

Quantification of Carbon Dioxide Gas Transfer Velocity by Scaling from Argon through Dual Tracer Gas Additions in Mountain Streams

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Abstract

Quantification of the rate of gas exchange across the air-water interface is essential in understanding the biogeochemical cycling of carbon in mountain streams. However, estimating the gas transfer velocity (k) is not trivial, due to high turbulence and subsequent bubble-mediated gas transfer. Schmidt scaling is often used to estimate gas transfer velocities of climate relevant gases (e.g. CO_2) from tracer gases (e.g. argon (Ar)), but this method has high uncertainty when scaling between gases of different solubilities in streams with bubble-mediated gas transfer. Here we explore a method for the estimation of gas exchange of CO_2 from Ar by performing dual tracer gas additions in mountain streams. Ar and CO_2 gas were simultaneously and continuously injected into streams and gas exchange rates were estimated using an exponential decline model. The mean ratio of gas exchange of Ar to CO_2 (α) was 1.7 (95% credible interval of 1.3 to 2.3), approximately equal to the theoretical value of 1.7 (based both on Schmidt scaling and solubility). This result indicates that Ar can be used to estimate gas transfer of CO_2 with scaling but with some uncertainty. Finally, modeled results suggest that the use CO_2 as a tracer gas to measure gas exchange in streams with environmental conditions favoring interconversion to bicarbonate (i.e, high pH and alkalinity), can result in an overestimation of the gas transfer velocity k .

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Key Points:

- The dual release tracer technique (Ar and CO₂) estimated the scaling factor a to be 1.69 (95% CI: 1.37-2.04), in agreement with literature.
- Schmidt scaling overestimates gas exchange of CO₂ in turbulent streams when scaling from Argon to CO₂, due to the high solubility of CO₂.
- Use of CO₂ as a tracer gas in streams with high pH and bicarbonate alkalinity results in an overestimation of the gas transfer velocity k .

Abstract

Quantification of the rate of gas exchange across the air-water interface is essential in understanding the biogeochemical cycling of carbon in mountain streams. However, estimating the gas transfer velocity (k) is not trivial, due to high turbulence and subsequent bubble-mediated gas transfer. Schmidt scaling is often used to estimate gas transfer velocities of climate relevant gases (e.g. CO₂) from tracer gases (e.g. argon (Ar)), but this method has high uncertainty when scaling between gases of different solubilities in streams with bubble-mediated gas transfer. Here we explore a method for the estimation of gas exchange of CO₂ from Ar by performing dual tracer gas additions in mountain streams. Ar and CO₂ gas were simultaneously and continuously injected into streams and gas exchange rates were estimated using an exponential decline model. The mean ratio of gas exchange of Ar to CO₂ (α) was 1.7 (95% credible interval of 1.3 to 2.3), approximately equal to the theoretical value of 1.7 (based both on Schmidt scaling and solubility). This result indicates that Ar can be used to estimate gas transfer of CO₂ with scaling but with some uncertainty. Finally, modeled results suggest that the use CO₂ as a tracer gas to measure gas exchange in streams with environmental conditions favoring interconversion to bicarbonate (i.e, high pH and alkalinity), can result in an overestimation of the gas transfer velocity k .

Plain Language Summary

Streams, rivers and lakes are key components of the global carbon cycle, acting as both sources and sinks for carbon dioxide (CO₂), a potent greenhouse gas. More specifically, mountain streams are significant sources of CO₂ due to their steep slopes and turbulent nature, which encourages the escape of CO₂ from the stream and into the atmosphere. Estimating the amount of CO₂ released from turbulent mountain streams is a challenging task due to the many processes that control this flux. This study tested a technique for estimating fluxes of CO₂ in mountain streams and found that the approach proved to be robust and in accordance with other studies, but that estimates should be corrected for chemical processes occurring in the stream that consume CO₂. These results will allow researchers to more accurately quantify CO₂ released from streams and improve existing global carbon models.

1 Introduction

The rate of gas exchange across the air-water interface is essential for quantifying the flux of climate relevant gases (e.g., carbon dioxide (CO₂), methane (CH₄), or nitrous oxide (N₂O)), a critical parameter involved in many biogeochemical processes (Katul et al., 2018; Ulseth et al., 2019; Wanninkhof et al., 2009). For instance, estimates of the global carbon (C) balance rely on accurate quantification of carbon fluxes into and out of ecosystems (Katul et al., 2018; Raymond et al., 2013). Among these fluxes, CO₂ evasion from freshwater ecosystems has received increasing attention due to the active roles that streams, rivers, lakes, and estuaries play transforming and reallocating terrestrially derived carbon (C) (Aufdenkampe et al., 2011; Battin et al., 2009). Streams and rivers contribute substantial amounts of CO₂ to the atmosphere (Raymond et al., 2012, 2013). More specifically, headwater streams are particularly active sites of CO₂ degassing because of their close connection to terrestrial ecosystems and increased gas exchange relative to that of larger streams and rivers (Raymond et al., 2012, 2013; Wallin et al., 2011).

The total flux of CO₂ evaded from mountain streams has been estimated at 3.5 kg C yr⁻¹ (CI: -0.5 and 23.5 kg C m⁻² yr⁻¹), which is equivalent to and/or exceed those in Amazonian and boreal streams (Horgby et al., 2019). We observe this high CO₂ flux in steep slope mountain streams due to the high gas transfer velocities in these locations, which is predominantly driving the flux, and not only because there are extremely high concentrations of total carbon in the stream, as is the case in streams draining organic-rich soils (Horgby, Boix Canadell, et al., 2019). In fact, because of the limited soil build up and vegetation cover typical in steep mountain terrain, carbon concentrations can actually be relatively low in streams as the source of carbon may be from groundwater upwelling only (Duvert et al., n.d.; Horgby, Segatto, et al., 2019).

The gas flux is a function of gas transfer velocity at the air–water interface (k , in units of distance per time), the gas solubility coefficient and the difference in gas concentrations (at equilibrium) between the air and water (Moog & Jirka, 1999). Quantification of the gas transfer velocity k is not trivial due to considerable amounts of uncertainty and high spatiotemporal variability (Schelker et al., 2016; Tobias et al., 2009; Ulseth et al., 2019; Wallin et al., 2011). The value of k is primarily a function of slope, which dictates stream channel geomorphology and varies significantly between streams, and associated hydraulics that vary through time (Kokic et al., 2018). There have been multiple attempts to scale estimates of gas exchange from physical stream properties such as slope, velocity, discharge, stream bed roughness, Reynolds number (Re) and energy dissipation (Katul et al., 2018; Kokic et al., 2018; Raymond et al., 2012; Ulseth et al., 2019; Wallin et al., 2011). However, the relevance of these physical scaling relationships depends largely on the size of the ecosystem in question. This is easily illustrated by comparison of a small mountain stream with a steep slope and high turbulence to a larger river with predominantly laminar flow. The increased turbulence in the small mountain stream is due to its steeper slope and shallower depth, resulting in partially submerged macroroughness and turbulence near the surface of the stream. This near surface turbulence drives high gas transfer velocity in mountain streams (Ulseth et al., 2019).

Several methods exist to measure air-water gas exchange in aquatic ecosystems, such as measuring diel curves of oxygen over time (Grace et al., 2015; Hall et al., 2016) direct measurements with chambers (Alin et al., 2011; Aufdenkampe et al., 2011; Beaulieu et al., 2012; Lorke et al., 2015; Vachon et al., 2010) and single (Tsivoglou et al., 1968) and dual tracer gas additions (Hall Jr. & Madinger, 2018; Heilweil et al., 2016; Knapp et al., 2019). Tracer gas additions have been shown to be an appropriate method for estimation of gas exchange in turbulent streams due to the relatively small width, depth and discharge of the system, which render the experimental set up practical (Kokic et al., 2018). Another advantage of the tracer gas addition method is that k can be estimated over a distance at a similar spatial scale of the turnover length of the gas in question (Hall Jr. & Madinger, 2018).

A downside of this method is that the gas exchange measured with the tracer gas must then be scaled to the gas in question, a non-trivial task due to differences in diffusivity (and therefore Schmidt scaling) and solubility between the tracer gas and the gas of ecological interest (in this case, CO₂) (Hall Jr. & Madinger, 2018). This is especially true in the presence of turbulence induced bubble-mediated gas exchange. Scaling between gases of differing solubilities, the rate of gas exchange is not only dependent on molecular diffusion through the water medium and turbulence, but also diffusion across the surface of the bubble and transportation to the surface by the bubble. Because of these effects, the role of bubbles in estimating gas exchange rates is

complex and difficult to model accurately (Asher & Wanninkhof, 1998; Cirpka et al., 1993; Woolf et al., 2007).

In addition, there are other processes that must be considered when estimating gas exchange rates of CO₂, such as biological respiration (a source of CO₂) and chemical interconversion of CO₂ to bicarbonate (a sink) (Hall & Ulseth, 2020). While the effect of respiration is likely negligible since the time scale over which gas exchange is measured is much shorter than what would be relevant for respiration (Duvert et al., n.d.), this is not the case for interconversion of CO₂ to HCO₃⁻. It has been shown through experimentation and modelling that the reaction kinetics for the interconversion occur at orders of magnitude and timescales that are relevant when using the tracer gas method (Schulz et al., 2006). While the role of chemical enhancement of CO₂ gas exchange across the air-water interface has been extensively explored (Bolin, 1960; Emerson, 1975; Quinn, J. A., Otto, 1971; Smith, 1985; Wanninkhof & Knox, 1996) the role of interconversion of CO₂ to HCO₃⁻ has not yet been accounted for in the estimation of the gas transfer velocity when the stream is artificially enriched with CO₂, as is the case when using CO₂ as the trace gas itself.

Common tracer gases used to scale CO₂ are sulfur hexafluoride (SF₆) (Hall et al., 2003; Maurice et al., 2017; Wanninkhof et al., 1990), propane (C₃H₈) (Marzolf et al., 2011; Mulholland et al., 2001; Raymond et al., 2012; Schelker et al., 2016), helium (He) (Vautier et al., 2020) and more recently argon (Ar) (Hall Jr. & Madinger, 2018; Ulseth et al., 2019). While SF₆ and C₃H₈ behave much more similarly to CO₂ in terms of solubility and Schmidt number, these gases are known greenhouse gases, making them less ideal for this type of study (Hall Jr. & Madinger, 2018; McDowell & Johnson, 2018). Helium is an inert gas, at relatively low background concentrations in nature and is conveniently commercially available, but differs significantly from CO₂ in terms of solubility. Ar has been used by Hall and Madinger (2018) to scale to O₂, a key parameter of gas exchange for ecosystem metabolism models, as it is very similar to O₂ in terms of Schmidt number and solubility and has been shown to accurately quantify gas transfer velocities in turbulent streams (Hall Jr. & Madinger, 2018; Ulseth et al., 2019). Additionally, Ar is another relatively inert noble gas, similarly to He, but is slightly more soluble, making it a better candidate for scaling to CO₂ (Asher & Wanninkhof, 1998).

Our objective was to estimate through dual tracer additions of Ar, a proven tracer gas, and soluble CO₂, a gas of ecological interest, the scalability of Ar to CO₂ for the purpose of estimating gas exchange rate of CO₂ (k_{CO_2}) in turbulent mountain streams. When scaling between gases of similar solubilities, gas exchange is predominantly controlled by diffusivity, in which case only using Schmidt scaling is appropriate. However, Ar and CO₂ differ significantly in terms of solubility, implying the need to correct for solubility in addition to the diffusivity effect. Finally, CO₂ also differs from Ar in that it is chemically reactive in the stream, which further complicates the ability to scale between these two gases. Based on solubility and diffusivity principles (Hall Jr. & Madinger, 2018; Woolf et al., 2007). We start with the primary hypothesis that scaling from Ar to CO₂ will be approximately equal to the theoretical value of 1.7, within an acceptable margin of error. Accordingly, we aim to answer the following questions: Can we empirically calculate the scaling factor and does it match the value obtained theoretically? What is the effect of the interconversion between CO₂ and HCO₃⁻ on the measured gas exchange rate of CO₂?

2 Materials and Methods

2.1 Study sites

We performed a total of 11 simultaneous dual releases of Ar and CO₂ between March 2018 and April 2019 at 4 different mountain streams in the Swiss Alps (Table 1). The four streams were steep-channel headwaters with step-pool morphology, where the gas exchange had been measured previously and were at the upper range of gas exchange rates (Ulseth et al., 2019). These sites are ideal systems to test our hypotheses as they are turbulent streams that also have substantial bubble-mediated gas exchange. Three of the stream sites (Richard, Veveyse and Vièze) were located below the tree line and thus covered by coniferous and mixed forests, while the Ferret stream drained a sparsely vegetated rocky terrain. To cover a wide range of predicted gas exchange rates, streams were chosen on the basis of differing geomorphological and hydraulic characteristics and sampled between 2 (Veveyse and Vièze) and 6 (Richard) occasions.

2.2. Experimental Set Up

Gas exchange rates were estimated by continuously adding CO₂ and Ar and measuring the downstream decline of gas concentrations (Figure 1a). Prior to addition of the trace gases, we collected pre-plateau samples for Ar and CO₂ at 5-6 stations downstream of the injection site, as well as one upstream location (Figure 1b). In situ measurements of atmospheric pressure, water temperature, pH, and conductivity were recorded at each station.

After collecting pre-plateau samples, we released a salt slug to estimate the discharge, travel time and velocity of the stream. A known mass of dissolved sodium chloride was added at the top of the reach and conductivity was continuously monitored and recorded at a frequency of 1 Hz at the last station in the reach using conductivity loggers (WTW, Xylem Inc.) until conductivity returned to background levels. The travel time was calculated as the time to peak conductivity at the end of the reach where time 0 corresponded to the addition of the salt slug at the top of the reach. The methods of estimation of discharge and velocity are provided in the *Supplementary Information*.

We then added Ar and CO₂ to the stream simultaneously using a micro bubble diffuser (PENTAIR, Aquatic Ecosystems, NC, USA), distributed evenly across the stream channel and waited for the concentrations to reach equilibrium at the downstream site, which was assumed to be 4 times the travel time estimated from the salt slug (Stream Solute Workshop, 1990). We repeated sampling for Ar and CO₂ gases at each station (one upstream and 5-6 downstream) and additionally collected water samples for alkalinity measurements. In situ measurements of atmospheric pressure, water temperature, pH, and conductivity were also repeated at each station.

2.3. Gas Sampling and Analysis

We measured CO₂ concentrations of the stream water in the laboratory and *in situ*. For all releases done prior to March 2019, duplicate samples for CO₂ were collected in glass vials (60 mL) that contained crystalized sodium azide (300 µL) for sample preservation. In the field, vials were carefully submerged in the water to avoid bubble formation and turbulence-induced CO₂ loss, and while still submerged, they were sealed with rubber stoppers and metal caps. In the

laboratory, a headspace with synthetic air (< 5 ppm CO₂) was created and the water phase and the headspace were allowed to equilibrate (2 hours). We measured the CO₂ concentrations using a cavity ring-down spectrometer (G2201-I, Picarro Instruments, USA) (Schelker et al., 2016). After March 2019, CO₂ concentrations were measured in situ using a Vaisala handheld CO₂ probe (GM70, Vaisala, Helsinki, Finland). This improved the efficiency of the fieldwork as the concentrations of CO₂ could be measured in real time. For each measurement of CO₂ with the Vaisala, the concentration was observed until it stabilized on the monitor of the device and an average value across 4-5 min of stable data was taken as the CO₂ concentration at that station. An intercalibration between the Vaisala and Picarro was done in the laboratory to check if corrections needed to be made such that the measured CO₂ concentrations could be comparable between them (see Figure S1 in the *Supplementary Information*). Measurements of temperature, pressure, pH, conductivity, stream depth and width were simultaneously recorded at each station.

Samples for dissolved Ar:N₂ were collected using a 3.8 cm diameter PVC pipe with an attached outlet vinyl tube (3.2 mm ID X 20 cm). As stream water flowed through the pipe, the downstream end was capped with a rubber stopper and the sample was collected from the vinyl tube, first overflowing the 12 mL Exetainer vial three times. The vials were capped immediately, without bubbles. Ar concentrations were measured as Ar:N₂ using membrane inlet mass spectrometry (MIMS) (Bay Instruments Inc., Easton, MD) within 24 hours.

We measured the ratio of Ar to N₂ as opposed to the concentration of Ar alone as this provided a much higher precision with the MIMS. The concentration of Ar in the stream was enriched by no more than 5%, preventing any N₂ degassing from the stream, and keeping the Ar:N₂ ratio as a reliable measurement of the increase in Ar concentration (Hall & Madinger, 2018; Ulseth et al., 2019). In addition, it was assumed that no biologically driven N₂ fluxes occurred during the release and that the concentration of N₂ in the stream remained constant throughout the sampling period.

Alkalinity samples were also stored at ~4°C and were analyzed the day after sampling. Alkalinity was measured using a titrator (916 Ti-Touch, Metrohm AG, Switzerland). The titrator was calibrated using standard solutions of pH = 4 and 7 and the slope was verified to be at least 96%. Samples were allowed to reach room temperature while being stored in a cupboard to protect them from light and were transferred to the beaker directly before measurement to avoid exposure to atmospheric CO₂. Samples of 100g were titrated with a solution of 0.05N HCl to an endpoint of 4.5 to determine total alkalinity.

2.4 Determination of k_{Ar} , k_{CO_2} and a

The exponential decline of Ar:N₂ and CO₂ was corrected for background concentrations and normalized to the ratio of Ar:N₂ or CO₂ concentration measured at the first station downstream of the injection site by:

$$\begin{aligned} An_x &= \frac{A_x}{A_0}, \\ Cn_x &= \frac{C_x}{C_0}, \end{aligned} \tag{1}$$

where An_x represents the ratio of Ar:N₂ (minus the background ratio) normalized to A_0 and C_0 , where A_0 and C_0 are the ratio of Ar:N₂ and the concentration of CO₂ measured at the first sampling station respectively. Exponential decay models were fit to the data according to

$$\begin{aligned} An_x &\sim N(An_0 \times e^{-K_{d,Ar}x}, \sigma_A) \\ Cn_x &\sim N(Cn_0 \times e^{\frac{-K_{d,Ar}}{a}x}, \sigma_C), \end{aligned} \quad (2)$$

where An_x is the normalized modeled ratio of Ar:N₂ at a distance x along the reach, An_0 is the y-intercept, $K_{d,Ar}$ is the decay rate of Ar at the stream water temperature in units of per distance, x is the distance along the reach of the stream (with the first station considered to be at 0 m) and a is the ratio of gas exchange rates between Ar and CO₂ (i.e. $a = K_{d,Ar}/K_{d,CO_2}$ at stream temperature). These statistical models assume that the residual errors are normally distributed with a standard deviation of σ_A and σ_C for Ar and CO₂ respectively.

A Bayesian statistical approach was used to fit equation 2 to the data by adjusting the parameters An_0 , Cn_0 , $K_{d,Ar}$, a , σ_A and σ_C , following the methods described by Hall & Madinger 2018 and Ulseth et al., 2019. The goal of this study was to determine if one can accurately scale from Ar to CO₂, i.e. we are interested in the value of $a = K_{d,Ar}/K_{d,CO_2}$, where $K_{d,Ar}$ and K_{d,CO_2} are in units per distance. The prior probability for a_j in each stream j was established as

$$a_j \sim N(a_{mean}, \sigma_a), \quad (3)$$

where a_{mean} had a prior distribution of $a_{mean} \sim N(1.6, 1)$, as 1.6 is the value found for a in Hall and Madinger (2018). Prior probabilities for the remaining parameters were the same as those in Hall and Madinger (2018) and Ulseth et al., 2019.

Estimates of uncertainty around the calculated value of K_d and a are provided as the 95% credible interval. Posterior distributions were generated using the *rstan* package in Rstudio (adapted from the supplementary information in Hall and Madinger, 2018) to obtain values for K_d and a (R Core Team, 2018; Stan Development Team, 2017).

Gas exchange rates (K_d) in m⁻¹ were converted to gas exchange velocity (k) in m d⁻¹ using

$$k = K_d \times v \times \bar{z} \times 86400, \quad (4)$$

where v is nominal stream velocity (m s⁻¹) and $\bar{z}$ is average stream depth (m) calculated from $\bar{z} = Q/(wv)$ (where Q and v were derived from the salt slug and w is the average width measured during sampling). The values of k (m d⁻¹) were standardized to a common Schmidt (Wanninkhof, 2014) number of 600 (k_{600} , m d⁻¹) such that they would be comparable among different streams, sampled on different days and therefore at varying stream temperatures.

2.5 Modelling the inter-conversion of CO₂ to HCO₃⁻ and correction of *a* (*a'*)

In addition to the gas exchange with the atmosphere, it is important to also consider other processes that are occurring in the stream, such a respiration and chemical interconversion of CO₂ to bicarbonate and HCO₃⁻, which may have an effect on the measured gas exchange rate. It is impossible to measure the changes in concentration that occur due chemical interconversion alone, as there are many processes happening in the stream simultaneously (e.g. outgassing and respiration). For this reason, we developed a model for the chemical interconversion of CO₂ to bicarbonate following the methods described by Schulz et al. (2006) which considered the following reactions:



The set of differential equations was implemented into the model and integrated numerically with the MATLAB function ‘ode15s’ solver for stiff problems (Shampine et al., 1997; Zeebe, 1999). Rate constants for the reaction equations used are provided in Table S1 in the *Supplementary Information*. Note that we could only apply this model to streams for which we had sufficient alkalinity and pH data (streams sampled from March 2019 onwards).

Initial conditions for the concentration of CO₂ in the stream was assumed to be equal to the value measured at station 1. This assumes that the gas injected into the stream at the diffusers has had time to dissolve and mix into the stream and is at its maximum concentration when measured at station one and is the same assumption that is made for the model that considers gas exchange only (described in section 2.3). The concentration of CO₂ was converted from ppm to mol/kg-soln using Henry’s Law and correcting for water vapor pressure (DOE, 1994).

Initial concentrations of carbonate and bicarbonate were calculated using CO2SYS (van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., Wallace, 2011) in MATLAB. This MATLAB function requires two of the three parameters we measured (pH, alkalinity and CO₂ concentration) in order to calculate concentrations of carbonate and bicarbonate as well as H⁺ and OH⁻. We provided estimates of the rate of inter-conversion of CO₂ to HCO₃⁻ using first the parameters pH and CO₂, and second using alkalinity and CO₂. The use of these different parameters provides us

with a proxy of uncertainty in our results as they should be identical in theory, but are not necessarily in practice due to uncertainties/errors associated with each measurement. Outputs of the function CO2SYS were then directly used to estimate reaction rate constants and initial concentrations for CO_3^{2-} , HCO_3^- , H^+ and OH^- . The temperature used for the estimation of equilibrium constants was taken as the average temperature in the stream during the release (Table 4).

3 Results & Discussion

3.1 Scaling of Ar to CO_2

Gas exchange rates for Ar (K_d (m^{-1})) ranged from a minimum of 0.008 m^{-1} in Veveyse to a maximum of 0.057 m^{-1} in Richard (Table 3) and are comparable to other estimate of gas exchange (Hall Jr. & Madinger, 2018; Hall & Ulseth, 2020; McDowell & Johnson, 2018). Precision on the Ar : N_2 measurements was high with a median standard deviation for the triplicate measurements of Ar : N_2 at each station of 5.36×10^{-5} .

For each of the releases the measured ratio of $K_{\text{Ar}} : K_{\text{CO}_2}$ was greater than one (Figure 2), which supports the theory that the gas exchange rate of Ar is greater than that of CO_2 . The variability in the ratio of $K_{\text{Ar}} : K_{\text{CO}_2}$ (a) was high among the 11 releases that we conducted and ranged from 1.12 to 1.99 with a standard deviation of 0.17 (Figure 2, Table 3). The average value for a ($\bar{a}$) was 1.69 with a 95% credible interval of 1.37 to 2.04, which is in agreement with the theoretical scaling value obtained using Eq. 13 in Woolf et al. (2007), where a was calculated to be equal to 1.74. The 95% confidence interval also encompasses the value for a estimated in Hall and Madinger (2018), which was found to be 1.6. Differences in these theoretical estimates of a are due to different values taken from the literature for both the Ostwald solubility coefficients and Schmidt numbers, as well as rounding error. The fact that a calculated from all three estimates was found to be much higher than the value of 1.36, which is the value one would obtain for a from Schmidt scaling alone, is also in agreement with the literature, which states that using Schmidt scaling is likely overestimating the gas exchange of CO_2 due to solubility effects (Hall Jr. & Madinger, 2018).

At high solubilities ($\alpha > \sim 0.01$), the scaling between gases depends on both the Schmidt number effects (diffusivity, temperature) and the solubility, while at low solubilities it is dependent on the Schmidt number only (Bell et al., 2017; Hall Jr. & Madinger, 2018; Wanninkhof, 2014; Woolf et al., 2007) (Figure 3). The contours vary as a function of both the Ostwald solubility coefficient (α) and the Schmidt number above an approximate threshold of $\alpha \sim 0.01$, while below this they vary as a function of Schmidt number only.

For the purposes of this study, we are interested in the ability to scale from Ar to CO_2 , which are two gases that behave differently in terms of solubility and Schmidt number (Figure 3). Scaling from Ar to O_2 can be easily done using Schmidt scaling alone as these two gases are similar in terms of solubility (i.e. moving parallel to the x-axis) and diffusivity (Schmidt number). However, for CO_2 there is the effect of solubility, in addition to the Schmidt number effect, complicating this scaling, especially in the presence of bubble mediated gas exchange (i.e. moving up both the x- and y-axes in Figure 3 to scale from Ar to CO_2). We can see that CO_2 is located on the contour equal to 1.74, and exists in the range where there are dependencies on

both Schmidt number and solubility ($\sim \alpha \gg 0.1$) (i.e. as one moves along the contour, both the solubility and the Schmidt number change) (Figure 3).

The theoretical scaling value of 1.36 using Schmidt scaling alone overestimates the gas exchange of CO₂ when scaling from Ar, is because CO₂ has a higher solubility and stays in solution rather than move into the gas phase and cross the air-water interface into bubbles to be quickly transported to the surface and out of the stream (Woolf et al., 2007). Because of this solubility effect, we obtain a relatively higher value for a when it is measured in the stream because it takes this effect into account. Ultimately, without correcting for the solubility effect, we would overestimate the gas exchange rate of CO₂ to the atmosphere when scaling from argon, particularly in turbulent streams where bubbles may dominate the gas exchange.

Therefore, scaling from Ar to CO₂ is not only dependent on the Schmidt number and solubility, but also the degree of turbulence and bubble-mediated gas transfer that is occurring in the stream, which could explain some of the uncertainty observed in the measured value for $\bar{a}$. Scaling from Ar to CO₂ could therefore be done with much less uncertainty using Eq. 13 in Woolf et al., 2006, if a measurement of the bubble flux (Q_b) for that particular stream, at a particular moment in time, is known. Measuring this parameter in the field is not trivial however and so a more feasible alternative could be to use a tracer gas with a similar solubility to that of CO₂. For instance, a good candidate can be helium (He) (Aeschbach, 2016), a tracer gas commonly used in oceanography. However, this gas is even farther away from CO₂ than Ar in terms of both Schmidt number and solubility (Figure 3).

3.2 Corrections for Interconversion of CO₂ to HCO₃⁻

In addition to the solubility effects, CO₂ also differs from Ar in that it is chemically reactive in the environment and the carbonate system has a significant role in how much CO₂ ultimately remains in solution upon addition of the tracer gas (DOE, 1994; Schulz et al., 2006)(Schulz et al., 2006, DOE 1994). All of the stream sites for this study are located in catchments with limestone bedrock (*map.geo.admin.ch*) and because of this, the average pH in the stream is relatively high (average pH: 8.14, sd: 0.15) (Table 4).

In general, at pH values above 5, some of the CO₂ will begin to convert to bicarbonate (HCO₃⁻) and at pH values around 8, like what we observe in the stream, the chemical equilibria almost entirely favor conversion of CO₂ to HCO₃⁻ (Riebesell et al., 2011), however in the stream there is some buffering capacity due to the alkalinity. Therefore, the CO₂ injected into the stream partially converts to bicarbonate (HCO₃⁻) and as a result the observed exponential decrease in CO₂ concentration has to necessarily be due to both the effect of gas exchange and chemical interconversion from CO₂ to HCO₃⁻. It is challenging to quantify the effect of chemical interconversion in the field as there are multiple processes occurring simultaneously (gas exchange, respiration and groundwater inputs (Hall & Ulseth, 2019). For this reason, we decided to model it following the methods described previously and according to Schulz et al. (2006). Measured values of CO₂ concentration, pH, pressure and temperature were input into the MATLAB script CO2SYS.m (van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., Wallace, 2011) to calculate the initial conditions for the model (Figure 4). Figure 4 is an example of an output of the model (Stream: RIC, Date: 21 March 2019), which shows the changes in

concentration of relevant components of the carbonate system vs. time upon the addition of CO₂ to the stream.

A key observation is that these changes in concentration occur at significant orders of magnitude and over relevant timescales. That is, the CO₂ added does not instantaneously convert to HCO₃⁻, but instead non-negligible quantities are converted over a period of time that is of the same time scale magnitude as the time it takes for the concentration of CO₂ in the stream to return to background conditions (~600 s). This means that the change in concentration that we observe in the stream is not only due to gas exchange, but is partially also due to chemical interconversion from CO₂ to HCO₃⁻.

Since these kinetic reactions are of significant proportions in relation to the overall decline in CO₂, we then attempted to correct our measured values for this effect so that the gas exchange rate of CO₂ (K_{d,CO_2} , m⁻¹) to the atmosphere due to physical processes alone could be estimated. This correction was made by subtracting the effect of chemical interconversion to bicarbonate (which was estimated from the model) such that we are left with an exponential decrease due to gas exchange with the atmosphere only, and not the combined effect (Figure 5).

In general, the effect of interconversion is mostly occurring in the first few stations, particularly in the Richard stream, and equilibrium is reached for the last few stations, where only gas exchange to the atmosphere is responsible for the observed decrease in CO₂ concentration (Figure 5). In release RIC-4, we see that initially the decay due to interconversion exceeds the measured decay rate. While it is not possible for the change in concentration due to interconversion to exceed what is observed in the field, this error is likely due to uncertainties in the measurements of ancillary data used in the model. In the releases done in the Veveyse stream, the flows were much higher, resulting in a lower initial concentration of CO₂, which could explain the more gradual decay rates observed. We see that in all of the releases, applying the correction results in a less steep curve, indicating a corrected K_{d,CO_2} that is lower than the initial measured gas exchange rate.

We reran the model using the values corrected for effects of chemical interconversion of CO₂ to bicarbonate, and found an average scaling factor (a') of 2.97 (95% CI: 1.82 – 4.73), which is much higher than the original estimate of 1.69 that accounted for diffusion and solubility effects only. We draw two main conclusions from these results. The first conclusion being that scaling from Ar to CO₂ can be done, but it is important to factor in the effects of solubility. The second conclusion being that using CO₂ as a tracer gas to measure gas exchange of CO₂ to the atmosphere may not be accurate, especially in streams that have a high pH and high bicarbonate alkalinity, as this causes much of the injected CO₂ to favor chemical interconversion to HCO₃⁻. As such, one would observe a decrease in CO₂ concentration that is due to chemical processes, and therefore the measured value of k obtained would not be an accurate estimate of gas exchange to the atmosphere.

5 Conclusions

Although Ar is abundant in the atmosphere and is present at relatively high background concentrations in streams, our findings agree with previous studies (Hall & Madinger, 2018; Ulseth et al., 2019) which state that Ar is a suitable tracer gas in the context of mountain streams. It has a low greenhouse gas effect and we are able to detect small changes in its concentration

with high precision (when measuring ratios Ar:N₂ when using the MIMS for analysis). Additionally, since only low concentrations are needed, only small quantities of Ar are required to be transported to the field study site, making the overall method much more convenient (Hall & Madinger, 2018). Furthermore, Ar:N₂ it is biologically and chemically inert at the time scale the gas release takes place, meaning that other processes occurring in the stream (groundwater inputs, respiration and chemical interconversion) would not impact the measurement of the gas exchange rate.

Our results show that it is possible to use Ar as a tracer gas to estimate the scaling of gas transfer velocities from Ar to CO₂. The measured value of a_{mean} (1.69) was approximately equal to the theoretical value calculated (1.74) based on the bubble mediated gas transfer model of Woolf et al., 2007. However, there is high uncertainty surrounding the measured gas transfer velocities of Ar and CO₂, and therefore substantial noise in the measured scaling factor a , resulting in errors when using these k_{CO_2} measurements to calculate CO₂ fluxes where bubbles dominate gas exchange. It is important to note however, that the amount of uncertainty observed in this study surrounding a (95% confidence interval varying from approximately 20% to 60% of the value of a), is comparable to results from other studies and most other methods for measuring gas exchange (Hall Jr. & Madinger, 2018; Hall & Ulseth, 2020; Knapp et al., 2019; Ulseth et al., 2019).

The dual release method of Ar and CO₂ described in this paper has shown that Ar can be used as a tracer gas and scaled to estimate gas transfer velocities of CO₂ when accounting for both solubility and diffusivity with measures of uncertainty that are comparable to other methods for measuring gas exchange (Knapp et al., 2015, 2019; Wanninkhof et al., 1990; Young & Huryn, 1999). Although estimating gas exchange rates remains highly uncertain, empirical methods, such as dual tracer gas additions, continue to constrain these uncertainties (Hall & Ulseth, 2020).

However, based on our findings, previously measured gas exchanges rates using CO₂ as a tracer gas may have been significantly affected by the process of chemical interconversion. Corrections to the scaling factor a that account for the chemical interconversion need to be better estimated in a laboratory setting to quantifiably address the uncertainty associated with using CO₂ as a tracer gas. We recommend future experiments that exclude the reaction kinetics altogether by avoiding adding CO₂, and instead using a DIC and total alkalinity (TA) enriched solution of the same pH and temperature as the stream in question. This way, when mixing occurs, no chemical disequilibrium will be created and the observed change in CO₂ concentration would only be a result of degassing and dilution. The latter can then be traced and corrected for by measuring changes in TA. A correct assessment of the coupled solubility and interconversion effects on scaling CO₂ gas exchange will be a valuable contribution towards more reliable carbon models as accurately quantifying CO₂ fluxes from streams to the atmosphere becomes of increasing importance in light of global change.

Acknowledgments, Samples, and Data

- The authors declare no conflict of interest
- All data used in this study has been made available on figshare.com (doi: <https://doi.org/10.6084/m9.figshare.13087472.v1>).

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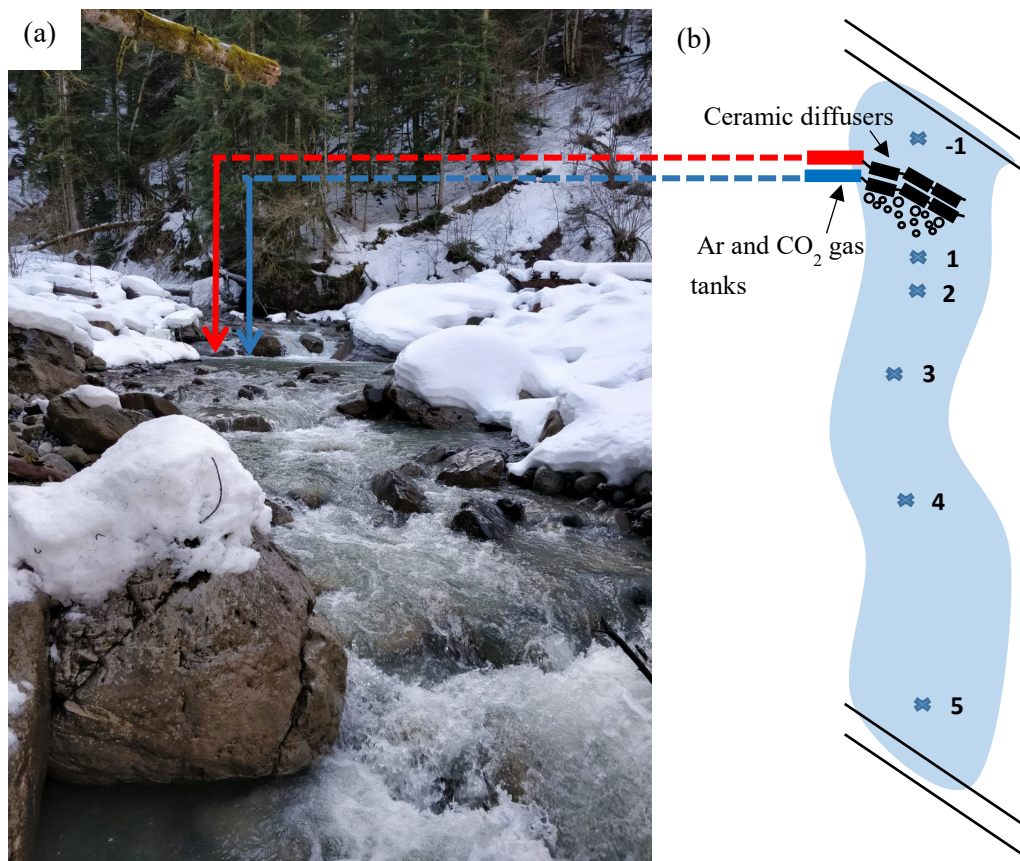
Figures

Figure 1. **a)** Photo of one of the experiment streams (Veveyse) taken on March 12th 2019 and **b)** Schematic of the experimental set up showing the stations -1 through 5. The ceramic diffusers for this particular release were placed at the location designated by the red and blue arrows in Figure 1. a).

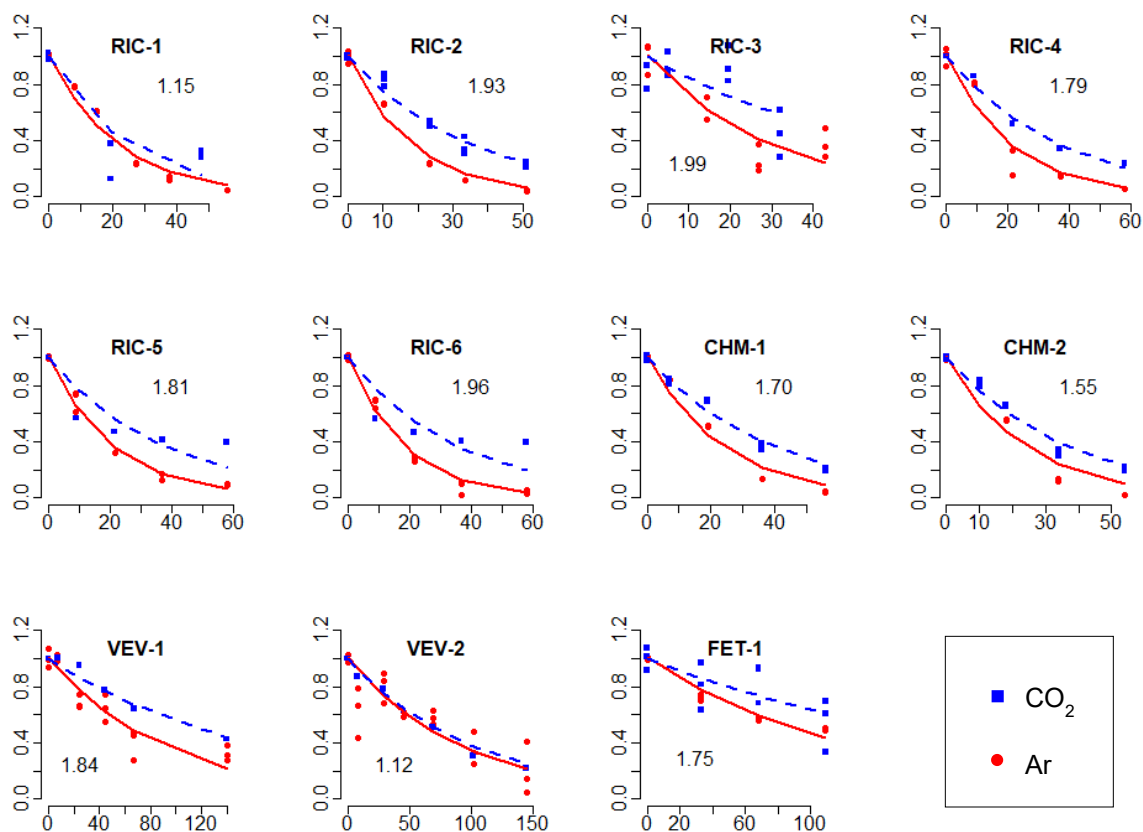


Figure 2. Exponential decline of normalized Ar (red) and CO₂ (blue), sampled at stations along the reach at each study site. Lines are exponential models fitted to the points of normalized gas concentration. Values for a estimated at each site are shown on each plot and ranged from 1.12 to 1.96.

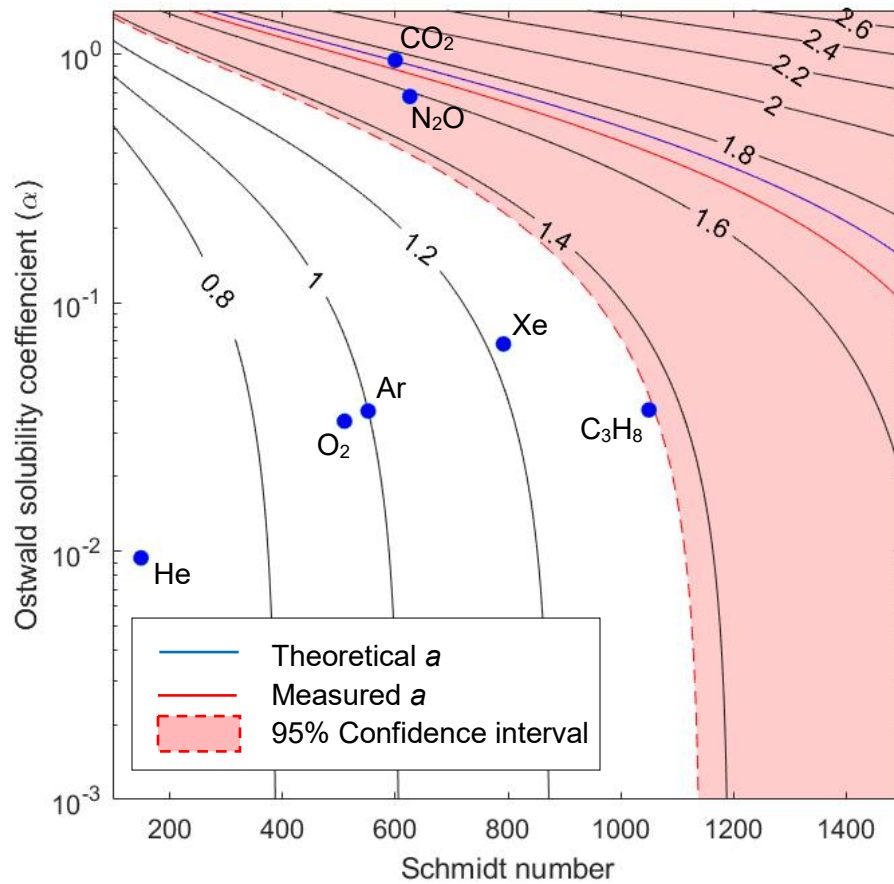


Figure 3. Contours are the ratio of the modeled bubble-mediated gas exchange rate (according to Woolf et al., 2007) of Ar to other gases ($K_{b,Ar}/K_{b,gas2}$) where $K_{b,gas2}$ is dependent on both solubility (represented by α , the Ostwald solubility coefficient) and Schmidt number. Ar falls on the contour equal to 1 as all values are referenced to Ar ($K_{b,Ar}/K_{b,gas2}$). The solid red line corresponds to the measured value for α , averaged across all the releases performed ($\bar{\alpha}$). The blue line represents the theoretical value for α calculated according to Hall & Madinger 2018. At high solubilities, scaling between gases depends on both the Schmidt number effects and the solubility, while at low solubilities it is dependent on the Schmidt number only.

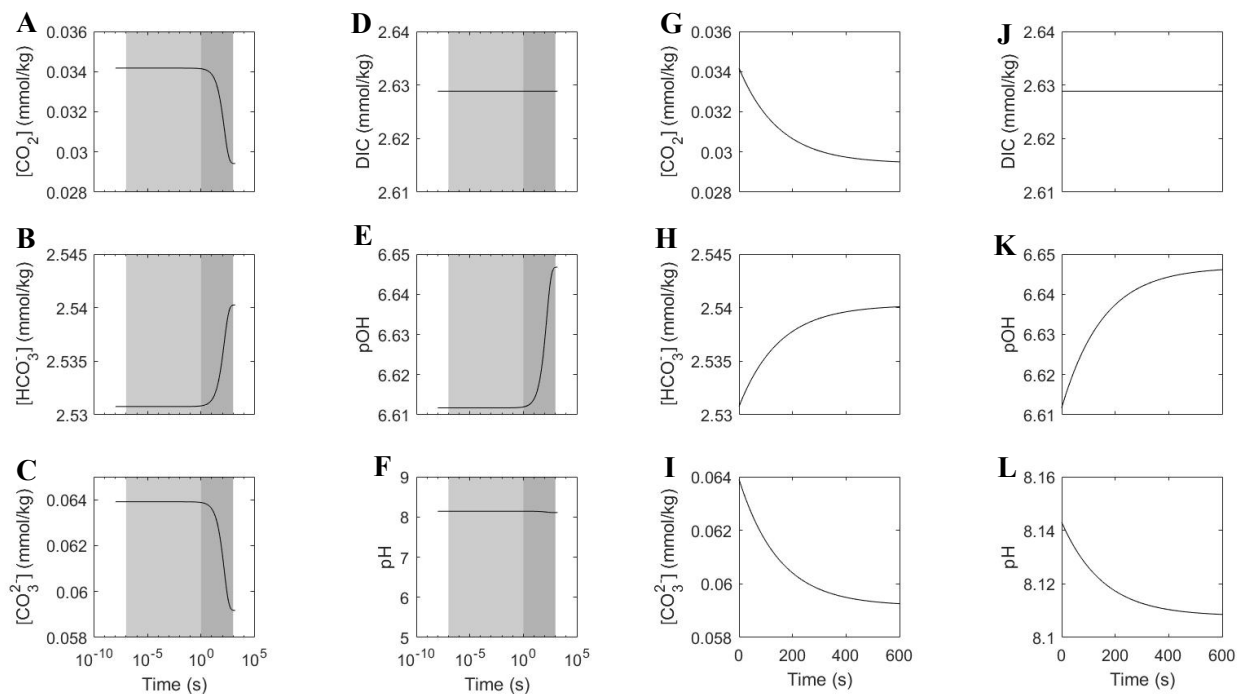


Figure 4. Example of an output of the reaction kinetics model (Stream: RIC, Date: 21 March 2019). Figures A-F depict changes in concentrations of [CO₂], [DIC], [HCO₃⁻], [CO₃²⁻], pOH and pH vs time (log-scaled) that occur at a logarithmic time scale (from 10^{-8} s to 600 s). Grey shaded areas show at what time scales we observe changes in concentrations (no change from 10^{-7} s to 10^0 s, but we observe changes in concentration from 10^0 to 10^3). Figures G-L show changes in concentration on a linear timescale (from 0 to 600 seconds) and are of the same order of magnitude as the timescales of gas exchange that occur in the stream. Measured values of [CO₂] and pH were used to estimate the initial conditions for the concentrations of [DIC], [HCO₃⁻], [CO₃²⁻] and pOH used in the kinetics model.

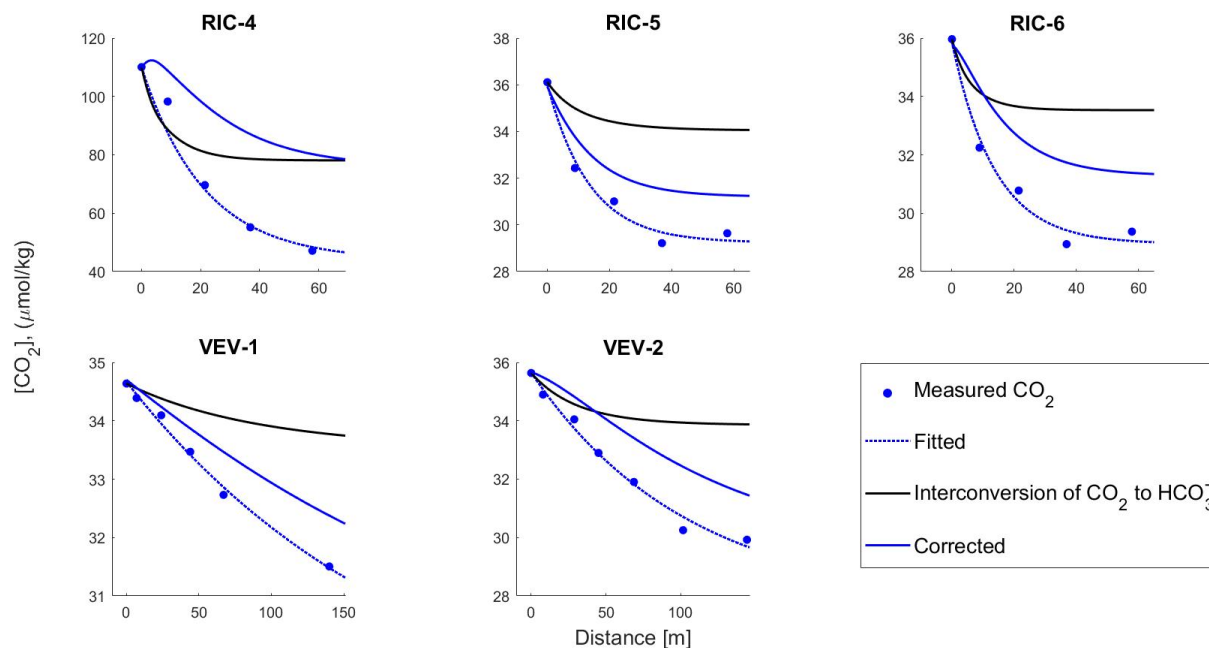


Figure 5. Modeled interconversion of CO_2 to HCO_3^- . The decrease in concentration of CO_2 that is due to chemical interconversion alone is shown in black. The corrected exponential decay of CO_2 in the stream is shown in blue and corresponds to $[\text{CO}_2]_{\text{corrected}} = [\text{CO}_2]_0 + [\text{CO}_2]_{\text{measured}} - [\text{CO}_2]_{\text{interconversion}}$. We observe that the effect of the chemical interconversion has the largest effect in the first few stations, as this is just after addition of the CO_2 gas to the stream. At stations farther from the addition site, the added CO_2 has theoretically had time to equilibrate, and therefore we observe changes in the concentration of CO_2 that are due to gas exchange with the atmosphere only. Therefore, the effect of interconversion is indirectly a function of stream flow rate (the faster the stream flow, the more stations will be affected).

Tables**Table 1.** Study sites and stream characteristics including stream name, code, date of release, slope, reach length (L), average stream width (w), average stream depth (z) discharge (Q), mean stream velocity (v) and salt slug travel time (t).

Stream	Code	Date	Slope*	L	w	z	Q	v	t
			[m m ⁻¹]	[m]	[m]	[m]	[m ³ s ⁻¹]	[m min ⁻¹]	[min]
Richard	RIC-1	29.Jan.18	0.14	65	1.9	0.11	0.030	8.6	8
Richard	RIC-2	16.Mar.18	0.14	65	1.4	0.11	0.011	4.2	16
Richard	RIC-3	30.May.18	0.14	57	4.8	0.98	1.023	13.0	4
Richard	RIC-4	21.Mar.19	0.14	69	1.7	0.13	0.016	4.1	17
Richard	RIC-5	15.Apr.19	0.14	65	2.4	0.08	0.017	5.3	11
Richard	RIC-6	30.Apr.19	0.14	65	2.5	0.44	0.050	2.7	5
Vièze	CHM-1	26.Jun.18	0.16	66	1.8	0.12	0.032	8.9	7
Vièze	CHM-2	04.Jul.18	0.16	67	2.5	0.08	0.021	6.4	11
Veveyse	VEV-1	12.Mar.19	0.10	151	6.7	0.17	0.591	30.5	5
Veveyse	VEV-2	28.Mar.19	0.10	146	6.1	0.34	0.411	12.0	6
Ferret	FET-1	08.Aug.18	0.06	142	3.1	0.12	0.143	23.7	6

*Slopes for all of the streams were measured using either digital GPS, a theolodite (Leica) and for one site (Veveyse) Google Earth by measuring the change in elevation from the top to the bottom of the reach and dividing by the length of the reach (m m⁻¹).

Table 2. Descriptions of symbols used for the calculation of k_{CO_2} and k_{Ar} for each release

Symbol	Description (units) [constant]
k	Gas transfer velocity (m d ⁻¹)
k_{Ar}	Gas transfer velocity for Ar (m d ⁻¹)
k_{CO_2}	Gas transfer velocity for CO ₂ (m d ⁻¹)
a	Ratio of gas exchange rate of Ar to that of CO ₂ [-]
A_x	Concentration ratio of Ar:N ₂ (Corrected for background concentrations) [-]
A_0	Concentration ratio of Ar:N ₂ at station 1 [-]
An_x	Concentration ratio of Ar:N ₂ Normalized to A_0 [-]
C_x	Concentration of CO ₂ (ppm)
C_0	Concentration of CO ₂ at station 1 (ppm)
Cn_x	Normalized concentration of CO ₂ [-]
An_0	Normalized concentration ratio of Ar:N ₂ at station 1 [-]
Cn_0	Normalized concentration of CO ₂ at station 1 [-]
K_d	Gas exchange rate (m ⁻¹)
$K_{d, Ar}$	Gas exchange rate for Ar (m ⁻¹)
K_{d, CO_2}	Gas exchange rate for CO ₂ (m ⁻¹)
K_{Ar}	Gas exchange rate for Ar (d ⁻¹)
K_{CO_2}	Gas exchange rate for CO ₂ (d ⁻¹)
σ_A	Standard deviation of normally distributed residual errors for the statistical model of Ar [-]
σ_C	Standard deviation of normally distributed residual errors for the statistical model of CO ₂ [-]
x	Distance along the reach (m)
a_j	Value of a in each stream j [-]
$\bar{a}$	Average value for a [-]
σ_a	Variation of a_j among streams, with a half-normal prior distribution
v	Nominal stream velocity (m s ⁻¹)
z	Average stream depth
k_{600}	Gas transfer velocity scaled to a common Schmidt number of 600 (m d ⁻¹)

Table 3. Measured gas exchange rates for Ar and CO₂ and calculated values. Scaling factors (*a*) are reported with 95% credible intervals.

Site	$K_{d,Ar}$ [m ⁻¹]	K_{Ar} [d ⁻¹]	k_{Ar} [m d ⁻¹]	K_{d,CO_2} [m ⁻¹]	K_{CO_2} [d ⁻¹]	k_{CO_2} [m d ⁻¹]	<i>a</i> [-]
RIC-1	0.046	566	65	0.044	543	62	1.15 (0.70,1.68)
RIC-2	0.056	336	36	0.028	169	18	1.93 (1.53,2.40)
RIC-3	0.035	650	640	0.016	308	302	1.99 (1.48,2.65)
RIC-4	0.049	289	39	0.027	159	21	1.79 (1.36,2.30)
RIC-5	0.057	436	34	0.028	214	17	1.80 (1.34,2.34)
RIC-6	0.057	224	99	0.028	109	48	1.96 (1.49,2.55)
CHM-1	0.043	559	66	0.026	332	39	1.70 (1.31,2.11)
CHM-2	0.043	392	32	0.028	256	21	1.55 (1.21,1.94)
VEV-1	0.011	496	86	0.006	260	45	1.84 (1.37,2.43)
VEV-2	0.008	145	49	0.010	176	59	1.12 (0.84,1.49)
FET-1	0.008	268	31	0.003	95	11	1.75 (1.27,2.36)

Table 4. Site chemistry data was recorded in the field for streams sampled March 2019 and onwards. These parameters were assessed at each station in the reach, however the averages for the entire reach are presented here for each release. The pH was measured on the free scale.

Code	Date	pH	Alkalinity (μmol/kg)	T (°C)	[CO ₂] ₀ (μmol/kg)
RIC-4	21.Mar.19	7.90	1384.55	3.76	110.05
RIC-5	15.Apr.19	8.67	1346.40	4.06	36.11
RIC-6	30.Apr.19	8.55	1327.43	4.37	35.96
VEV-1	12.Mar.19	8.24	1658.31	2.01	34.64
VEV-2	28.Mar.19	8.26	1672.41	2.66	35.64

SUPPORTING INFORMATION FOR:
**Quantification of Gas Transfer Velocity of CO₂ by Scaling from Argon through
Dual Tracer Gas Additions in Mountain Streams**

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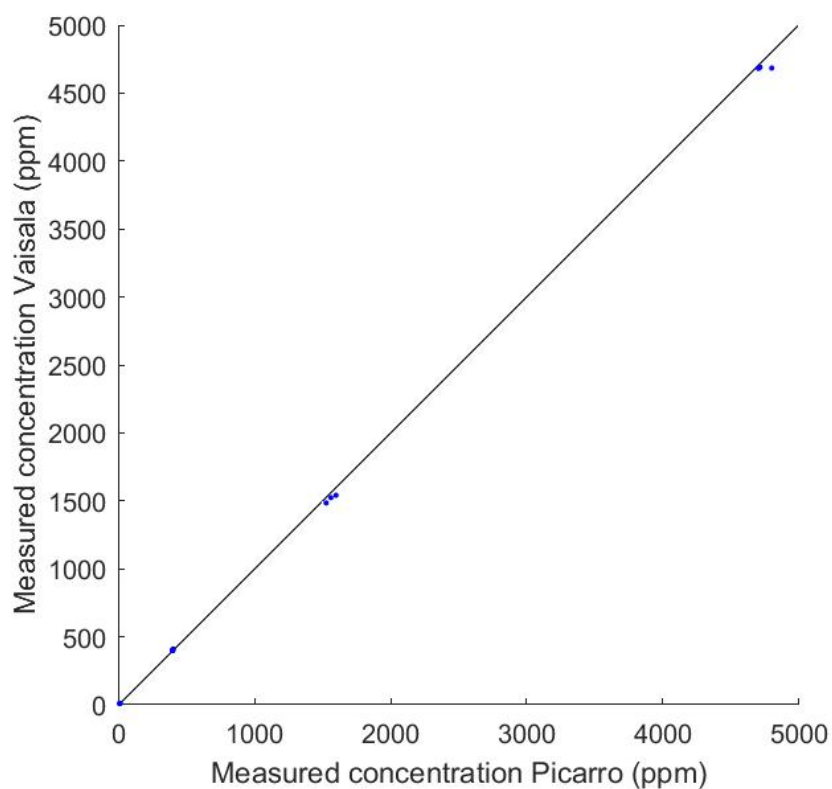


Figure S1. Intercalibration check for CO₂ data obtained using the Picarro CRDS analyzer and the Vaisala hand held probe. The same known concentration of CO₂ in a sealed container was measured using both instruments in triplicate at 4 different concentrations: 0 ppm, 500 ppm, 1500 ppm and 5000 ppm. The results are plotted alongside a 1:1 line. Measurements performed with the Vaisala were found to be comparable to those measured with the Picarro and no correction was deemed necessary.

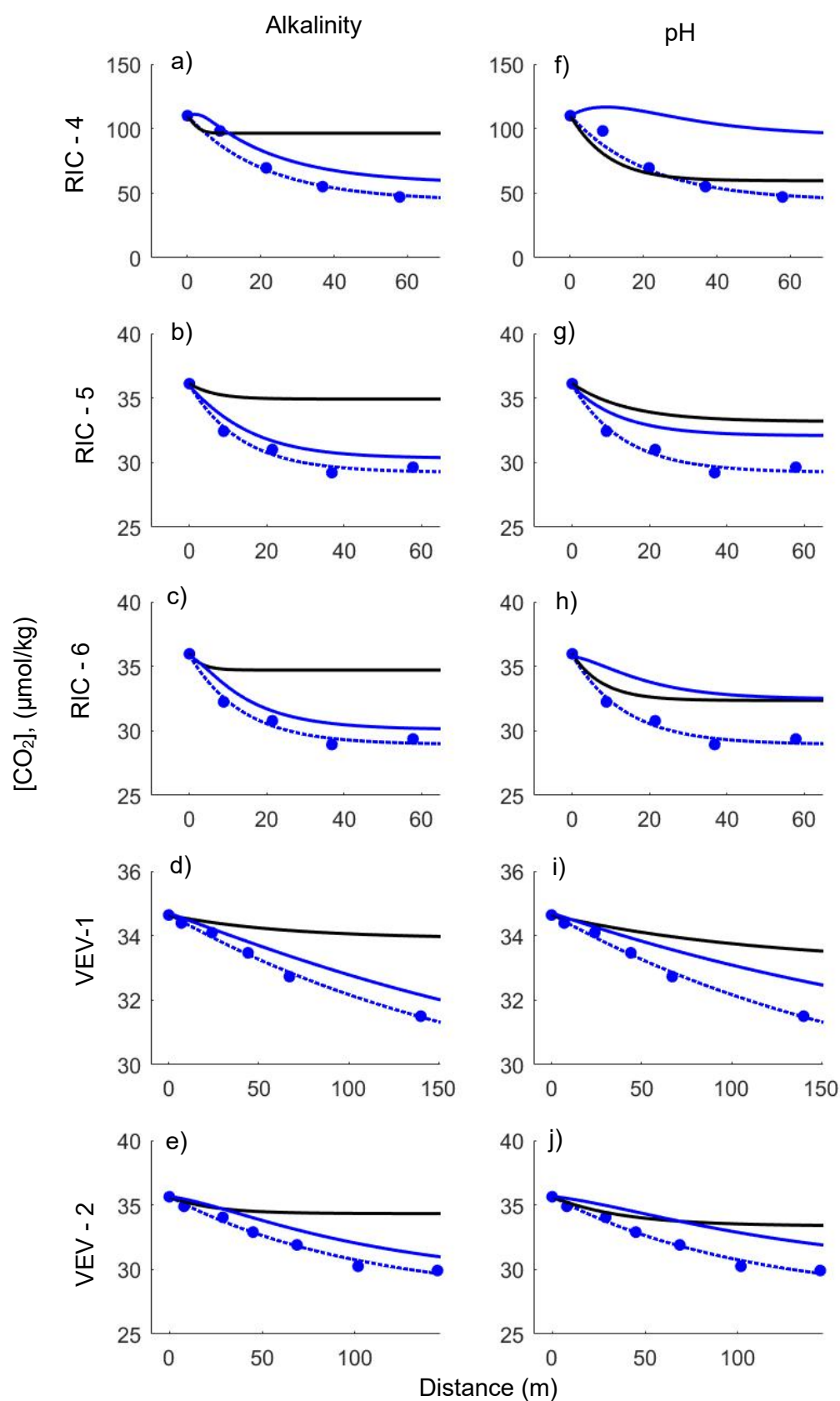


Figure S2. Modeled interconversion of CO_2 to HCO_3^- for each of the releases using alkalinity (a-e) and pH (f-k). The measured CO_2 concentrations are shown by the blue points, to which an exponential decay is fitted (dashed line). The decrease in concentration of CO_2 that is due to chemical interconversion alone is shown in black. The corrected exponential decay of CO_2 in the stream is shown in blue and corresponds to $[\text{CO}_2]_{\text{corrected}} = [\text{CO}_2]_0 + [\text{CO}_2]_{\text{measured}} - [\text{CO}_2]_{\text{interconversion}}$.

Supplementary Tables

Table S1. Reaction rate constants and their respective check values used in this study

Rate constant	Check value ($T = 298.15$ K, $S = 35$)	Dependence on T and S	Reference
k_{+1}	$3.71 \times 10^{-2} \text{ s}^{-1}$	$\exp(1246.98 - 6.19 \times 10^4/T - 183.0 \ln(T))$	1
k_{-1}	$2.67 \times 10^4 \text{ kg mol}^{-1} \text{ s}^{-1}$	k_{+1}/K_1^*	Calculated
k_{+4}	$2.23 \times 10^3 \text{ kg mol}^{-1} \text{ s}^{-1}$	$A_4 \exp(-90,166.83/(RT))/K_w^*$	3
k_{-4}	$9.71 \times 10^{-5} \text{ s}^{-1}$	$k_{+4} \times K_w^*/K_1^*$	Calculated
$k^{H^+}_{+5}$	$5.0 \times 10^{10} \text{ kg mol}^{-1} \text{ s}^{-1}$	None	2
$k^{H^+}_{-5}$	59.44 s^{-1}	$k^{H^+}_{+5} \times K_2^*$	Calculated
$k^{OH^-}_{+5}$	$6.0 \times 10^9 \text{ kg mol}^{-1} \text{ s}^{-1}$	None	2
$k^{OH^-}_{-5}$	$3.06 \times 10^5 \text{ s}^{-1}$	$k^{OH^-}_{+5} \times K_w^*/K_2^*$	Calculated
k_{+6}	$1.40 \times 10^{-3} \text{ kg mol}^{-1} \text{ s}^{-1}$	None	2
k_{-6}	$2.31 \times 10^{-10} \text{ kg mol}^{-1} \text{ s}^{-1}$	k_{+6}/K_w^*	Calculated

Reference 1 refers the work of Johnson (1982), reference 2 refers to Eigen (1964) and reference 3 refers to Schulz et al. (2006). T refers to temperature in Kelvin and S refers to salinity, R denotes the universal gas constant of 8.31451 J/mol, K_w^* the equilibrium constant for the ion product of water calculated using the methods described in DOE (1994), K_1^* and K_2^* the first and second dissociation constants of carbonic acid from Roy et al. (1993).

Supplementary Methods

Methods S1. Estimation of discharge and velocity

The methods used for the estimation of discharge and velocity follow closely the methods described in Ulseth et al. (2019). We used slug releases of sodium chloride to estimate flow (Q), travel time and velocity (v). We dissolved sodium chloride in a bucket of stream water, ensuring that the known mass of salt had completely dissolved before releasing it into the stream. Enough salt was dissolved to increase conductivity by 50-100% (0.5-500 kg, depending on stream size and background conductivity). The conductivity was continuously recorded at the bottom of the reach using conductivity loggers (WTW, Xylem, Inc.) until the conductivity returned to background conditions.

Travel time was defined as the time it took to reach peak conductivity. The velocity was calculated by dividing the length of the reach (m) by the travel time (s).

The stream Q (m^3/s) was estimated by integrating under the specific conductivity curve according to equation 1:

$$Q = \frac{SC_{add}}{\sum_{i=1}^n (SC_{meas} \times \Delta t)} \quad (1)$$

Where SC_{add} is the specific conductivity of the salt slug added to the stream. We calculated SC_{add} using an empirical relationship calculated in the lab that relates the mass of the salt to the specific conductivity. SC_{meas} is the specific conductivity measured at the end of the reach and Δt is the time step of the conductivity measurements (1s).

Supplementary References

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