al., 2010). Studies commonly use gas tracer tests to estimate K, for example, using propane or SF_6 (Cook et al., 2006; Schade et al., 2016; Wanninkhof et al., 1990), usually injected into streams together with a conservative tracer such as salt (NaCl).

Gas transfer coefficients or gas transfer velocities have been shown to increase with decreasing stream order (Butman & Raymond, 2011; Raymond et al., 2012; Schelker et al., 2016; Wallin et al., 2011), with low order, headwater streams having the largest gas transfer rates. This may be because they tend to be steeper and more turbulent (Butman & Raymond, 2011). Previous studies have demonstrated the importance of slope and discharge on gas transfer from streams and rivers (Billett & Harvey, 2013; Hope et al., 2001; Natchimuthu et al., 2017; Raymond et al., 2012; Schelker et al., 2016; Wallin et al., 2011). It has been shown that stream energy dissipation rate (ε_d), based on stream power per unit weight of water, varies linearly with the reaeration coefficient (k_2) of streams (Tsivoglou & Neal, 1976). In some studies, gas transfer has been measured in the same stream under different discharge conditions. Most of these reported an increase in gas transfer rates with increasing discharge using tracer testing (Billett & Harvey, 2013; Kokic et al., 2015; Natchimuthu et al., 2017; Peter et al., 2014), or the floating chamber method (Khadka et al., 2014). Other studies have reported that gas transfer is not influenced by flow conditions (Genereux & Hemond, 1992), or contrary to expectations, that gas transfer rates can sometimes be smaller under increased flows (Öquist et al., 2009; Wallin et al., 2011).

There is currently limited understanding of controls on gas transfer in steep (>10%) headwater streams (Long et al., 2015), and importantly, predictive models need to be tested and improved in these systems under varying flow conditions. Steep streams occur across a substantial proportion of the terrestrial landscape. Based on a 3 arc sec data set of global terrestrial slope values presented by Larsen et al. (2014), we estimate that around 18% of slopes have a gradient of more than 10%, and so streams with such slopes will account for a sizeable proportion of freshwater channels globally.

Much of the work on gas transfer in streams and rivers has been carried out in relation to evasion of CO_2, the greenhouse gas which currently accounts for the largest proportion of global radiative forcing (Myhre et al., 2013). Considerable work has been undertaken to understand controls on K_{CO2} for use in models that upscale estimates of total carbon export from streams and rivers to the atmosphere. In a recent study, the total quantity of carbon evaded to the atmosphere from rivers and streams was estimated to be 1,800 Tg C yr^{-1} globally (Raymond et al., 2013). Studies have shown that variations in K_{CO2} can have more impact on CO_2 evasion rates than stream water pCO_2 (Kokic et al., 2015; Wallin et al., 2011). Accurate estimates of K_{CO2} and k_{CO2} are needed to improve predictions of CO_2 evasion (Kokic et al., 2015).

The aims of the study are to investigate gas transfer rates in steep streams and specifically to establish the relationship between gas transfer and slope and flow in steeper streams, and under more varied flow conditions, than those that have generally been studied to date. The experimental design differs from previous studies in that sites were selected to enable comparison between four very steep streams (>15%) and four moderately steep streams, and the tracer experiments were specifically planned to investigate how gas transfer rates obtained during high-discharge events differ from those obtained under low flow conditions. The streams were in the same geology and had similar topographic positions and vegetation characteristics, enabling a focused investigation of slope and flow.

We undertook SF_6 tracer tests in four steep streams (slopes of 18.4 to 29.4%) and four shallower streams (slopes of 3.7 to 7.6%) under both high and low flow conditions. The shallower sloping stream sections (3.7 to 7.6%) for which we made measurements are at the upper end of the slope values reported in previous studies (Billett & Harvey, 2013; Wallin et al., 2011). The study aimed to investigate the physical process of gas transfer, and not to measure actual evasion of greenhouse gases, and therefore, in-stream greenhouse gas concentrations were not measured. However, due to the primary importance of CO_2 as a greenhouse gas and the large number of studies which estimate its evasion from freshwater, we converted our K_{SF6} estimates to K_{CO2} so we could compare them with other measurements and apply models that estimate both K_{CO2} and k_{CO2} using site properties and flow data (Raymond et al., 2012). We present new models and test existing models for the prediction of K_{CO2} and k_{CO2} for these steeper streams under varying flow conditions. We discuss the implications of our findings for the prediction of CO_2 losses from streams.

2. Methods and Study Area

The field measurements were carried out in an unforested, upland area of South Wales, UK (Figure 1). Tracer tests were carried out in eight headwater tributary streams approximately 1 m wide within two river valleys (the Llia and Tawe valleys) approximately 7 km apart. The tested sites lie at elevations of 330 to 435 m above sea level and are all on the Devonian Old Red Sandstone, which forms the boulders making up the beds and banks of the streams. The vegetation cover and type was similar at all the sites and was dominated by vegetation from the "acid grassland" category as defined in the UK wide 25 m resolution "Land Cover Map 2007" (Morton et al., 2011). There are occasional superficial glacial till and peat deposits mapped in the vicinity.

2.1. Local Site Selection

A total of 16 tracer tests were carried out, with repeated tests in the same reach under high and low flow conditions, in each of the eight streams. The gas transfer coefficients were determined using the methods

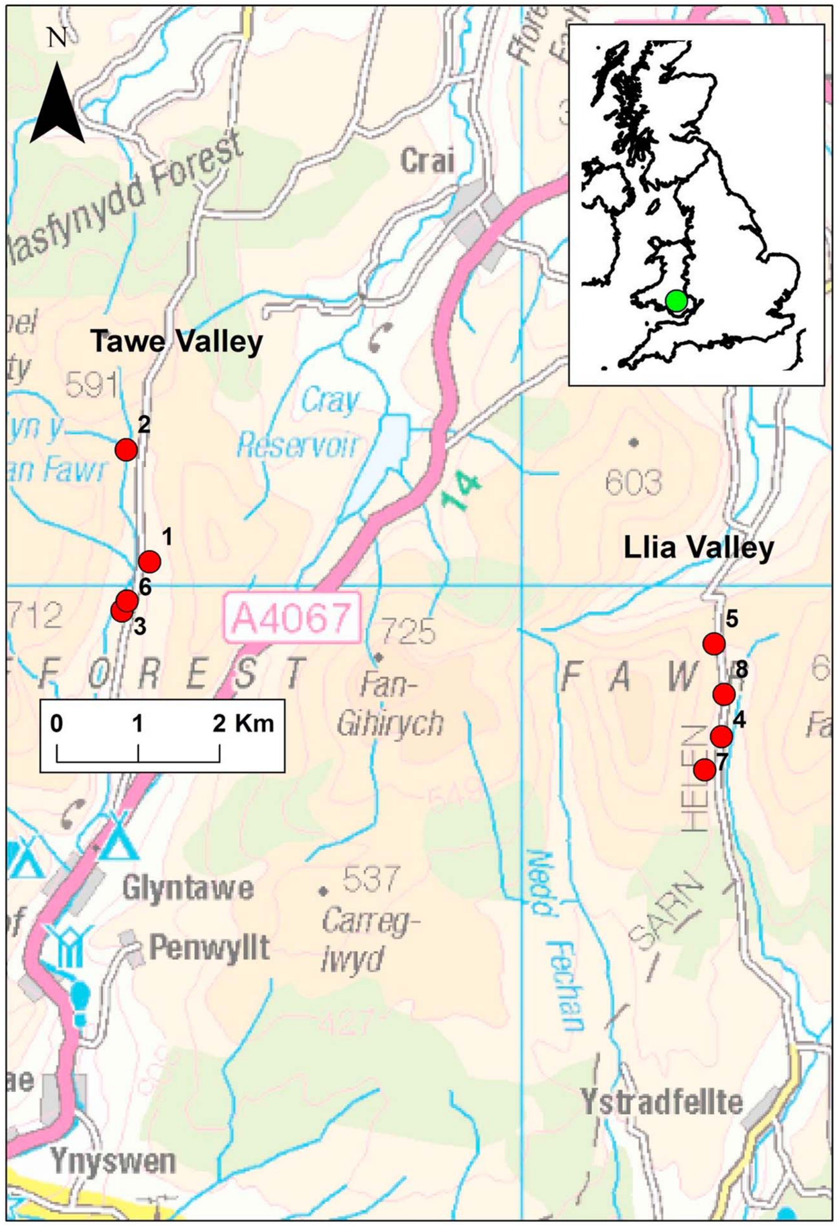

Figure 1. Map of the study area and stream sampling locations with UK map inset. *Contains Ordnance Survey data ©Copyright and database rights 2016.*

described in Hope et al. (2001) and Wallin et al. (2011). The study was designed to ensure as much consistency as possible to enable the effect of flow and slope on *K* to be investigated. Streams that had a suitable injection point above an accessible 45 m length section with no obvious inflows or outflows were selected. Injection sites were chosen ensuring that there was sufficient depth to install the gas injection system and that they were just upstream of a constriction/cascade to facilitate tracer mixing. At all sites a mixing reach of 25 m was used because during preliminary tests (not reported), mixing reaches of 15–20 m were often insufficient to ensure full mixing. Any remaining sites where full mixing was not achieved within the 25 m mixing reach were omitted from the data set.

Final results were obtained for four steeper and four shallower streams. It was not possible to use a randomized site selection procedure as there were few stream sections that met all the criteria outlined above. To enable a comparison between high and low flows, tracer tests were planned in response to prevailing weather conditions and were carried out once at each site after a prolonged dry period (at least 1 week), and once following and during periods of heavy rainfall.

2.2. Tracer Testing Methodology

Field tests involved constant-rate simultaneous injections of a gas tracer (SF_6) and a saline tracer. Successful estimation of gas transfer coefficients from tracer tests depends upon steady state conditions and full tracer mixing throughout the stream channel at the upstream and downstream sampling points. It is not possible to determine this with the gas tracer (which is measured later in the laboratory), and therefore, the salt tracer is used to ensure that there is full tracer mixing and that the gas samples are only taken once steady state has been reached. The salt tracer results are also used to estimate the flow, and the reach travel time.

The saline tracer comprised table salt (NaCl) mixed with tap water to a concentration equivalent to either 0.5 kg or 1 kg of salt in 10 L of water, with smaller concentrations used in tests with smaller flows. The saline tracer was injected using a peristaltic pump that discharged tracer into the center of the stream channel through a 5 mm diameter tube. The tracer injection rate was measured using a measuring cylinder and stop watch to determine the time taken to pump a volume of 30 mL. Repeated measurements were made at the start and end of the tracer test to ensure that the injection rate was constant.

The gas tracer was injected using weighted porous tubing distributed across the stream channel. The gas injection pressure was set at around 13.8 kPa using a regulator, and regular pressure readings were made to ensure that injection rates remained constant.

Gas sampling and monitoring for the saline tracer was undertaken at upstream and downstream monitoring points 20 m apart (25 and 45 m downstream of the injection site). Specific Electrical Conductance (SEC) measurements were made with a Mettler Toledo conductivity probe with readings noted down at regular time intervals ensuring a detailed tracer breakthrough curve was obtained prior to the onset of steady state conditions. The probes have an accuracy of 0.5% and were calibrated on a daily basis. When steady state conditions were reached, the SEC probes were used to check that the tracer was fully mixed across the width and depth of the stream channel. Measurements were made with both SEC probes at both the upstream and downstream site to ensure consistent readings. The reach travel time was estimated as the difference in the time taken for the saline tracer to reach 75% of the steady state concentration at the upstream and downstream monitoring points (Billett & Harvey, 2013).

Gas samples were taken after SEC measurements indicated that the saline tracer concentrations had reached steady state concentrations at the downstream monitoring point. Water samples for gas analysis were taken with a syringe which was used to inject the water into empty gas sample cylinders, with inlet and outlet valves ensuring that no air was introduced into the sample (see supporting information Figure S1). Upstream and downstream gas samples were taken at a time interval equal to the reach travel time to ensure that the same water was sampled at both measurement sites. Three sets of samples were taken, with each set of upstream and downstream samples taken after the preceding set (i.e., the sequence was upstream 1, downstream 1; upstream 2, downstream 2; and upstream 3, downstream 3). Stream temperature and SEC were also measured when each gas sample was taken.

Water levels in the stream were monitored using a temporary stage post. The saline tracer was used to calculate the stream discharge using the constant-rate injection method outlined by Moore (2004). This required calibration solutions to be made up in the field by mixing known volumes of stream water measured with volumetric flasks, with known volumes of the saline tracer injection solution added using pipettes.

A Leica SmartRover GPS was used to survey the positions (±0.02 m) and elevations (±0.02 m) of the upstream and downstream monitoring points for slope calculation.

The width and depth of the stream channel was measured using a tape measure. These measurements were made at 2.5 m intervals between the upstream and downstream sampling points. The width was measured as the distance between the point nearest the bank with water in on one side of the channel, and the point nearest the opposite bank which had water in. Dry areas within the channel were not subtracted from the width measurement but should be in future tests. At each measurement point the depth was measured three times: once near the middle and once near each edge. The width and depth measurements were used to estimate the average width and depth over the 20 m tracer sampling reach.

2.3. Laboratory Measurement of SF_6

SF_6 was measured by gas chromatography attached to an electron capture detector using a 5 m stainless steel column packed with PorpakQ and held isothermally at 50°C for 3 min. Measurement precision was ±2.5% and the detection limit was 1 ng L^{-1}.

2.4. Calculation of Stream Discharge

The constant-rate injection dilution gauging method outlined by Moore (2004) was used to calculate the stream discharge from the saline tracer test:

$$Q = \frac{q}{k(\mathrm{ECss} - \mathrm{ECbg})} \tag{1}$$

where Q is stream discharge (L s^{-1}), q is tracer injection rate (L s^{-1}), ECss is the steady state electrical conductivity (μS cm^{-1}), ECbg is the background electrical conductivity (μS cm^{-1}), and k is the slope of the relationship between the electrical conductivity and the relative tracer concentration in the stream calculated using the field calibration method, see Moore (2004). Errors in salt dilution gauging estimates of discharge are generally around 4–7% (Day, 1976).

2.5. Estimation of Downstream Gas Evasion

For each upstream and downstream stream length, the change in SF_6 concentration was calculated as a percentage, and for each of the 16 tests the mean percentage change for the three repeat measurements was determined. Each of the 16 test results was assigned to one of four classes: (i) steep stream (>18%) under high flow conditions, (ii) steep stream (>18%) under low flow conditions, (iii) shallower stream (3–8%) under high flow conditions, and (iv) shallower stream (3–8%) under low flow conditions. The mean change (%) over 20 m was determined for each class, and this rate of gas loss over a 20 m reach was extrapolated to determine how quickly gas concentrations will decline, assuming this evasion rate for every 20 m in a downstream direction.

2.6. Calculation of the Gas Transfer Coefficient

Gas transfer coefficients were calculated using methods in Hope et al. (2001) and Wallin et al. (2011). The gas transfer coefficient for SF_6 was estimated using

$$K_{\mathrm{SF6}}\left(\mathrm{min}^{-1}\right) = \tau^{-1} \times \ln[(G_1 \times C_2)/(G_2 \times C_1)] \tag{2}$$

where k_{SF6} is the gas transfer coefficient for SF_6, τ is the reach travel time (seconds), G_1 and G_2 are the integrated SF_6 peak areas (i.e., relative concentrations) for the upstream and downstream measurement locations where C_1 and C_2 are the specific conductance values (μS cm^{-1}) at the upstream and downstream locations on the reach.

The SF_6 transfer coefficients were converted to CO_2 transfer coefficients using

$$K_{\mathrm{CO2}}/K_{\mathrm{SF6}} = (D_{\mathrm{CO2}}/D_{\mathrm{SF6}})^n \tag{3}$$

where K is the gas transfer coefficient (min^{-1}), D is the diffusion coefficient (m^2 s^{-1}), and n is an exponent based on stream water surface characteristics (Macintyre et al., 1995). The value of n is reported as varying from −0.66 to 1 (Hope et al., 2001). We used an n value of 0.5 that was used in similar studies (Billett & Harvey, 2013; Wallin et al., 2011). Wallin et al. (2011) suggest that 0.5 is a conservative estimate because turbulence varied among the streams they tested.

As the value of n is related to turbulence, we might expect that a higher value of n might be required for steep streams compared to shallow streams, or for streams tested under higher compared to lower flow conditions. It is possible that by using a constant value of 0.5 for n, K_{CO2} may be overestimated under lower flows or in shallow gradient streams when compared to tracer tests conducted under higher flows, or streams with steeper gradients. However, varying values of n between 0.5 and −0.5 in our calculations resulted in only a minor (0.36%) change in K_{CO2} for our first stream site.

The diffusion coefficient for CO_2 was estimated using the equation in Wallin et al. (2011) based on Jähne et al. (1987) and Wise and Houghton (1966):

$$D_{CO2} = 0.9477\ \exp^{(0.0274T)} \tag{4}$$

where D_{CO2} is the diffusion coefficient for CO_2 ($m^2\ s^{-1}$) and T is the stream temperature during the tracer test (°C). Although a slightly different equation was presented in Hope et al. (2001). for the estimation of D_{CO2}, these two approaches gave very similar estimates (difference in K_{CO2} of 0.01%).

The diffusion coefficient for SF_6 was estimated using the equation in King and Saltzman (1995) from which the values of the constants were taken:

$$D_{SF6} = Ae^{-\frac{Ea}{RT}} \tag{5}$$

where A is the preexponential factor 0.029 cm s^{-1}, Ea is the activation energy for diffusion in water (19.3 kJ/mol^{-1}), R has a value of 8.314×10^{-6} kJ mol^{-1} K^{-1}, T is the stream temperature in kelvin (measured during the test). Finally, the CO_2 gas transfer coefficients were corrected for temperature effects as outlined in Wallin et al. (2011):

$$K_{CO2}(20°) = K_{CO2}(T)\varnothing^{20-T} \tag{6}$$

where T is the water temperature of the stream reach and $\varnothing$ is a temperature coefficient with a value of 1.01 (Metzger & Dobbins, 1967). We converted the K_{CO2} values (at 20°C) to gas transfer velocities (k_{CO2}; m d^{-1}) by multiplying the former by stream depth.

2.7. Statistical Analysis and Models for the Prediction of K_{CO2} and k_{CO2}

We assessed the significance of the differences in K_{CO2} between steeper and shallower streams using the Mann-Whitney test. Stream parameters such as slope, flow velocity, or discharge are commonly used to form statistical models for the estimation of gas transfer from streams in both space and time (Raymond et al., 2012; Wallin et al., 2011). We explored these variables for estimating K_{CO2} by creating scatterplots of the values of these predictors versus the associated K_{CO2} values, and we included in these plots the median values for the tracer tests published by Wallin et al. (2011). We found no other studies which presented raw data that included both streambed slope and flow values (velocity or discharge) for headwater streams.

We used ordinary least squares to form regression models for predicting K_{CO2} for our data set based on the following predictors: slope, velocity, discharge, and slope × discharge. We also applied the regression models presented by Raymond et al. (2012) for the prediction of gas transfer velocity (k_{CO2}) to our data based on stream velocity, slope, and depth. For comparison we also formed a regression model for estimating k_{CO2} using the same predictors fitted to our data.

3. Results and Their Interpretation

3.1. Stream Characteristics

The streams are all of similar size, with channel widths ~1 m and average water depths of ~0.1 m during the tests (Table 1). Four streams have very steep slopes (18 to 29.4%) and four have shallower but still moderately steep slopes (3.7 to 7.6%). There were substantial differences in the measured flows during the two tests undertaken at each site (Table 1), and streams appeared substantially more turbulent during the high flow tests (see images in supporting information Figure S2). Discharge during the low flow tests varied from 0.8 to 4.6 L s^{-1} and those during the high flow tests from 12 to 88 L s^{-1} (Table 1). As expected, reach travel times were substantially faster under higher flow conditions (Table 1).

3.2. Salt Tracer

The specific electrical conductivity measurements were used to determine tracer mixing, and all reported results were for tests in which the salt tracer was fully mixed throughout the stream channel at both the upstream and downstream monitoring sites.

Steady state conditions (indicated by constant SEC), or conditions very close to steady state, were achieved in all reported tests. This is illustrated in time series plots of SEC concentrations at the upstream and

Table 1
K_{CO2} Average Values, Stream and Flow Characteristics for Eight Streams Under High and Low Flow Conditions

Stream (flow)	Date	Flow (L s^{-1})	Mean width[a] (m)	Mean depth (cm)	Velocity (m s^{-1})	Reach travel time (s)	Mean K_{CO2} min^{-1} (SD)[b]	Slope (%)
1 (high)	4/11/2013	12	0.92	10.9	0.12	165	0.343 (0.074)	23.2
1 (low)	24/06/2014	2.4	0.58	6.0	0.04	450	0.175 (0.020)	23.2
2 (high)	16/11/2015	38	1.02	19.3	0.19	105	0.056 (0.027)	3.7
2 (low)	9/09/2015	4.6	0.99	10.3	0.05	445	0.039 (0.012)	3.7
3 (high)	17/11/2015	37	1.14	14.5	0.20	100	1.471 (0.073)	29.4
3 (low)	10/09/2015	0.8	0.98	3.1	0.008	2400	0.093 (0.065)	29.4
4 (high)	11/11/2014	88	1.07	29.3	0.25	80	0.367 (0.255)	5.6
4 (low)	15/09/2014	2.2	1.04	10.4	0.01	1410	0.018 (0.010)	5.6
5 (high)	12/11/2014	43	0.98	12.1	0.22	90	0.172 (0.022)	5.6
5 (low)	16/09/2014	0.8	0.78	4.6	0.17	1230	0.045 (0.025)	5.6
6 (high)	13/11/2014	13	0.92	12.2	0.09	220	0.380 (0.043)	18.0
6 (low)	17/09/2014	3.1	0.82	6.4	0.01	1575	0.072 (0.005)	18.0
7 (high)	14/11/2014	35	1.22	13.6	0.20	100	1.044 (0.303)	24.9
7 (low)	18/09/2014	2.2	1.20	7.7	0.03	795	0.139 (0.013)	24.9
8 (high)	18/11/2015	25	1.09	13.0	0.13	150	0.139 (0.092)	7.6
8 (low)	11/09/2015	1.0	0.93	6.8	0.01	1440	0.037 (0.006)	7.6

[a]Note that width measurements are from the extreme edges of water flow and may include dry areas within the streambed. [b]SD is the standard deviation based on the measurement of SF_6 gas tracer concentrations in three samples taken during the tracer test under steady state flow conditions.

downstream sampling site which are presented in supporting information Figures S3 and S4, and the supporting information includes further discussion of these results. These SEC results illustrating steady state conditions provide evidence that the gas results, and the estimates of reach travel time, are reliable.

3.3. SF_6 Tracer

SF_6 tracer concentrations reduced substantially between the upstream and downstream sampling points, and there was reasonable consistency in the concentrations observed in the three samples taken at each sampling point (see supporting information Figures S5 and S6 and supporting information Tables S1 and S2).

The mean change (%) over 20 m was determined for each class (steep and high flow, steep and low flow, shallower and high flow, and shallower and low flow). The mean % changes over the 20 m reach were larger in steeper streams (66.9% and 78.2% changes) than in shallower streams (16.9% and 36.4% changes). Within these classes of steep and shallower streams there was a larger percentage change under low compared to high flow conditions, which reflects the longer reach travel time providing more time for gas evasion.

This mean rate of gas loss over a 20 m reach for each of the four classes was extrapolated to determine how quickly gas concentrations will decline, assuming this rate of gas transfer rate is consistent in a downstream direction (Figure 2). Although this approach is theoretical—in reality the slope and stream characteristics will vary downstream causing changes in gas transfer—it shows that the majority of the tracer is evaded within a short distance of the injection site. In steep streams, SF_6 gas concentrations are negligible within 100 m, while in the shallower streams they are greatly reduced within 200 to 400 m. Given that SF_6 has a higher Schmidt number than other gases of environmental interest (CO_2, CH_4, N_2O, and O_2), transfer rates for these gases will be larger than those of SF_6, and their concentrations would therefore decline more rapidly over the same distance.

3.4. K_{CO2} Transfer Coefficients

Mean (0.465 min^{-1}) and median (0.259 min^{-1}) K_{CO2} values in the four steeper streams were larger than mean (0.109 min^{-1}) and median (0.051 min^{-1}) K_{CO2} in the four shallower streams (Table 1 and Figures 3 and 4), and the difference between sites with steep and shallow slopes was statistically significant ($P = 0.028$) based on the Mann-Whitney test.

At all sites, K_{CO2} values were larger (mean 0.497 min^{-1}) under high compared to low (mean 0.077 min^{-1}) flow conditions (Figure 3). The difference between the two tests was generally greater in the steeper streams (Sites 1, 3, 6, and 7) compared to the streams with the shallower slopes (Sites 2, 4, 5, and 8). Estimated K_{CO2} was

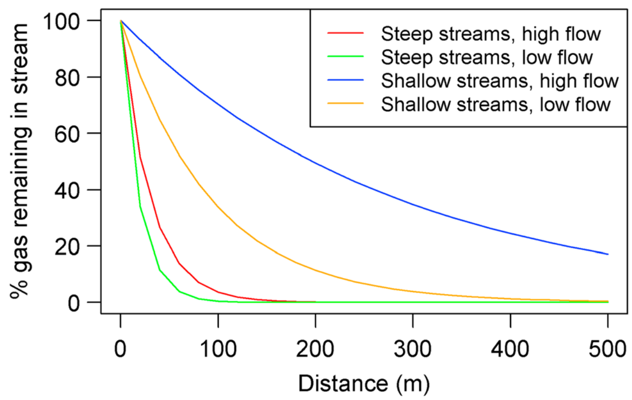

Figure 2. Extrapolation of the percentage of SF_6 gas remaining in stream based on measurements over a 20 m reach length, using an average of four measurements within each of four stream classes. Steep streams are those with bed slope 18.4–29.4%, while shallow streams have bed slopes 3.7–7.6%. The quantities for low and high flow conditions are reported in Table 1.

largest in steeper streams under high flow conditions, but for both steep and shallower sloping streams, K_{CO2} was significantly larger under high compared to low flow conditions (Figure 4). In steep streams, mean (0.809 min^{-1}) and median (0.712 min^{-1}) K_{CO2} values under high flow conditions were larger than mean (0.120 min^{-1}) and median (0.116 min^{-1}) values under low flow conditions, and this difference was statistically significant (P = 0.029) using the Mann-Whitney Rank Sum Test. In shallower streams, mean (0.184 min^{-1}) and median (0.156 min^{-1}) K_{CO2} values under high flow conditions were larger than mean (0.034 min^{-1}) and median (0.036 min^{-1}) K_{CO2} values under low flow conditions (one-tailed t test ; P = 0.032).

The best regression model (with the largest adjusted R^2 value) for the prediction of K_{CO2} from all 16 tests was for a single predictor of stream discharge multiplied by slope angle (expressed as the percentage value); the model coefficients are presented in Table 2, and the model is plotted in Figure 5. This model accounted for 94% of the variance in K_{CO2} (adjusted R^2 = 0.939).

3.5. k_{CO2} Gas Transfer Velocities

Estimated and measured values of the gas transfer velocities (k_{CO2}) are shown in Figure 6 using a new least squares ordinary regression model from the 16 observations in this study, and also for a range of nonlinear, predictive equations presented by Raymond et al. (2012). The new regression model based on stream velocity, slope, and depth accounted for 83% of the variance in k_{CO2} (adjusted R^2 = 0.827). Of the models presented by Raymond et al. (2012), equations (5) and (2) based on stream velocity and slope had the smallest overall prediction errors. The mean prediction error (untransformed units; m d^{-1}) for the linear regression model applied to the 16 samples was −3.41, while the mean prediction error for equation (5) and (2) were 18.2 and 21.9 (m d^{-1}), respectively. The mean squared errors (which provide a better assessment of bias than the mean error) were 1,065, 2,575, and 2,596 for the linear model, equations (5) and (2), respectively. The

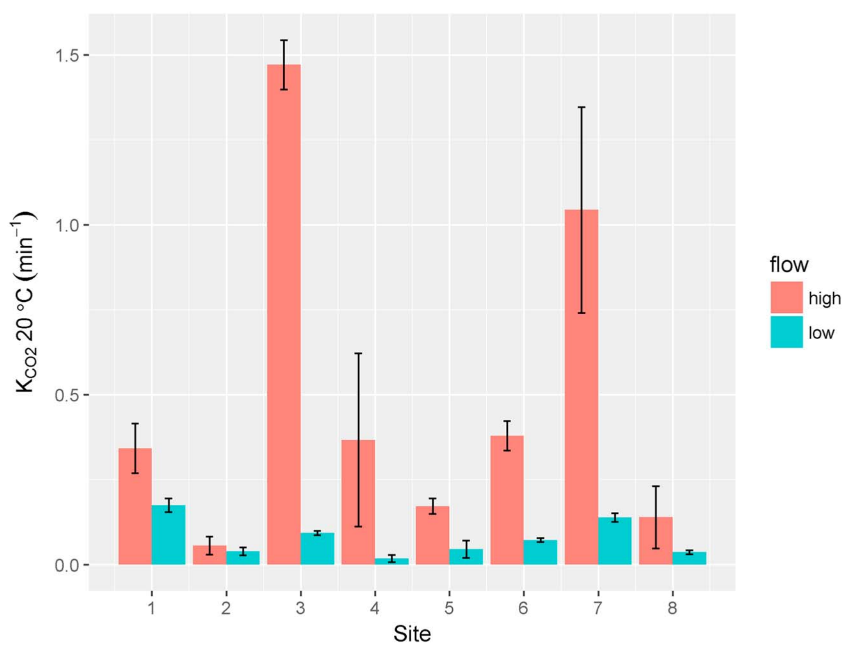

Figure 3. Barplot of K_{CO2} 20°C (min^{-1}) for the eight study sites under high and low flow conditions (see Table 1). The error bars (one standard deviation) are based on three measurements of gas tracer concentration during each test (high or low flow) at each site.

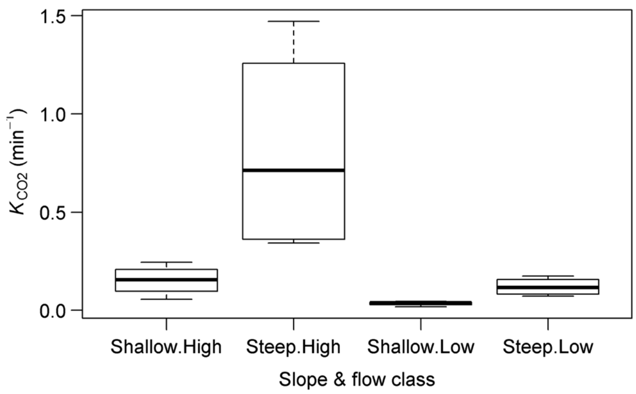

Figure 4. Boxplot showing the variations in K_{CO2} for four groups of sites based on streambed slope and flow conditions (see Table 1); each group has four sets of measurements. Steep streams are those with bed slope 18.4–29.4%, while shallow streams have bed slopes 3.7–7.6%.

mean error and mean squared errors for equations (2) and (5) are reasonably small given they were developed for a limited range of k_{CO2} (0–100 m d^{-1}). The two other models we applied from Raymond et al. (2012) (equations (1) and (7)) were more biased and had significantly larger prediction errors.

4. Discussion

Our results show that SF_6 gas transfer (and by inference CO_2 and other greenhouse gas transfer) occurs over short length scales: ~100 m in steep (18.4–29.4%) streams and ~200–400 m in streams with moderately steep slopes (3.7–7.6%). Previous studies have shown that loss of CO_2 by evasion to the atmosphere can be greater than downstream transport (Billett & Moore, 2008) and that substantial gas losses can occur over short distances. Öquist et al. (2009) estimated that up to 90% of soil dissolved inorganic carbon from groundwater was evaded as CO_2 within 200 m of the groundwater entering a small boreal stream in Sweden. Kokic et al. (2015) also reported substantial loss of CO_2 from small boreal streams in Sweden within a reach length of 150 m. In such streams and rivers where all gases are quickly evaded to the atmosphere, understanding the inputs and sources of gases and identifying any local hot spots of dissolved CO_2 input or instream production may be critical, as gases may be lost to the atmosphere between sampling locations (Venkiteswaran et al., 2014) leading to substantial underestimation of total evasion.

The K_{CO2} values from this study are generally in the range observed in other studies, but values from other studies tend to be lower (Table 3). This may in part reflect the shallower gradients of the streams and rivers in other studies which leads to less turbulent flow and lower evasion rates (Kokic et al., 2015; Schelker et al., 2016; Wallin et al., 2011). The steepest streams in our study included small waterfall sections which are known to increase turbulence and local evasion rates (Leibowitz et al., 2017; Natchimuthu et al., 2017).

Discharge is an important factor in determining gas transfer as turbulence generally increases with larger flows (Butman & Raymond, 2011; Hope et al., 2001; Zappa et al., 2007). The effect of larger flows leading to increased turbulence was easy to observe at our study sites. At each of our sites, K_{CO2} values were substantially larger under high compared to low flows (Figure 3). This relationship was not well established in other studies; Wallin et al. (2011) reported both increases and decreases in K_{CO2} with flow. In some cases K_{CO2} may not increase with discharge because the increase in depth offsets the effect of the greater turbulence (Genereux & Hemond, 1992). However, it is also possible that these studies did not observe an increase in K_{CO2} with increased flow because they investigated sites with shallower slopes where the relationship between flow and K_{CO2} may not be as strong (Natchimuthu et al., 2017) or because they did not encompass such a large flow range.

Billett and Harvey (2013) presented clear evidence of increasing K_{CO2} as discharge increased at two sites, and the three largest K_{CO2} values they reported were from streams under high flow conditions. It is clear from the results of our study, and that of Billett and Harvey (2013), that differences in K_{CO2} at a single site under different flow conditions are greater than those for streams with different slopes, suggesting that temporal variability is higher than spatial variability. Natchimuthu et al. (2017) found particularly high gas transfer velocities during high-discharge events. Overall, it appears that a substantial proportion of gas evasion may occur under high flow conditions, and therefore, large-scale estimates of gas evasion from streams and rivers should take account of temporal variability in discharge rather than using mean discharge.

Table 2
Coefficients for the Least Squares Regression Model Fitted to the 16 Estimates of K_{CO2} (See Figure 5) and k_{CO2}, Made in This Study (See Figure 6)

	Estimate	Std error	*t* value	*P* value
	K_{CO2}			
Intercept	9.93e-04	3.12e-02	0.032	0.975
Discharge[a] × slope[b]	1.21e-03	7.95e-05	15.2	<0.001
	k_{CO2}			
Intercept	−35.9	19.12	−1.878	0.083
Velocity[c] × slope[b]	4211.8	568.9	7.40	<0.001
Depth (m)	3.235	1.536	2.107	0.05

[a]Units L s^{-1}. [b]Percentage value. [c]Units m s^{-1}.

Figure 6 provides a comparison between previous estimates of K_{CO2} in similar sized streams by Wallin et al. (2011) and Billett and

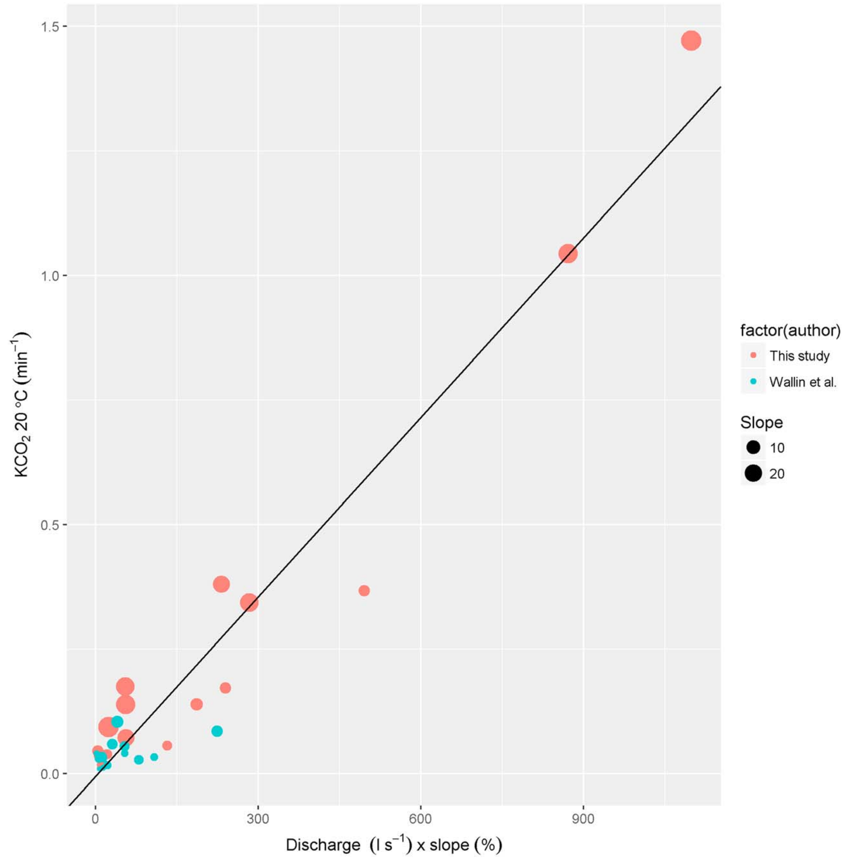

Figure 5. Scatterplot of discharge × slope (% values) versus K_{CO2} 20°C (min^{-1}) for the data from this study and that of Wallin et al. (2011). The diameter of the disk symbol is proportional to the stream slope angle at each site. The solid line is the ordinary least squares regression model fitted to the data from this study (see Table 2).

Harvey (2013). For each study the maximum and minimum reported K_{CO2} for each stream reach is plotted against stream slope. The four steep streams (range 18–29%) in this study are substantially steeper than the streams investigated in these two previous studies (slope range 0.2–11%), while the four shallow streams (3.7–7.6%) in this study are at the steeper end of the stream slopes reported in these previous studies. Figure 7 shows that maximum K_{CO2} values in our study are generally larger than those reported by Wallin et al. (2011), which may be because our study streams are steeper. However, some of the maximum values obtained by Billett and Harvey (2013) were similar to the maximum values in this study, and the data from Billett and Harvey (2013) illustrate that even in lower gradient streams, gas transfer coefficients can be as large as those in steeper reaches during high-discharge events.

Our models suggest that a combination of slope and either discharge or velocity can provide an effective prediction of K_{CO2} and k_{CO2}. For large-scale studies, stream or river discharge may be an easier parameter to estimate than stream velocity, because it can be predicted from rainfall and catchment area, while velocity also depends on the local stream characteristics. However, our models are based on a limited set of 16 measurements from eight sites, and although they account for much of the observed variation, further measurements are required in different geological and topographic settings, and in varying flow conditions, before they could be applied with confidence. We did not attempt to account for the effect of channel bed roughness (Bicudo & Giorgetti, 1991) on gas transfer because this varies considerably across short, step-pool sequences in steep stream sections (Lee & Ferguson, 2002) where we undertook tracer measurements and would therefore be difficult to incorporate into predictive models.

We were unable to use data from some published tracer studies to evaluate models for the prediction of either K_{CO2} or k_{CO2} because the authors had either reported summary statistics without results of individual measurements or had omitted important site characteristics (e.g., slope). It is essential that authors publish all

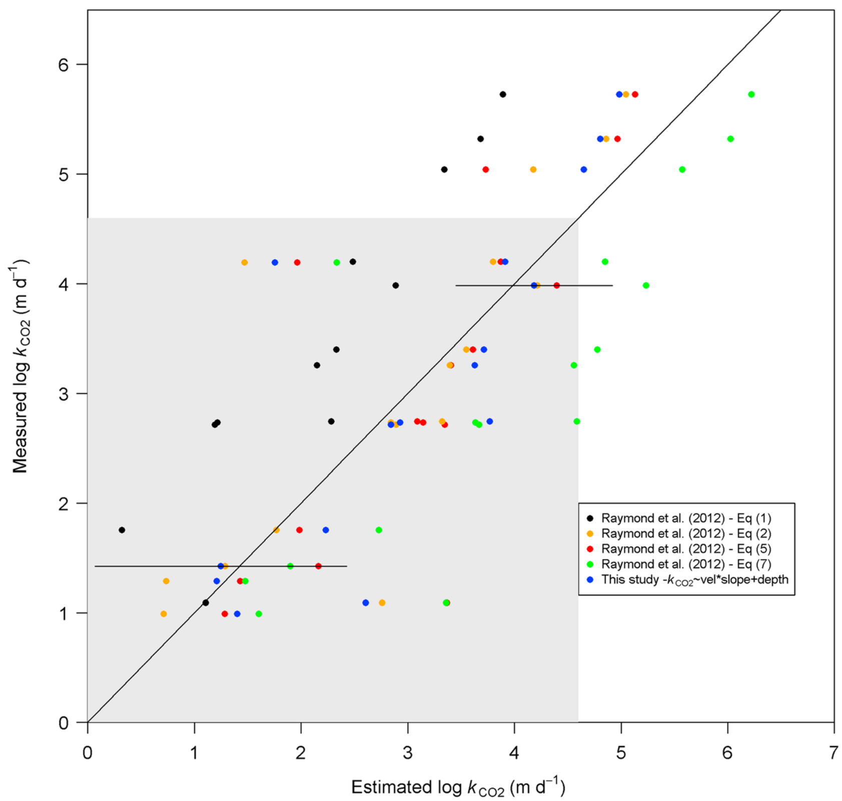

Figure 6. Estimated and measured values of log k_{CO2} for the 16 measurements made in this study for a range of predictive equations from Raymond et al. (2012). The parameters of the regression model fitted to the data from this study are shown in Table 2. The shaded region shows the approximate range of k_{CO2} over which the models by Raymond et al. (2012) were developed (0–100 m d^{-1}). The horizontal black lines show the 95% confidence intervals predictions at two sites using the model from this study (the prediction values are the locations of the blue disks).

relevant data so that models can be developed and tested across the widest possible range of landscape settings and flow conditions. Further tracer measurements to estimate gas transfer are required in a range of steep stream settings under varying flow conditions to test and refine models for the prediction of k_{CO2}.

Obtaining accurate estimates of gas transfer coefficients from tracer tests is difficult, and there are many potential sources of error (Knapp et al., 2015). In this study we ensured that (i) there was full tracer mixing within the stream channel at the sampling points, (ii) steady state was reached during the tracer tests,

Table 3
Comparison of Features and Mean K_{CO2} Values Obtained From a Range of Experimental Studies, Modified and Updated From Wallin et al. (2011)

K_{CO2} range (min^{-1})	Mean K_{CO2} (min^{-1})[a]	Number of tests	Slope range (%)	Discharge range (L s^{-1})	Location	Reference
0.039–1.471	0.327	16	3.7–24.9	0.8 to 88	S Wales, UK	This study
0.025–0.076[b]	Not reported	26	Not reported	3–33	Tennessee, USA	Genereux and Hemond (1992)
0.04–0.07[b]	Not reported	31	Not reported	5–57	Tennessee, USA	Roberts et al. (2007)
0–0.1[b]	Not reported	11	0.1–5	10–770	Alaska, USA	(Morse et al. (2007)
0.0004–0.003[b]	Not reported	3	0.11–0.28	47–425	Wisconsin, USA	House and Skavroneck (1981)
0.023–0.061[b]	Not reported	7	Not reported	12.9	Maine, USA	Maprani et al. (2005)
0.005–0.151	0.08	3	Not reported	36–137	Scotland, UK	Billett et al. (2004)
0.015–0.344	Not reported	8	3.2–11.3	4.3–24.1	Scotland, UK	Hope et al. (2001)
0–1.29	0.157	49	1.4–11	0.8 to 374.4	N England, UK	Billett and Harvey (2013)
0–0.0482	0.0255	8		0–10	N Sweden	Öquist et al. (2009)
0.001–0.207	0.041	114	0.2–6.8	0.4–154.1	N Sweden	Wallin et al. (2011)

[a]All studies used tracer methods for estimating K_{CO2}, except Morse et al. (2007). [b]Where necessary values were transformed from original values into values of K_{CO2} min^{-1} by Wallin et al. (2011).

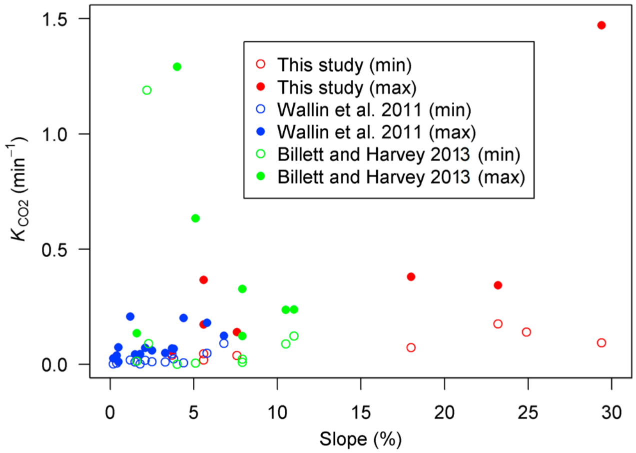

Figure 7. Comparison of K_{CO2} values from this study, Wallin et al. (2011) and Billett and Harvey (2013). Separate data are plotted for the minimum and maximum K_{CO2} values (min^{-1}) for each site in each study.

(iii) there were no substantial inflows in the study reaches, and (iv) there was a steady state tracer input. All these factors are important; if any of these conditions are not fulfilled there will be variability in tracer concentrations at the upstream and downstream sampling points, and so gas transfer estimates will include errors that are avoidable. As recommended (Knapp et al., 2015), we undertook temperature correction using temperature measurements made simultaneously with sample collection. We presented the variation in our gas transfer estimates based on repeated tracer gas concentration measurements which show that despite all the precautions outlined above, there is significant variability which should be considered. Many previous studies have only briefly reported the methods and results of the tracer tests used to estimate the gas transfer coefficient (e.g., Kokic et al., 2015; Peter et al., 2014; Schade et al., 2016) or have not discussed errors associated with replicate analyses (Hope et al., 2001; Kokic et al., 2015; Schelker et al., 2016; Wallin et al., 2011). While these studies may have avoided the sources of error listed above, it would be useful to develop a consistent method for future studies and assess the errors and uncertainties in the gas transfer coefficient estimates.

5. Conclusions

We used a combination of SF_6 and salt tracer testing to investigate gas transfer in eight streams (slope range 3.7–29.4%) under both high and low flow conditions (range 0.8–88 L s^{-1}). We observed that the vast majority of SF_6 tracer was lost within a maximum reach length of 100 to 400 m for our 16 measurements, and because SF_6 evades more slowly than CO_2, (and Ch_4, N_2O, and O_2) these would be lost over even shorter stream reach lengths. High-spatial resolution measurements of $p$$CO_2$ would be needed to ensure that groundwater inputs or hot spots of in-stream CO_2 generation are not overlooked in estimates of CO_2 evasion from such streams and rivers.

When the estimates of K_{CO2} were grouped by slope (shallow or steep) and flow condition (low and high), both factors were statistically significant. Steep streams, which make up a substantial proportion of freshwater channels globally, clearly have the potential to be extremely important in gas transfer between the land and atmosphere. At each of our eight sites, the largest K_{CO2} values occurred under the highest flows. Our findings suggest that much gas evasion may take place under high flow conditions and highlight the need to take into account temporal variations in discharge when upscaling estimates of gas evasion from streams and rivers.

We created a statistical model to predict K_{CO2} (min^{-1}) using values of streambed slope × discharge for our 16 measurements which accounted for 94% of the variation in the estimates of K_{CO2} from the tracer testing. We also used our measurements to estimate their k_{CO2} (m d^{-1}) transfer velocities and formed a statistical model based on stream slope and velocity which accounted for 83% of the variation in k_{CO2}. Two of the models presented by Raymond et al. (2012) for the prediction of k_{CO2}, developed from a larger number of tracer measurements (largely from streams with smaller slopes), also provided reasonable estimates based on slope and flow velocity.

Given the complicated nature of gas injection tracer tests in freshwater channels, and the many potential sources of error that arise from the field methodology, we recommend that our standard protocol is used and applied in future tests.

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