SUPPORTING INFORMATION FOR:

Quantification of Gas Transfer Velocity of CO_2 by Scaling from Argon through Dual Tracer Gas Additions in Mountain Streams

K. H. Schuler[1,4], L. Gómez Gener[1], A. J. Ulseth[2], K. G. Schulz[3], N. Deluigi[1] and T. J. Battin[1]

[1]Stream Biofilm and Ecosystem Research Laboratory (SBER), Polytechnique Fédérale de Lausanne (EPFL).

[2]Department of Biological Sciences, Sam Houston State University.

[3]School of Environment, Science and Engineering Southern Cross University.

[4]Department of Earth Ocean and Atmospheric Sciences, University of British Columbia

Corresponding author: Katrina Schuler (kschuler@eoas.ubc.ca)

Table of Contents

Supplementary Figures

Figure S1. Intercalibration check: A performance comparison of the Picarro and Vaisala probe for measuring CO_2 concentrations

Figure S2. Summary of modeled corrections applied to the measured data (pH and Alkalinity)

Supplementary Tables

Table S1. Rate constants and respective check values used in this study

Supplementary Methods

Methods S1. Estimation of discharge and velocity

Supplementary References

Supplementary Figures

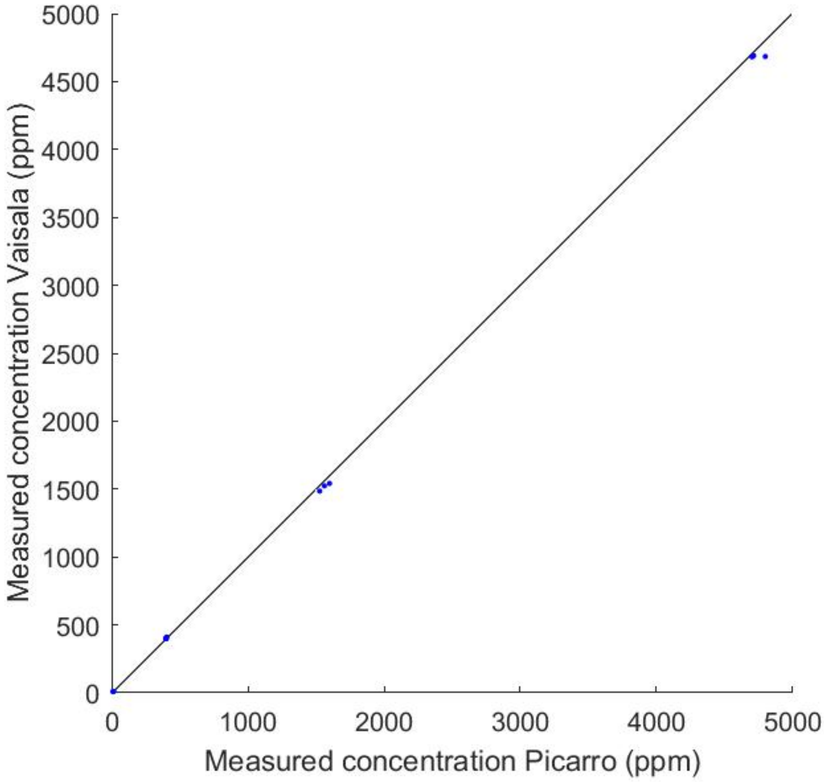

Figure S1. Intercalibration check for CO_2 data obtained using the Picarro CRDS analyzer and the Vaisala hand held probe. The same known concentration of CO_2 in a sealed container was measured using both instruments in triplicate at 4 different concentrations: 0 ppm, 500 ppm, 1500 ppm and 5000 ppm. 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.

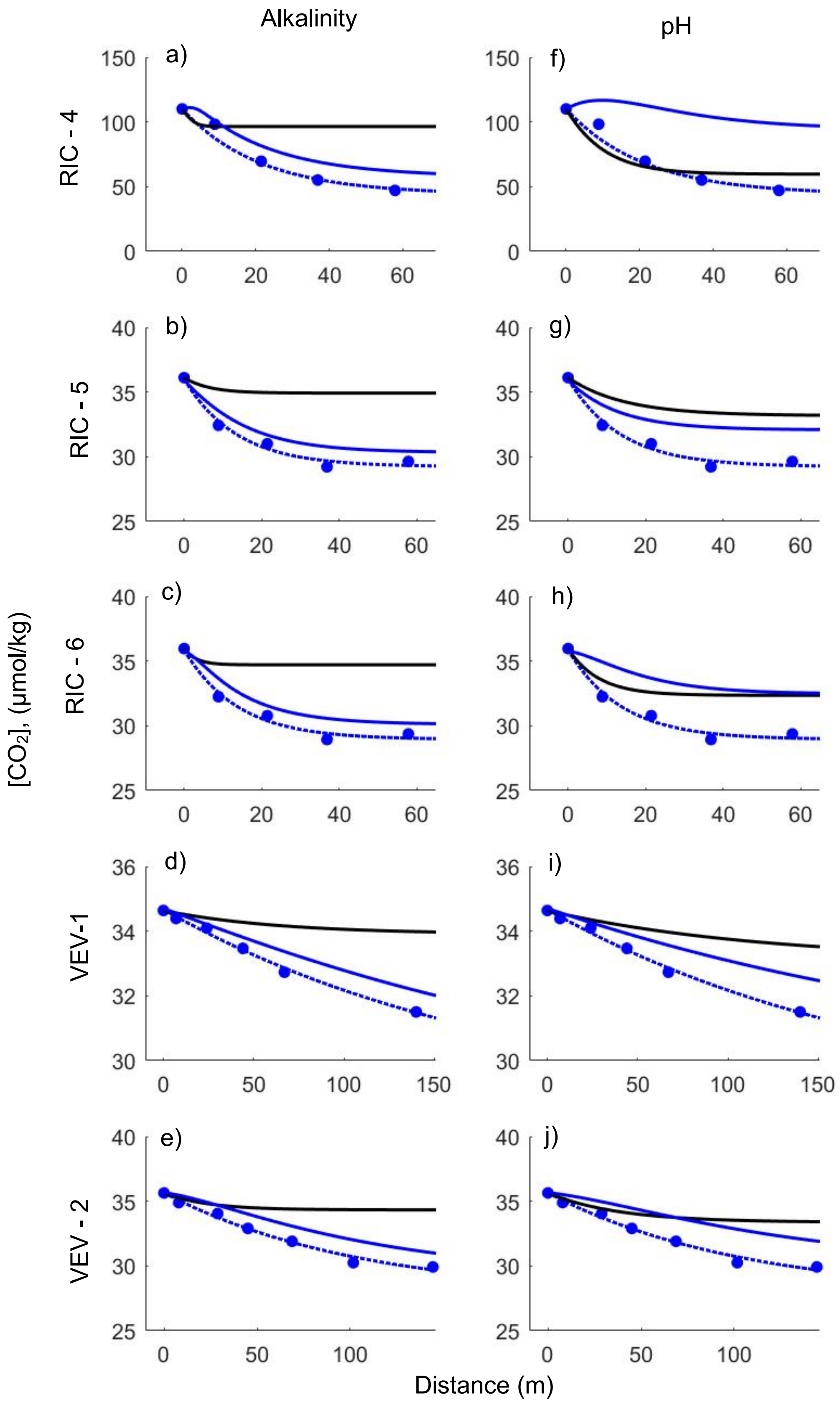

Figure S2. Modeled interconversion of CO_2 to HCO_3^- for each of the releases using alkalinity (a-e) and pH (f-k). The measured CO_2 concentrations are shown by the blue points, to which an exponential decay is fitted (dashed line). The decrease in concentration of CO_2 that is due to chemical interconversion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

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}	3.71×10^{-2} s^{-1}	exp $(1246.98\text{-}6.19 \times 10^4/T - 183.0 \ln(T))$	1
k_{-1}	2.67×10^4 kg mol^{-1} s^{-1}	k_{+1}/K_1^*	Calculated
k_{+4}	2.23×10^3 kg mol^{-1} s^{-1}	$A_4 \exp(-90{,}166.83/(RT))/K_w^*$	3
k_{-4}	9.71×10^{-5} s^{-1}	$k_{+4} \times K_w^*/K_1^*$	Calculated
$k^{H+}{}_{+5}$	5.0×10^{10} kg mol^{-1} s^{-1}	None	2
$k^{H+}{}_{-5}$	59.44 s^{-1}	$k^{H+}{}_{+5} \times K_2^*$	Calculated
$k^{OH-}{}_{+5}$	6.0×10^9 kg mol^{-1} s^{-1}	None	2
$k^{OH-}{}_{-5}$	3.06×10^5 s^{-1}	$k^{OH-}{}_{+5} \times K_w^*/K_2^*$	Calculated
k_{+6}	1.40×10^{-3} kg mol^{-1} s^{-1}	None	2
k_{-6}	2.31×10^{-10} kg mol^{-1} 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

DOE. (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater. *Version 2A, Dickson, A.G. Goyet, C. (Eds.), ORNL/CDIAC-74*.

Eigen, M. (1964). Proton Transfer, Acid-Base Catalysis, and Enzymatic Hydrolysis. Part I: ELEMENTARY PROCESSES. *Angewandte Chemie International Edition in English*, *3*(1), 1–19. https://doi.org/10.1002/anie.196400011

Johnson, K. S. (1982). Carbon dioxide hydration and dehydration kinetics in seawater. *Limnology and Oceanography*, *27*(5), 849–855. https://doi.org/10.4319/lo.1982.27.5.0849

Roy, R. N., Roy, L. N., Vogel, K. M., Porter-Moore, C., Pearson, T., Good, C. E., et al. (1993). The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Marine Chemistry*, *44*(2–4), 249–267. https://doi.org/10.1016/0304-4203(93)90207-5

Schulz, K. G., Riebesell, U., Rost, B., Thoms, S., & Zeebe, R. E. (2006). Determination of the rate constants for the carbon dioxide to bicarbonate inter-conversion in pH-buffered seawater systems. *Marine Chemistry*, *100*(1–2), 53–65. https://doi.org/10.1016/j.marchem.2005.11.001

Ulseth, A. J., Hall, R. O., Boix Canadell, M., Madinger, H. L., Niayifar, A., & Battin, T. J. (2019). Distinct air–water gas exchange regimes in low- and high-energy streams. *Nature Geoscience*, *12*(4), 259–263. https://doi.org/10.1038/s41561-019-0324-8