1 **Quantification of Carbon Dioxide Gas Transfer Velocity by Scaling from Argon through**

2 **Dual Tracer Gas Additions in Mountain Streams**

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14 **Key Points:**

15 - The dual release tracer technique (Ar and CO_2) estimated the scaling factor a to be 1.69
16   (95% CI: 1.37-2.04), in agreement with literature.

17 - Schmidt scaling overestimates gas exchange of CO_2 in turbulent streams when scaling
18   from Argon to CO_2, due to the high solubility of CO_2.

19 - Use of CO_2 as a tracer gas in streams with high pH and bicarbonate alkalinity results in
20   an overestimation of the gas transfer velocity k.

21 **Abstract**

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

38

39 **Plain Language Summary**

40 Streams, rivers and lakes are key components of the global carbon cycle, acting as both sources
41 and sinks for carbon dioxide (CO_2), a potent greenhouse gas. More specifically, mountain
42 streams are significant sources of CO_2 due to their steep slopes and turbulent nature, which
43 encourages the escape of CO_2 from the stream and into the atmosphere. Estimating the amount of
44 CO_2 released from turbulent mountain streams is a challenging task due to the many processes
45 that control this flux. This study tested a technique for estimating fluxes of CO_2 in mountain
46 streams and found that the approach proved to be robust and in accordance with other studies,
47 but that estimates should be corrected for chemical processes occurring in the stream that
48 consume CO_2. These results will allow researchers to more accurately quantify CO_2 released
49 from streams and improve existing global carbon models.

50 **1 Introduction**

51 The rate of gas exchange across the air-water interface is essential for quantifying the flux of
52 climate relevant gases (e.g., carbon dioxide (CO_2), methane (CH_4), or nitrous oxide (N_2O)), a
53 critical parameter involved in many biogeochemical processes (Katul et al., 2018; Ulseth et al.,
54 2019; Wanninkhof et al., 2009). For instance, estimates of the global carbon (C) balance rely on
55 accurate quantification of carbon fluxes into and out of ecosystems (Katul et al., 2018; Raymond
56 et al., 2013). Among these fluxes, CO_2 evasion from freshwater ecosystems has received
57 increasing attention due to the active roles that streams, rivers, lakes, and estuaries play
58 transforming and reallocating terrestrially derived carbon (C) (Aufdenkampe et al., 2011; Battin
59 et al., 2009). Streams and rivers contribute substantial amounts of CO_2 to the atmosphere
60 (Raymond et al., 2012, 2013). More specifically, headwater streams are particularly active sites
61 of CO_2 degassing because of their close connection to terrestrial ecosystems and increased gas
62 exchange relative to that of larger streams and rivers (Raymond et al., 2012, 2013; Wallin et al.,
63 2011).

64   The total flux of CO_2 evaded from mountain streams has been estimated at 3.5 kg C yr^{-1} (CI:
65   −0.5 and 23.5 kg C m^{-2} yr^{-1}), which is equivalent to and/or exceed those in Amazonian and
66   boreal streams (Horgby et al., 2019). We observe this high CO_2 flux in steep slope mountain
67   streams due to the high gas transfer velocities in these locations, which is predominantly driving
68   the flux, and not only because there are extremely high concentrations of total carbon in the
69   stream, as is the case in streams draining organic-rich soils (Horgby, Boix Canadell, et al., 2019).
70   In fact, because of the limited soil build up and vegetation cover typical in steep mountain
71   terrain, carbon concentrations can actually be relatively low in streams as the source of carbon
72   may be from groundwater upwelling only (Duvert et al., n.d.; Horgby, Segatto, et al., 2019).

73   The gas flux is a function of gas transfer velocity at the air–water interface (k, in units of distance
74   per time), the gas solubility coefficient and the difference in gas concentrations (at equilibrium)
75   between the air and water (Moog & Jirka, 1999). Quantification of the gas transfer velocity k is
76   not trivial due to considerable amounts of uncertainty and high spatiotemporal variability
77   (Schelker et al., 2016; Tobias et al., 2009; Ulseth et al., 2019; Wallin et al., 2011). The value of k
78   is primarily a function of slope, which dictates stream channel geomorphology and varies
79   significantly between streams, and associated hydraulics that vary through time (Kokic et al.,
80   2018). There have been multiple attempts to scale estimates of gas exchange from physical
81   stream properties such as slope, velocity, discharge, stream bed roughness, Reynolds number
82   (Re) and energy dissipation (Katul et al., 2018; Kokic et al., 2018; Raymond et al., 2012; Ulseth
83   et al., 2019; Wallin et al., 2011). However, the relevance of these physical scaling relationships
84   depends largely on the size of the ecosystem in question. This is easily illustrated by comparison
85   of a small mountain stream with a steep slope and high turbulence to a larger river with
86   predominantly laminar flow. The increased turbulence in the small mountain stream is due to its
87   steeper slope and shallower depth, resulting in partially submerged macroroughness and
88   turbulence near the surface of the stream. This near surface turbulence drives high gas transfer
89   velocity in mountain streams (Ulseth et al., 2019).

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

100   A downside of this method is that the gas exchange measured with the tracer gas must then be
101   scaled to the gas in question, a non-trivial task due to differences in diffusivity (and therefore
102   Schmidt scaling) and solubility between the tracer gas and the gas of ecological interest (in this
103   case, CO_2) (Hall Jr. & Madinger, 2018). This is especially true in the presence of turbulence
104   induced bubble-mediated gas exchange. Scaling between gases of differing solubilities, the rate
105   of gas exchange is not only dependent on molecular diffusion through the water medium and
106   turbulence, but also diffusion across the surface of the bubble and transportation to the surface by
107   the bubble. Because of these effects, the role of bubbles in estimating gas exchange rates is

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

110   In addition, there are other processes that must be considered when estimating gas exchange
111   rates of CO_2, such as biological respiration (a source of CO_2) and chemical interconversion of
112   CO_2 to bicarbonate (a sink) (Hall & Ulseth, 2020). While the effect of respiration is likely
113   negligible since the time scale over which gas exchange is measured is much shorter than what
114   would be relevant for respiration (Duvert et al., n.d.), this is not the case for interconversion of
115   CO_2 to HCO_3^-. It has been shown through experimentation and modelling that the reaction
116   kinetics for the interconversion occur at orders of magnitude and timescales that are relevant
117   when using the tracer gas method (Schulz et al., 2006). While the role of chemical enhancement
118   of CO_2 gas exchange across the air-water interface has been extensively explored (Bolin, 1960;
119   Emerson, 1975; Quinn, J. A., Otto, 1971; Smith, 1985; Wanninkhof & Knox, 1996) the role of
120   interconversion of CO_2 to HCO_3^- has not yet been accounted for in the estimation of the gas
121   transfer velocity when the stream is artificially enriched with CO_2, as is the case when using CO_2
122   as the trace gas itself.
123
124   Common tracer gases used to scale CO_2 are sulfur hexafluoride (SF_6) (Hall et al., 2003; Maurice
125   et al., 2017; Wanninkhof et al., 1990), propane (C_3H_8) (Marzolf et al., 2011; Mulholland et al.,
126   2001; Raymond et al., 2012; Schelker et al., 2016), helium (He) (Vautier et al., 2020) and more
127   recently argon (Ar) (Hall Jr. & Madinger, 2018; Ulseth et al., 2019). While SF_6 and C_3H_8 behave
128   much more similarly to CO_2 in terms of solubility and Schmidt number, these gases are known
129   greenhouse gases, making them less ideal for this type of study (Hall Jr. & Madinger, 2018;
130   McDowell & Johnson, 2018). Helium is an inert gas, at relatively low background concentrations
131   in nature and is conveniently commercially available, but differs significantly from CO_2 in terms
132   of solubility. Ar has been used by Hall and Madinger (2018) to scale to O_2, a key parameter of
133   gas exchange for ecosystem metabolism models, as it is very similar to O_2 in terms of Schmidt
134   number and solubility and has been shown to accurately quantify gas transfer velocities in
135   turbulent streams (Hall Jr. & Madinger, 2018; Ulseth et al., 2019). Additionally, Ar is another
136   relatively inert noble gas, similarly to He, but is slightly more soluble, making it a better
137   candidate for scaling to CO_2 (Asher & Wanninkhof, 1998).

138   Our objective was to estimate through dual tracer additions of Ar, a proven tracer gas, and
139   soluble CO_2, a gas of ecological interest, the scalability of Ar to CO_2 for the purpose of
140   estimating gas exchange rate of CO_2 (k_{CO_2}) in turbulent mountain streams. When scaling
141   between gases of similar solubilities, gas exchange is predominantly controlled by diffusivity, in
142   which case only using Schmidt scaling is appropriate. However, Ar and CO_2 differ significantly
143   in terms of solubility, implying the need to correct for solubility in addition to the diffusivity
144   effect. Finally, CO_2 also differs from Ar in that it is chemically reactive in the stream, which
145   further complicates the ability to scale between these two gases. Based on solubility and
146   diffusivity principles (Hall Jr. & Madinger, 2018; Woolf et al., 2007). We start with the primary
147   hypothesis that scaling from Ar to CO_2 will be approximately equal to the theoretical value of
148   1.7, within an acceptable margin of error. Accordingly, we aim to answer the following
149   questions: Can we empirically calculate the scaling factor and does it match the value obtained
150   theoretically? What is the effect of the interconversion between CO_2 and HCO_3^- on the measured
151   gas exchange rate of CO_2?

152 **2 Materials and Methods**

153 2.1 Study sites

154 We performed a total of 11 simultaneous dual releases of Ar and CO_2 between March 2018 and
155 April 2019 at 4 different mountain streams in the Swiss Alps (Table 1). The four streams were
156 steep-channel headwaters with step-pool morphology, where the gas exchange had been
157 measured previously and were at the upper range of gas exchange rates (Ulseth et al., 2019).
158 These sites are ideal systems to test our hypotheses as they are turbulent streams that also have
159 substantial bubble-mediated gas exchange. Three of the stream sites (Richard, Veveyse and
160 Vièze) were located below the tree line and thus covered by coniferous and mixed forests, while
161 the Ferret stream drained a sparsely vegetated rocky terrain. To cover a wide range of predicted
162 gas exchange rates, streams were chosen on the basis of differing geomorphological and
163 hydraulic characteristics and sampled between 2 (Veveyse and Vièze) and 6 (Richard) occasions.

164

165 2.2. Experimental Set Up

166 Gas exchange rates were estimated by continuously adding CO_2 and Ar and measuring the
167 downstream decline of gas concentrations (Figure 1a). Prior to addition of the trace gases, we
168 collected pre-plateau samples for Ar and CO_2 at 5-6 stations downstream of the injection site, as
169 well as one upstream location (Figure 1b). In situ measurements of atmospheric pressure, water
170 temperature, pH, and conductivity were recorded at each station.

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

179 We then added Ar and CO_2 to the stream simultaneously using a micro bubble diffuser
180 (PENTAIR, Aquatic Ecosystems, NC, USA), distributed evenly across the stream channel and
181 waited for the concentrations to reach equilibrium at the downstream site, which was assumed to
182 be 4 times the travel time estimated from the salt slug (Stream Solute Workshop, 1990). We
183 repeated sampling for Ar and CO_2 gases at each station (one upstream and 5-6 downstream) and
184 additionally collected water samples for alkalinity measurements. In situ measurements of
185 atmospheric pressure, water temperature, pH, and conductivity were also repeated at each
186 station.

187 2.3. Gas Sampling and Analysis

188 We measured CO_2 concentrations of the stream water in the laboratory and *in situ*. For all
189 releases done prior to March 2019, duplicate samples for CO_2 were collected in glass vials (60
190 mL) that contained crystalized sodium azide (300 µL) for sample preservation. In the field, vials
191 were carefully submerged in the water to avoid bubble formation and turbulence-induced CO_2
192 loss, and while still submerged, they were sealed with rubber stoppers and metal caps. In the

193   laboratory, a headspace with synthetic air (< 5 ppm CO2) was created and the water phase and
194   the headspace were allowed to equilibrate (2 hours). We measured the CO_2 concentrations using
195   a cavity ring-down spectrometer (G2201-*I*, Picarro Instruments, USA) (Schelker et al., 2016).
196   After March 2019, CO_2 concentrations were measured in situ using a Vaisala handheld CO_2
197   probe (GM70, Vaisala, Helsinki, Finland). This improved the efficiency of the fieldwork as the
198   concentrations of CO_2 could be measured in real time. For each measurement of CO_2 with the
199   Vaisala, the concentration was observed until it stabilized on the monitor of the device and an
200   average value across 4-5 min of stable data was taken as the CO_2 concentration at that station.
201   An intercalibration between the Vaisala and Picarro was done in the laboratory to check if
202   corrections needed to be made such that the measured CO_2 concentrations could be comparable
203   between them (see Figure S1 in the *Supplementary Information*). Measurements of temperature,
204   pressure, pH, conductivity, stream depth and width were simultaneously recorded at each station.

205   Samples for dissolved $Ar:N_2$ were collected using a 3.8 cm diameter PVC pipe with an attached
206   outlet vinyl tube (3.2 mm ID X 20 cm). As stream water flowed through the pipe, the
207   downstream end was capped with a rubber stopper and the sample was collected from the vinyl
208   tube, first overflowing the 12 mL Exetainer vial three times. The vials were capped immediately,
209   without bubbles. Ar concentrations were measured as $Ar:N_2$ using membrane inlet mass
210   spectrometry (MIMS) (Bay Instruments Inc., Easton, MD) within 24 hours.

211   We measured the ratio of Ar to N_2 as opposed to the concentration of Ar alone as this provided a
212   much higher precision with the MIMS. The concentration of Ar in the stream was enriched by no
213   more than 5%, preventing any N_2 degassing from the stream, and keeping the $Ar:N_2$ ratio as a
214   reliable measurement of the increase in Ar concentration (Hall & Madinger, 2018; Ulseth et al.,
215   2019). In addition, it was assumed that no biologically driven N_2 fluxes occurred during the
216   release and that the concentration of N_2 in the stream remained constant throughout the sampling
217   period.

218   Alkalinity samples were also stored at ~4°C and were analyzed the day after sampling.
219   Alkalinity was measured using a titrator (916 Ti-Touch, Metrohm AG, Switzerland). The titrator
220   was calibrated using standard solutions of pH = 4 and 7 and the slope was verified to be at least
221   96%. Samples were allowed to reach room temperature while being stored in a cupboard to
222   protect them from light and were transferred to the beaker directly before measurement to avoid
223   exposure to atmospheric CO_2. Samples of 100g were titrated with a solution of 0.05N HCl to an
224   endpoint of 4.5 to determine total alkalinity.

225   *2.4 Determination of k_{Ar}, k_{CO_2} and a*

226   The exponential decline of $Ar:N_2$ and CO_2 was corrected for background concentrations and
227   normalized to the ratio of $Ar:N_2$ or CO_2 concentration measured at the first station downstream
228   of the injection site by:

229

230    $An_x = \dfrac{A_x}{A_0}$,

231    $Cn_x = \dfrac{C_x}{C_0}$,   (1)

232

233   where An_x represents the ratio of Ar:N$_2$ (minus the background ratio) normalized to A_0 and C_0,
234   where A_0 and C_0 are the ratio of Ar:N$_2$ and the concentration of CO_2 measured at the first
235   sampling station respectively. Exponential decay models were fit to the data according to

236

237    $An_x \sim N(\ An_0 \times e^{-K_{d,Ar}x}, \sigma_A)$

238    $Cn_x \sim N(\ Cn_0 \times e^{\frac{-K_{d,Ar}}{a}x}, \sigma_C),$ (2)

239

240   where An_x is the normalized modeled ratio of Ar:N$_2$ at a distance x along the reach, An_0 is the y-
241   intercept, $K_{d,\ Ar}$ is the decay rate of Ar at the stream water temperature in units of per distance, x
242   is the distance along the reach of the stream (with the first station considered to be at 0 m) and a
243   is the ratio of gas exchange rates between Ar and CO_2 (i.e. $a = K_{d,\ Ar}/K_{d,\ CO2}$ at stream
244   temperature). These statistical models assume that the residual errors are normally distributed
245   with a standard deviation of σ_A and σ_C for Ar and CO_2 respectively.

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

251

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

253   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
254   and Madinger (2018). Prior probabilities for the remaining parameters were the same as those in
255   Hall and Madinger (2018) and Ulseth et al., 2019.

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

260   Gas exchange rates (K$_d$) in m^{-1} were converted to gas exchange velocity (k) in m d^{-1} using

261

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

263

264   where v is nominal stream velocity (m s^{-1}) and $\bar{z}$ is average stream depth (m) calculated from $\bar{z} =$
265    $Q/(wv)$ (where Q and v were derived from the salt slug and w is the average width measured
266   during sampling). The values of k (m d^{-1}) were standardized to a common Schmidt (Wanninkhof,
267   2014) number of 600 (k_{600}, m d^{-1}) such that they would be comparable among different streams,
268   sampled on different days and therefore at varying stream temperatures.

269

270   2.5 Modelling the inter-conversion of CO_2 to HCO_3^- and correction of a (a')

271   In addition to the gas exchange with the atmosphere, it is important to also consider other
272   processes that are occurring in the stream, such a respiration and chemical interconversion of
273   CO_2 to bicarbonate and HCO_3^-, which may have an effect on the measured gas exchange rate. It
274   is impossible to measure the changes in concentration that occur due chemical interconversion
275   alone, as there are many processes happening in the stream simultaneously (e.g. outgassing and
276   respiration). For this reason, we developed a model for the chemical interconversion of CO_2 to
277   bicarbonate following the methods described by Schulz et al. (2006) which considered the
278   following reactions:

279

$$280 \quad CO_2 + H_2O \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} HCO_3^- + H^+ \tag{5}$$

$$281 \quad CO_2 + OH^+ \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} HCO_3^- \tag{6}$$

$$282 \quad CO_3^{2-} + H^+ \underset{k_{-5}^{H^+}}{\overset{k_{+5}^{H^+}}{\rightleftharpoons}} HCO_3^- \tag{7}$$

$$283 \quad HCO_3^- + OH^- \underset{k_{-5}^{OH^-}}{\overset{k_{+5}^{OH^-}}{\rightleftharpoons}} CO_3^{2-} + H_2O \tag{8}$$

$$284 \quad H_2O \underset{k_{-6}}{\overset{k_{+6}}{\rightleftharpoons}} H^+ + OH^- \tag{9}$$

285

286   The set of differential equations was implemented into the model and integrated numerically
287   with the MATLAB function 'ode15s' solver for stiff problems (Shampine et al., 1997; Zeebe,
288   1999). Rate constants for the reaction equations used are provided in Table S1 in the
289   *Supplementary Information*. Note that we could only apply this model to streams for which we
290   had sufficient alkalinity and pH data (streams sampled from March 2019 onwards).

291   Initial conditions for the concentration of CO_2 in the stream was assumed to be equal to the value
292   measured at station 1. This assumes that the gas injected into the stream at the diffusers has had
293   time to dissolve and mix into the stream and is at its maximum concentration when measured at
294   station one and is the same assumption that is made for the model that considers gas exchange
295   only (described in section 2.3). The concentration of CO_2 was converted from ppm to mol/kg-
296   soln using Henry's Law and correcting for water vapor pressure (DOE, 1994).

297   Initial concentrations of carbonate and bicarbonate were calculated using CO2SYS (van Heuven,
298   S., Pierrot, D., Rae, J. W. B., Lewis, E., Wallace, 2011) in MATLAB. This MATLAB function
299   requires two of the three parameters we measured (pH, alkalinity and CO_2 concentration) in
300   order to calculate concentrations of carbonate and bicarbonate as well as H^+ and OH^-. We
301   provided estimates of the rate of inter-conversion of CO_2 to HCO_3^- using first the parameters pH
302   and CO_2, and second using alkalinity and CO_2. The use of these different parameters provides us

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

309

310 **3 Results & Discussion**

311 3.1 Scaling of Ar to CO_2

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

317 For each of the releases the measured ratio of K_{Ar} : K_{CO2} was greater than one (Figure 2), which
318 supports the theory that the gas exchange rate of Ar is greater than that of CO_2. The variability in
319 the ratio of K_{Ar} : K_{CO2} (a) was high among the 11 releases that we conducted and ranged from
320 1.12 to 1.99 with a standard deviation of 0.17 (Figure 2, Table 3). The average value for a ($\bar{a}$)
321 was 1.69 with a 95% credible interval of 1.37 to 2.04, which is in agreement with the theoretical
322 scaling value obtained using Eq. 13 in Woolf et al. (2007), where a was calculated to be equal to
323 1.74. The 95% confidence interval also encompasses the value for a estimated in Hall and
324 Madinger (2018), which was found to be 1.6. Differences in these theoretical estimates of a are
325 due to different values taken from the literature for both the Ostwald solubility coefficients and
326 Schmidt numbers, as well as rounding error. The fact that a calculated from all three estimates
327 was found to be much higher that the value of 1.36, which is the value one would obtain for a
328 from Schmidt scaling alone, is also in agreement with the literature, which states that using
329 Schmidt scaling is likely overestimating the gas exchange of CO_2 due to solubility effects (Hall
330 Jr. & Madinger, 2018).

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

337 For the purposes of this study, we are interested in the ability to scale from Ar to CO_2, which are
338 two gases that behave differently in terms of solubility and Schmidt number (Figure 3). Scaling
339 from Ar to O_2 can be easily done using Schmidt scaling alone as these two gases are similar in
340 terms of solubility (i.e. moving parallel to the x-axis) and diffusivity (Schmidt number).
341 However, for CO_2 there is the effect of solubility, in addition to the Schmidt number effect,
342 complicating this scaling, especially in the presence of bubble mediated gas exchange (i.e.
343 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
344 located on the contour equal to 1.74, and exists in the range where there are dependencies on

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

347 The theoretical scaling value of 1.36 using Schmidt scaling alone overestimates the gas exchange
348 of CO_2 when scaling from Ar, is because CO_2 has a higher solubility and stays in solution rather
349 than move into the gas phase and cross the air-water interface into bubbles to be quickly
350 transported to the surface and out of the stream (Woolf et al., 2007). Because of this solubility
351 effect, we obtain a relatively higher value for a when it is measured in the stream because it takes
352 this effect into account. Ultimately, without correcting for the solubility effect, we would
353 overestimate the gas exchange rate of CO_2 to the atmosphere when scaling from argon,
354 particularly in turbulent streams where bubbles may dominate the gas exchange.

355 Therefore, scaling from Ar to CO_2 is not only dependent on the Schmidt number and solubility,
356 but also the degree of turbulence and bubble-mediated gas transfer that is occurring in the
357 stream, which could explain some of the uncertainty observed in the measured value for $\bar{a}$.
358 Scaling from Ar to CO_2 could therefore be done with much less uncertainty using Eq. 13 in
359 Woolf et al., 2006, if a measurement of the bubble flux (Q_b) for that particular stream, at a
360 particular moment in time, is known. Measuring this parameter in the field is not trivial however
361 and so a more feasible alternative could be to use a tracer gas with a similar solubility to that of
362 CO_2. For instance, a good candidate can be helium (He) (Aeschbach, 2016), a tracer gas
363 commonly used in oceanography. However, this gas is even farther away from CO_2 than Ar in
364 terms of both Schmidt number and solubility (Figure 3).

365

366 3.2 Corrections for Interconversion of CO_2 to HCO_3^-

367 In addition to the solubility effects, CO_2 also differs from Ar in that it is chemically reactive in
368 the environment and the carbonate system has a significant role in how much CO_2 ultimately
369 remains in solution upon addition of the tracer gas (DOE, 1994; Schulz et al., 2006)(Schulz et
370 al., 2006, DOE 1994). All of the stream sites for this study are located in catchments with
371 limestone bedrock (*map.geo.admin.ch*) and because of this, the average pH in the stream is
372 relatively high (average pH: 8.14, sd: 0.15) (Table 4).

373 In general, at pH values above 5, some of the CO_2 will begin to convert to bicarbonate (HCO_3^-)
374 and at pH values around 8, like what we observe in the stream, the chemical equilibria almost
375 entirely favor conversion of CO_2 to HCO_3^- (Riebesell et al., 2011), however in the stream there is
376 some buffering capacity due to the alkalinity. Therefore, the CO_2 injected into the stream
377 partially converts to bicarbonate (HCO_3^-) and as a result the observed exponential decrease in
378 CO_2 concentration has to necessarily be due to both the effect of gas exchange and chemical
379 interconversion from CO_2 to HCO_3^-. It is challenging to quantify the effect of chemical
380 interconversion in the field as there are multiple processes occurring simultaneously (gas
381 exchange, respiration and groundwater inputs (Hall & Ulseth, 2019). For this reason, we decided
382 to model it following the methods described previously and according to Schulz et al. (2006).
383 Measured values of CO_2 concentration, pH, pressure and temperature were input into the
384 MATLAB script CO2SYS.m (van Heuven, S., Pierrot, D., Rae, J. W. B., Lewis, E., Wallace,
385 2011) to calculate the initial conditions for the model (Figure 4). Figure 4 is an example of an
386 output of the model (Stream: RIC, Date: 21 March 2019), which shows the changes in

387   concentration of relevant components of the carbonate system vs. time upon the addition of CO_2
388   to the stream.

389   A key observation is that these changes in concentration occur at significant orders of magnitude
390   and over relevant timescales. That is, the CO_2 added does not instantaneously convert to HCO_3^-,
391   but instead non-negligible quantities are converted over a period of time that is of the same time
392   scale magnitude as the time it takes for the concentration of CO_2 in the stream to return to
393   background conditions (~600 s). This means that the change in concentration that we observe in
394   the stream is not only due to gas exchange, but is partially also due to chemical interconversion
395   from CO_2 to HCO_3^-.

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

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

413   We reran the model using the values corrected for effects of chemical interconversion of CO_2 to
414   bicarbonate, and found an average scaling factor (*a'*) of 2.97 (95% CI: 1.82 – 4.73), which is
415   much higher than the original estimate of 1.69 that accounted for diffusion and solubility effects
416   only. We draw two main conclusions from these results. The first conclusion being that scaling
417   from Ar to CO_2 can be done, but it is important to factor in the effects of solubility. The second
418   conclusion being that using CO_2 as a tracer gas to measure gas exchange of CO_2 to the
419   atmosphere may not be accurate, especially in streams that have a high pH and high bicarbonate
420   alkalinity, as this causes much of the injected CO_2 to favor chemical interconversion to HCO_3^-.
421   As such, one would observe a decrease in CO_2 concentration that is due to chemical processes,
422   and therefore the measured value of *k* obtained would not be an accurate estimate of gas
423   exchange to the atmosphere.

424   **5 Conclusions**

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

429   with high precision (when measuring ratios $Ar:N_2$ when using the MIMS for analysis).
430   Additionally, since only low concentrations are needed, only small quantities of Ar are required
431   to be transported to the field study site, making the overall method much more convenient (Hall
432   & Madinger, 2018). Furthermore, $Ar:N_2$ it is biologically and chemically inert at the time scale
433   the gas release takes place, meaning that other processes occurring in the stream (groundwater
434   inputs, respiration and chemical interconversion) would not impact the measurement of the gas
435   exchange rate.

436   Our results show that it is possible to use Ar as a tracer gas to estimate the scaling of gas transfer
437   velocities from Ar to CO_2. The measured value of a_{mean} (1.69) was approximately equal to the
438   theoretical value calculated (1.74) based on the bubble mediated gas transfer model of Woolf et
439   al., 2007. However, there is high uncertainty surrounding the measured gas transfer velocities of
440   Ar and CO_2, and therefore substantial noise in the measured scaling factor a, resulting in errors
441   when using these k_{CO2} measurements to calculate CO_2 fluxes where bubbles dominate gas
442   exchange. It is important to note however, that the amount of uncertainty observed in this study
443   surrounding a (95% confidence interval varying from approximately 20% to 60% of the value of
444   a), is comparable to results from other studies and most other methods for measuring gas
445   exchange (Hall Jr. & Madinger, 2018; Hall & Ulseth, 2020; Knapp et al., 2019; Ulseth et al.,
446   2019).

447   The dual release method of Ar and CO_2 described in this paper has shown that Ar can be used as
448   a tracer gas and scaled to estimate gas transfer velocities of CO_2 when accounting for both
449   solubility and diffusivity with measures of uncertainty that are comparable to other methods for
450   measuring gas exchange (Knapp et al., 2015, 2019; Wanninkhof et al., 1990; Young & Huryn,
451   1999). Although estimating gas exchange rates remains highly uncertain, empirical methods,
452   such as dual tracer gas additions, continue to constrain these uncertainties (Hall & Ulseth, 2020).

453   However, based on our findings, previously measured gas exchanges rates using CO_2 as a tracer
454   gas may have been significantly affected by the process of chemical interconversion. Corrections
455   to the scaling factor a that account for the chemical interconversion need to be better estimated in
456   a laboratory setting to quantifiably address the uncertainty associated with using CO_2 as a tracer
457   gas. We recommend future experiments that exclude the reaction kinetics altogether by avoiding
458   adding CO_2, and instead using a DIC and total alkalinity (TA) enriched solution of the same pH
459   and temperature as the stream in question. This way, when mixing occurs, no chemical
460   disequilibrium will be created and the observed change in CO_2 concentration would only be a
461   result of degassing and dilution. The latter can then be traced and corrected for by measuring
462   changes in TA. A correct assessment of the coupled solubility and interconversion effects on
463   scaling CO_2 gas exchange will be a valuable contribution towards more reliable carbon models
464   as accurately quantifying CO_2 fluxes from streams to the atmosphere becomes of increasing
465   importance in light of global change.

466

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