



HAL
open science

Mapping gas exchanges in headwater streams with membrane inlet mass spectrometry

Camille Vautier, Ronan Abherve, Thierry Labasque, Anniet M. Laverman, Aurélie Guillou, Eliot Chatton, Patrick Dupont, Luc Aquilina, Jean-Raynald de Dreuzy

► **To cite this version:**

Camille Vautier, Ronan Abherve, Thierry Labasque, Anniet M. Laverman, Aurélie Guillou, et al.. Mapping gas exchanges in headwater streams with membrane inlet mass spectrometry. *Journal of Hydrology*, 2020, 581, <10.1016/j.jhydrol.2019.124398>. <insu-02403865>

HAL Id: insu-02403865

<https://insu.hal.science/insu-02403865v1>

Submitted on 11 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Journal Pre-proofs

Research papers

Mapping gas exchanges in headwater streams with membrane inlet mass spectrometry

Camille Vautier, Ronan Abhervé, Thierry Labasque, Anniet M. Laverman, Aurélie Guillou, Eliot Chatton, Pascal Dupont, Luc Aquilina, Jean-Raynald de Dreuzy

PII: S0022-1694(19)31133-3
DOI: <https://doi.org/10.1016/j.jhydrol.2019.124398>
Reference: HYDROL 124398

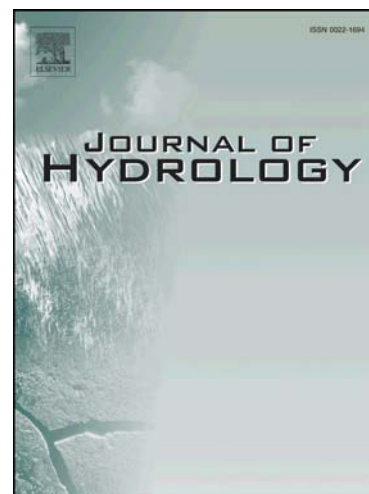
To appear in: *Journal of Hydrology*

Received Date: 26 July 2019
Revised Date: 20 November 2019
Accepted Date: 22 November 2019

Please cite this article as: Vautier, C., Abhervé, R., Labasque, T., Laverman, A.M., Guillou, A., Chatton, E., Dupont, P., Aquilina, L., de Dreuzy, J-R., Mapping gas exchanges in headwater streams with membrane inlet mass spectrometry, *Journal of Hydrology* (2019), doi: <https://doi.org/10.1016/j.jhydrol.2019.124398>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier B.V.



1 Mapping gas exchanges in headwater streams with membrane inlet mass
2 spectrometry

3 *Camille Vautier* ^{a*}, *Ronan Abhervé* ^{a,b}, *Thierry Labasque* ^{a,c}, *Anniét M.*
4 *Laverman* ^d, *Aurélié Guillou* ^c, *Eliot Chatton* ^{a,1}, *Pascal Dupont* ^e, *Luc Aquilina* ^a,
5 *Jean-Raynald de Dreuzy* ^{a,c}

6 ^a Univ Rennes, CNRS, Géosciences Rennes, UMR 6118, 35000 Rennes, France

7 ^b Centre Eau Terre Environnement, INRS, Quebec City, Canada

8 ^c Univ Rennes, CNRS, OSUR (Observatoire des sciences de l'univers de Rennes),
9 UMS 3343, 35000 Rennes, France

10 ^d Univ Rennes, CNRS, Ecobio, UMR 6553, 35000 Rennes, France

11 ^e LGCGM, INSA Rennes, 35000 Rennes, France

12 **Corresponding Author**

13 * camille.vautier@univ-rennes1.fr

14 **Present Addresses**

15 ¹ Sorbonne Universités, UPMC Univ Paris 06, CNRS, Laboratoire d'Océanographie
16 Microbienne (LOMIC), Observatoire Océanologique, Banyuls/mer, France

17 **ABSTRACT**

18 Using continuous injections of helium coupled to *in-situ* continuous flow membrane
19 inlet mass spectrometry (CF-MIMS), we mapped the gas exchanges along two low-
20 slope headwater streams having discharges of 25 L s⁻¹ and 90 L s⁻¹. Mean reaeration
21 rate coefficients (k_2) were estimated at 130 d⁻¹ and 60 d⁻¹, respectively. Our study
22 revealed that gas exchanges along headwater streams are highly heterogeneous. The
23 variable morphology of the streambed causes gas exchanges to be focused into small
24 areas, namely small cascades made up of stones or wood, with reaeration rate
25 coefficients up to 40 times higher than in low-turbulent zones. As such, cascades
26 appear to be hot spots for both oxygenation and greenhouse gases emissions.
27 Additional O₂ and CO₂ measurements effectively showed fast exchanges between
28 the stream and the atmosphere in the cascades, following the partial pressure
29 gradients. These cascades allow a fast oxygenation of the eutrophic streams depleted
30 in O₂, which sustains respiration. Simultaneously, cascades release the oversaturated
31 CO₂ originating from groundwater inputs to the atmosphere. By comparing
32 measured reaeration rate coefficients to ten predictive equations from literature, we
33 showed that all equations systematically underestimate reaeration rate coefficients,
34 with significantly higher discrepancies in cascades than in low-turbulent zones. The
35 inadequate characterization of the processes occurring in cascades causes empirical

- 36 equations to have poor predictive capabilities, leading to a global underestimation
37 of CO₂ emission from headwater streams.

Journal Pre-proofs

38 KEY-WORDS

- 39 - headwater stream
- 40 - membrane inlet mass spectrometry (MIMS)
- 41 - reaeration
- 42 - gas exchange
- 43 - greenhouse gas emission
- 44 - CO₂ evasion

45 HIGHLIGHTS

- 46 - *In-situ* membrane inlet mass spectrometry allows real-time mapping of gas
47 exchanges along headwater streams.
- 48 - Gas exchange rate coefficients are highly heterogeneous along low-slope
49 headwater streams.
- 50 - Predictive equations of gas exchanges are generally reliable in low-turbulent
51 zones, but underestimate gas exchanges in small cascades.
- 52 - Small cascades can be viewed as hot spots for both stream oxygenation and
53 CO₂ emission.
- 54 - Overlooking small cascades in global CO₂ calculations leads to an
55 underestimation of CO₂ emissions from headwater catchments.

56 1. INTRODUCTION

57 Streams continuously exchange gases with the atmosphere. The reaeration process,
58 which characterizes the exchange of oxygen between streams and atmosphere,
59 provides ecosystem services by sustaining in-stream respiration (Aristegi et al. 2009;
60 Knapp et al. 2015). Air-water gas exchanges also control CO₂, CH₄ and N₂O release
61 or uptake by streams (Tranvik et al. 2009) and thus influence the global greenhouse
62 gas budgets of terrestrial systems. Global CO₂ emissions from inland water,
63 estimated at 2.9 PgC y⁻¹, are of the same order of magnitude as terrestrial C sinks of
64 3.1 PgC y⁻¹. Among inland water CO₂ fluxes, recent studies highlighted the
65 importance of inputs from headwater streams, because of their ubiquity (Bishop et
66 al. 2008), their connection to biologically active compartments and their high level
67 of turbulence (Duvert et al. 2018; Natchimuthu et al. 2017; Öquist et al. 2009; Wallin
68 et al. 2011). Crawford et al. (2014) showed that even in a lake-rich landscape of the
69 Northern Highland Lake District (Michigan, US), streams emitted roughly the same
70 CO₂ mass as lakes. The same study highlighted that streams may also be substantial
71 sources of CH₄ (Crawford et al. 2014). With respect to warming potential, CH₄
72 emissions by streams corresponded to 26% of the total estimated CO₂ flux. All these
73 studies call for a better quantification of greenhouse gas emissions in lower-order
74 streams.

75 Quantification of gas exchanges is also crucial in surface water ecology, especially
76 for open-channel metabolism calculations (Aristegi et al. 2009; Knapp et al. 2015).
77 It is a key-point in many hydrogeochemical studies as well, such as radon-based

78 groundwater discharge estimations (Avery et al. 2018; Cartwright et al. 2014; Cook
79 et al. 2003; Gilfedder et al. 2019; Gleeson et al. 2018). Gas exchange rate
80 coefficients can be measured directly by performing gas tracer release
81 experiments (Benson et al. 2014; Genereux and Hemond 1992; Hall and Madinger
82 2018; Knapp et al. 2019; Wanninkhof et al. 1990). Inert gases such as propane, SF₆
83 or helium are injected in the stream, often in conjunction with a non-volatile tracer
84 to account for dispersion and dilution effects. Since these injections are time- and
85 cost-intensive, predictive equations, either empirical (Churchill et al. 1964;
86 Goncalves et al. 2017; Melching and Flores 1999; Tsivoglou and Neal 1976) or
87 process-based (Gualtieri and Gualtieri 2000; Gualtieri et al. 2002), have been
88 developed to propose straightforward estimates of gas exchange rate coefficients.
89 The gas exchange rate coefficients are expressed as a function of hydrodynamic
90 characteristics such as water depth, flow velocity, slope, discharge and in some cases
91 dimensionless numbers (e.g. Froude, Reynolds, Sherwood numbers). A wide
92 diversity of equations may be found in literature, but each equation appears to be
93 specific to the hydrological conditions for which it has been defined, making them
94 poorly reliable at a large scale or in different settings (Melching and Flores 1999;
95 Palumbo and Brown 2014).

96 The diversity of empirical equations existing in literature reflects the variability of
97 gas exchanges in headwater catchments. Lower-order streams are characterized by
98 the great diversity in small-scale morphological structures, including pools, riffles,
99 and cascades that can change over time and that are difficult to represent at larger

100 scales. In larger rivers, cascades have been shown to trigger gas exchanges by
101 creating air bubbles (Cirpka et al. 1993). High tracer gas losses have been measured
102 in dams (Caplow et al. 2004). Flume experiments have evidenced that spillways and
103 cascades critically increase water oxygenation (Baylar et al. 2006; Khdhiri et al.
104 2014; Tebbutt 1972), generating gas exchanges that may be several orders of
105 magnitudes higher than in low-turbulent channels (Baylar et al. 2006). Drops in CO₂
106 partial pressure downstream from waterfalls have additionally been shown in studies
107 focused on global carbon budget estimates (Wallin et al. 2011) and on river water
108 hardness in karstic systems (Chen et al. 2004). In most studies focused on headwater
109 streams, though, a unique gas exchange rate coefficient is estimated for the whole
110 stream, whatever the diversity of its hydrodynamic conditions.

111 Here we focus on headwater streams and investigate the impact of small-scale
112 morphological traits on global predictions of gas exchange rate coefficients and CO₂
113 evasion fluxes. We hypothesize that the heterogeneity of the streambed, which is a
114 characteristic feature of headwater streams, explains the difficulty in predicting gas
115 exchanges and CO₂ emissions. By coupling continuous helium injections and
116 membrane inlet mass spectrometry, we map gas exchanges along two low slope
117 headwater streams that display a diversity of morphological structures. We
118 additionally measure dissolved O₂ and CO₂ to characterize the impact of natural
119 cascades and riffles on stream oxygenation and greenhouse gas emissions in
120 headwater catchments.

121 **2. MATERIAL AND METHODS**

122 The two headwater streams were selected based on the diversity of their
123 morphological structures (i.e. the presence of low-turbulent zones and cascades).
124 Helium (an inert gas tracer) and NaCl (a conservative tracer) were injected
125 continuously and monitored at several distances from the injection site using a
126 continuous flow membrane inlet mass spectrometer (CF-MIMS) and an electrical
127 conductivity (EC) probe. Experiments were performed in spring 2018.

128 **2.1. Study site**

129 The two streams belong to a crystalline catchment located in Pleine-Fougères
130 (Brittany, Western France) (Kolbe et al. 2016). The catchment (figure 1a) is part of
131 the Long-Term Socio-Ecological Research (LTSER) site “Zone Atelier Armorique”.
132 Both streams present typical low-slope headwater stream morphologies, featuring
133 small cascades and low-turbulent areas (figure 1c). Both streams are located in
134 agricultural fields and have riverine vegetation dominated by brambles and diverse
135 herbaceous species such as Kentucky bluegrass and buttercups. Stream A (locally
136 called “Le Ronan”) is a first-order stream with a mean depth of 0.16 m, a mean width
137 of 0.8 m, and a discharge rate of 25 L s^{-1} , as measured by the NaCl slug injection
138 performed the day of the experiment. Stream B (“Le Petit Hermitage”) is a second
139 order stream with a mean depth of 0.25 m, a mean width of 1.8 m, and a discharge
140 rate of 90 L s^{-1} . Their streambeds were covered by heterogeneous detrital elements,
141 such as coarse-grain sediments, small rocks and decaying branches, which led their
142 small-scale morphology to be variable (figure 1b). The global slope of the streams

143 was deduced from the altitude of the upstream and downstream ends of the reach.
144 The precise topography was then determined by measuring the height of each
145 cascade with a tape. Each reach was divided into several uniform sub-reaches (e.g.
146 low-turbulent zone, cascade). Reach A (total length of 52 m) showed a succession
147 of low-turbulent zones and small cascades (5 to 15 cm high). It was divided into 6
148 sub-reaches (A_1 to A_6) measuring 3 to 12 meters. Reach B (total length of 98 m) was
149 flat and homogeneous along its first 95 meters, and displayed a 35 cm high cascade
150 at its downstream end, between 95 and 98 meters. It was divided into 3 sub-reaches
151 (B_1 to B_3): two similar segments in the flat zone (B_1 and B_2), and one short segment
152 around the fall (B_3) (figure 1b).

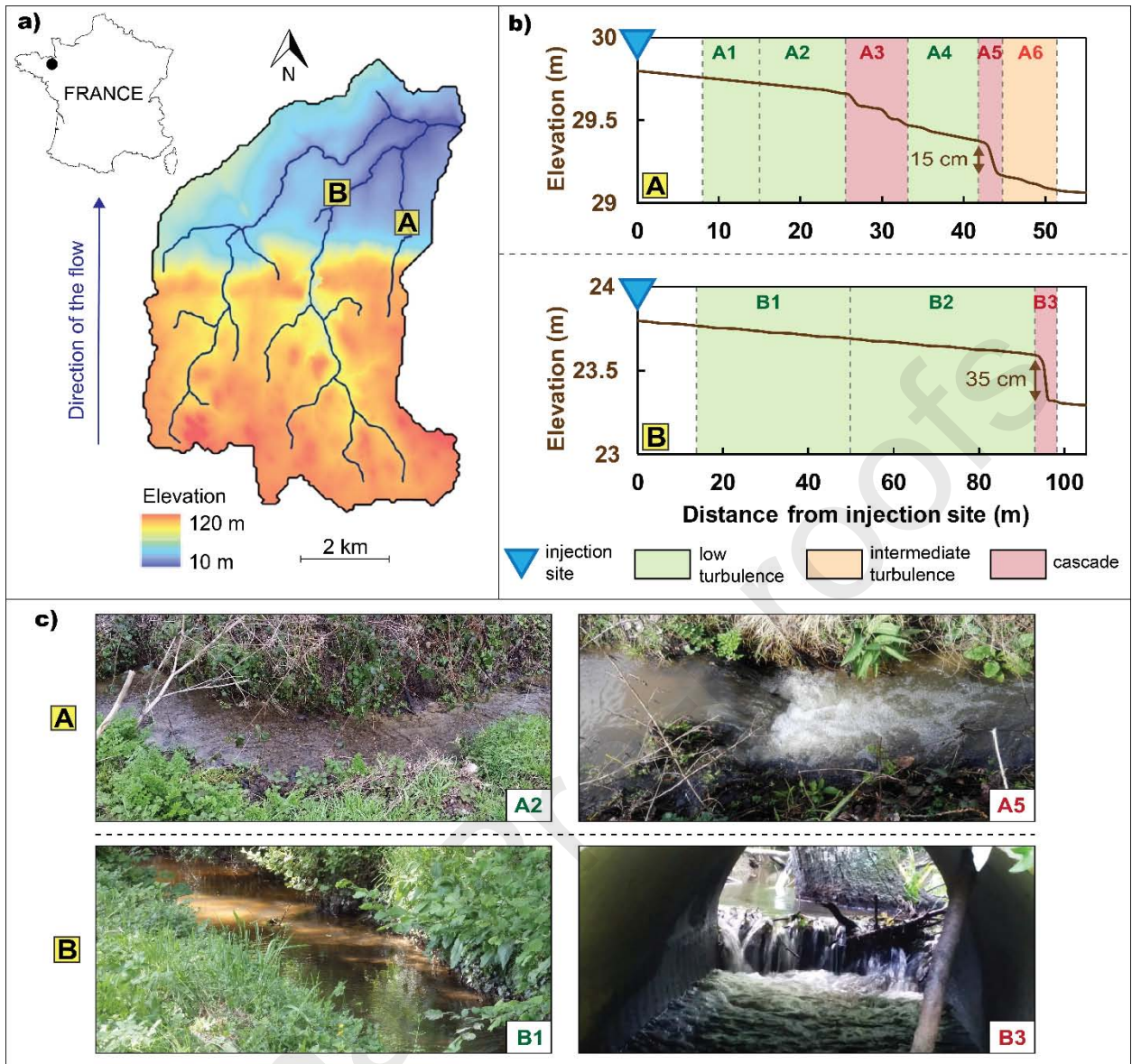


Figure 1. (a) Localization and map of the Pleine-Fougères catchment, (b) Streambed topographic profiles of reaches A and B, and (c) Pictures of the less turbulent zone (left) and of the highest cascade (right) in reach A (up) and in reach B (down). On the topographic profiles (b), dashed lines indicate sub-reaches limits, colors indicate visually-determined turbulence levels of each sub-reach.

153 **2.2. Tracer injection**

154 Helium was chosen as gaseous tracer for the following reasons. (1) As a noble gas,
155 it is non-reactive. (2) It is non-toxic. (3) Its concentration in the atmosphere is very
156 low (around 5 ppm), allowing a high concentration difference between stream and
157 atmosphere during injections. (4) It can be accurately measured with CF-MIMS and
158 gas chromatography. (5) It is highly volatile, increasing the accuracy of degassing
159 estimations. (6) It is not expensive. (7) Unlike other tracers such as SF₆ (Benson et
160 al. 2014), it is not a greenhouse gas. A non-volatile conservative tracer was also
161 needed to account for potential dilution due to groundwater discharge (Genereux and
162 Hemond 1990; Kilpatrick et al. 1987; Tobias et al. 2009). We used chloride from
163 NaCl, which is classically chosen for its low cost and simple use (Genereux and
164 Hemond 1990; Genereux and Hemond 1992).

165 Helium and NaCl were injected continuously at a constant rate for 2 hours in
166 stream A and for 1 hour in stream B. Helium was injected from a 100% liquid
167 helium bottle through bubbling on the stream bottom (Supplementary data, Figure
168 A.1). A precision manometer and a pressure regulator ensured the stability of the
169 injection. The background helium concentration of both streams was around
170 $8 \cdot 10^{-9} \text{ mol L}^{-1}$. Upon injection, it increased to $1 \cdot 10^{-7} \text{ mol L}^{-1}$ in stream A and to
171 $8 \cdot 10^{-7} \text{ mol L}^{-1}$ in stream B. 10 kg of NaCl were dissolved in a 300 L can filled with
172 stream water. The NaCl solution was then injected into the stream at a flow rate of
173 2 L min^{-1} using a peristaltic pump. The background electrical conductivity,
174 measured at the injection site, before and after the experiments, was $270 \mu\text{S cm}^{-1}$ in

175 stream A and $204 \mu\text{S cm}^{-1}$ in stream B. Upon injection, it increased to $330 \mu\text{S cm}^{-1}$
176 in stream A and to $229 \mu\text{S cm}^{-1}$ in stream B.

177 **2.3. Measurement**

178 *In-situ* measurements of helium were performed using continuous flow membrane
179 inlet mass spectrometry (CF-MIMS). *In-situ* membrane inlet mass spectrometry has
180 been shown to improve the determination of gas exchange rate coefficients based on
181 tracer injections (Knapp et al. 2019). It was also used recently by Weber et al. (2019)
182 to derive gas exchange rate coefficients from direct measurements of dissolved
183 atmospheric gases. The CF-MIMS used here (modified from HPR40 - Hiden
184 Analytical) is described in details in Chatton et al. (2017). The gas inlet is ensured
185 by a membrane (X44® 99) connected to the vacuum of a Quadrupole Mass
186 Spectrometer (QMS around 10^{-5} Torr), allowing the direct permeation of dissolved
187 gases from water to spectrometer. Inside the QMS, gases are ionized using an oxide
188 coated iridium filament that allows the selection of ionization energies (between 4
189 and 150 eV) and emission intensities (between 20 and 5000 μA). Ionized gases are
190 then separated by the quadrupole according to their mass to charge ratios. Then, the
191 detection of gases is performed either by a Faraday cup or a single channel electron
192 multiplier (SCEM). The instrumental relative standard deviation is 2% for He and
193 0.2% for N_2 , O_2 and CO_2 , indicating high measurement sensitivity.

194 The spectrometer was installed a few meters away from the stream. Stream water
195 was pumped continuously (MP1 Grunfoss pump, 5 L min^{-1}) and brought to the
196 spectrometer membrane through a nylon tubing system preventing any contact with

197 the air. The pump was attached to a float so that stream water was pumped at a
198 constant depth, approximately 10 cm below the surface. Helium was measured by
199 the spectrometer in real time, with a 10 second timestep. During injection, the pump
200 feeding the CF-MIMS was moved step by step from the downstream end to the
201 upstream end of the reach to map the loss of helium along the stream. To make sure
202 that the injection rate was constant, the pump was first installed at the downstream
203 end of the reach until helium concentrations reached a stable plateau for 20 minutes.
204 Then, the pump was moved a few meters upstream to the next measurement location.
205 After a few minutes of unstable measurements due to pump and tubing manipulation,
206 the helium concentration stabilized at a new stable plateau. From that time, the pump
207 was maintained at this location during 10 minutes to gather a significant number of
208 helium measurements (60 to 70) and make sure the injection rate was constant. Then
209 the pump was moved upstream to the next measurement location, and the procedure
210 was reiterated up to the uppermost measurement location. Moving the pump
211 upstream avoided perturbation from one measurement location to the next one. The
212 stability of the injection and the consistency of the measurements were checked
213 continuously using real-time data visualization provided by the *in-situ* CF-MIMS
214 system. This system allowed real-time mapping of the degassing taking place along
215 the streams. Major atmospheric gas concentrations (N_2 , O_2 , Ar, CO_2), water vapor
216 pressure (H_2O) and temperature were simultaneously measured with the CF-MIMS
217 to correct helium data for external and instrumental deviations. CF-MIMS data,
218 expressed in partial pressures in air, were converted into concentrations in water by

219 external calibration with micro-gas chromatography (μ GC) measurements on grab
220 samples. Two samples intended for μ GC analysis were taken at each location, in
221 500 mL glass bottles. To ensure the synchronicity of CF-MIMS and μ GC data,
222 samples were collected directly at the CF-MIMS outlet. The tube filling the glass
223 bottles was immersed in a bucket to avoid any contact with the atmosphere. All μ GC
224 measurements were performed less than 48 hours after sampling. The instrument
225 relative standard deviation of the μ GC is 3%. Detailed description of CF-MIMS
226 measurements, corrections and the calibration procedure can be found in Chatton et
227 al. (2017). As a proxy for NaCl, electrical conductivity was monitored using two
228 Hatch[®] probes. The relative standard deviation of EC measurements is 5%. One EC
229 probe was moved together with the pump. The probe and the pump were attached to
230 the same float to ensure they sampled the same water. The second EC probe was
231 permanently installed 10 meters downstream from the injection site to check the
232 stability of salt injection. The experimental set-up is summarized in figure 2.

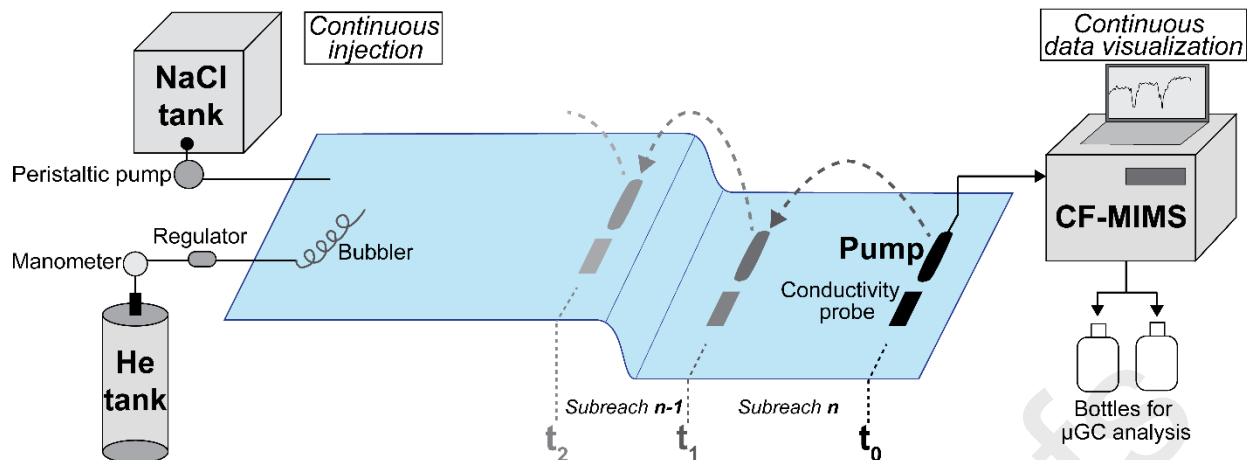


Figure 2. Experimental set up. Upstream, helium and salt are injected continuously at a stable level during the whole duration of the experiment. Downstream, at decreasing distances from the injection site, helium concentrations are measured continuously and visualized in real-time using a CF-MIMS fed by a pump. Chloride concentrations are measured with an EC probe. First, the pump and the EC probe are installed at the downstream end of the reach (t_0). Once the concentration in helium reaches a plateau, the pump and the EC probe are moved upstream to the next measurement location (t_1). Once a new plateau in concentration is reached, instruments are moved upstream again (t_2). The procedure is reiterated up until the last measurement location to map helium losses along the whole length of the reach. In order to calibrate CF-MIMS measurements, two bottles are sampled from the CF-MIMS outlet at each measurement location for μ GC analysis.

234 Degassing is commonly assumed to be linearly proportional to the air-water
 235 concentration difference (Kilpatrick et al. 1987). Thus, the variation in helium
 236 concentrations through time can be expressed by the 1D advection-dispersion
 237 equation:

$$\frac{\partial C_{He}}{\partial t} + U \frac{\partial C_{He}}{\partial x} = D_x \frac{\partial^2 C_{He}}{\partial x^2} - k_{He}(C_{He} - C_{He}^{eq}) \quad (1)$$

238 where C_{He} (mol L⁻¹) is the helium concentration, C_{He}^{eq} (mol L⁻¹) is the helium
 239 concentration in a stream at equilibrium with the atmosphere, k_{He} (s⁻¹) is the air-water
 240 gas exchange rate coefficient of helium, U (m s⁻¹) is the water velocity and D_x
 241 (m² s⁻¹) is the longitudinal dispersion coefficient. Since helium has a low
 242 atmospheric concentration, its equilibrium concentration in stream is low (around
 243 8.10⁻⁹ mol L⁻¹). Thus, during helium injections, stream helium concentration
 244 becomes at least one order of magnitude higher than the equilibrium concentration,
 245 and C_{He}^{eq} can be neglected. The variations in chloride concentrations through time can
 246 be expressed using the same advection-dispersion equation without the degassing
 247 term:

$$\frac{\partial C_{Cl}}{\partial t} + U \frac{\partial C_{Cl}}{\partial x} = D_x \frac{\partial^2 C_{Cl}}{\partial x^2} \quad (2)$$

248 where C_{Cl} (mol L⁻¹) is the chloride concentration. Assuming that the advection and
 249 dispersion parameters for chloride are similar than for helium (Genereux and
 250 Hemond 1992; Tobias et al. 2009; Wanninkhof et al. 1990), combining equations 1

251 and 2 leads to the solution proposed by Kilpatrick et al. (1987), in which dilution
 252 effects are taken into account by the ratio in chloride concentrations:

$$k_{He} = \frac{U}{L} \ln \left(\frac{C_{He}^{up}}{C_{He}^{down}} \frac{C_{Cl}^{up}}{C_{Cl}^{down}} \right) \quad (3)$$

253 where C_{He}^{up} and C_{Cl}^{up} (mol L⁻¹) are the upstream concentrations, C_{He}^{down} and C_{Cl}^{down}
 254 (mol L⁻¹) are the downstream concentrations, U (m s⁻¹) is the mean stream velocity
 255 and L (m) is the distance between the two locations.

256 The gas exchanges depend on the nature of the gas and on water temperature. Gas
 257 exchange rate coefficients can be scaled from one gas to another using the ratio of
 258 their Schmidt numbers (Jähne et al. 1987b). The Schmidt number (Sc) is a
 259 dimensionless number corresponding to the ratio of kinematic viscosity to mass
 260 diffusivity. To enable comparison with previously published results, gas exchange
 261 rate coefficients calculated for helium, k_{He} , are scaled to the reaeration rate
 262 coefficient k_2 , defined as the gas exchange rate coefficient for O₂ at 20°C:

$$k_2 = k_{He} \left(\frac{Sc_{O_2}}{Sc_{He}} \right)^{-0,5} \quad (4)$$

263 where Sc_{O_2} is the Schmidt number for oxygen at 20°C and Sc_{He} is the Schmidt
 264 number for helium at stream temperature. The equations from which the Schmidt
 265 numbers used in this study were obtained are featured in table 1.

266 **Table 1.** Schmidt numbers used in this study.

| Gas | Reference | Equation |
|-----------------|---|--|
| He | Wanninkhof (1992) based on data from Jähne et al. (1987a) | $Sc_{He} = 377.09 - 19.154 T + 0.50137 T^2 - 0.005669 T^3$ |
| O ₂ | Baird and Davidson (1962); Carlson (1911); Raymond et al. (2012); Wise and Houghton (1966) | $Sc_{O_2} = 1568 - 86.04 T + 2.142 T^2 - 0.0216 T^3$ |
| CO ₂ | Wanninkhof (1992) | $Sc_{CO_2} = 1911 - 118.11 T + 3.453 T^2 - 0.0413 T^3$ |

267 **2.5. Comparison with predictive equations**

268 Gualtieri et al. (2002) performed a dimensional analysis to identify the physical
269 parameters that control gas exchange rate coefficients in streams. They showed that
270 gas exchange rate coefficients k (d⁻¹) can be expressed as a direct function of the
271 Froude number Fr , the channel slope i , the Reynolds number Re , the ratio between
272 the stream depth h (m), the mean velocity U (m s⁻¹), and a dimensionless gas
273 exchange factor λ :

$$k = \frac{U}{h} \lambda[Fr, i, Re] \quad (5)$$

with: $Fr = \frac{U}{\sqrt{gh}}$; $Re = \frac{U h}{\nu}$

274 where g (m s^{-2}) is the gravitational acceleration and ν ($\text{m}^2 \text{s}^{-1}$) is the kinematic
275 viscosity. Gualtieri et al. (2002) reformulated 20 empirical and semi-empirical
276 equations from literature as a function of these parameters. It was shown that all
277 equations physically contain the velocity over depth ratio, the slope and the Froude
278 number. Some of them additionally involve the Reynolds number. Their process-
279 based analysis pointed out that stream depth is a crucial parameter in any gas
280 exchange rate coefficient equation: it influences in the velocity over depth ratio as
281 well as the Froude and Reynolds numbers. Thus, application of these equations
282 implicitly assumes the existence of a water layer with a well-defined thickness. In
283 cascades, such a layer cannot be defined. A cascade can be seen as a succession of a
284 ramp, where gas exchanges occur at the free surface of the water layer, and a
285 receiving basin, in which gas exchanges are controlled by air bubbles (Cirpka et al.
286 1993). In the ramp section of the cascade, the supercritical flow regime implies that
287 the water layer is very thin and uneven. In the receiving basin portion of the cascade,
288 the falling jet penetrating the water generates high turbulence and uneven flows.
289 Thus, the empirical and semi-empirical equations of gas exchange rate coefficient
290 are theoretically not applicable in cascades. Cirpka et al. (1993) developed
291 alternative semi-empirical equations to describe gas exchanges specifically within
292 cascades in large rivers. Their equations account for gas exchanges through the free
293 surface and via air bubbles. They rely on four parameters, the calibration of which

294 requires extensive in-situ tracer experiments with the simultaneous injections of four
295 different gases.

296 This raises the question of the suitability of predictive equations for global
297 estimations of gas exchange rate coefficients. Indeed, since most headwater streams
298 display both cascades and low turbulent zones, the unreliability of equations in
299 cascades is likely to distort the gas exchange rate coefficient at the stream scale. To
300 test if the presence of a few cascades significantly distorts global gas exchange
301 predictions over a stream reach, we compared measured k_2 values with values
302 calculated using predictive equations developed for small streams (table 2). We
303 considered the historical equation of O'Connor and Dobbins (1958). Among the
304 many other empirical equations that have been proposed ever since, we chose the
305 relationships that were calibrated with the largest datasets. The semi-empirical
306 equation from Melching and Flores (1999) is based on a large USGS data set and
307 was further used in several studies (Haider et al. 2013; Ritz et al. 2017). The seven
308 semi-empirical equations from Raymond et al. (2012) are based on the same USGS
309 data set and on four additional data sets (Bernot et al. 2010; Bott et al. 2006;
310 Mulholland et al. 2001; Tsivoglou and Neal 1976), making them, to our knowledge,
311 the equations based on the largest amount of data (Lauerwald et al. 2015). We also
312 considered the process-based equation proposed by Gualtieri and Gualtieri (2000)
313 and Gualtieri et al. (2002).

Table 2. Predictive equations considered in this study. All formulas were converted into the reaeration rate coefficient k_2 (d^{-1}).

| Reference | Equation type | Equation |
|---|----------------|--|
| O'Connor and Dobbins (1958) | Semi-empirical | $k_2 = 3.93 U^{0.5} h^{-1.5}$ |
| Melching and Flores (1999) | Semi-empirical | $k_2 = 517 (Ui)^{0.524} Q^{-0.242}$ |
| Gualtieri and Gualtieri (2000) Gualtieri et al. (2002) | Process-based | $k_2 = 86400 \frac{U}{h} \frac{2^{1/3}}{Sc^{2/3} R_{m-t}^{2/3}} Re^{-1/3} Fr^{-2/3} i^{1/3}$ |
| | | [1] $k_2 = 5354 (Ui)^{0.89} h^{-0.46}$ |
| | | [2] $k_2 = 6311 (Ui)^{0.89} h^{-0.42} (1 - 2.54 Fr^2)$ |
| | | [3] $k_2 = 1235 U^{0.85} s^{0.77} h^{-1}$ |
| Raymond et al. (2012) | Semi-empirical | [4] $k_2 = 1011 (Ui)^{0.76} h^{-1}$ |
| | | [5] $k_2 = (3020 Ui + 2.15) h^{-1}$ |
| | | [6] $k_2 = 988 (Ui)^{0.75} Q^{0.011} h^{-1}$ |
| | | [7] $k_2 = 5023 (Ui)^{0.86} Q^{-0.14} h^{-0.34}$ |

314 To compare measured gas exchange rate coefficients with gas exchange rate
 315 coefficients obtained using predictive equations, the hydraulic parameters of each
 316 stream were measured. (Supplementary data, Table A.1). Global parameters were

317 evaluated at the reach scale and local parameters were evaluated for each sub-reach.
318 Stream discharge was calculated using a NaCl slug injection. Velocity was measured
319 using a field velocimeter (FP111 Global Water Flow Probe). The slope was derived
320 from the altitude gradient between upper and lower reach ends. Depth was measured
321 at several points across and along each reach, and averaged for each reach.

322 **2.6. Reactive gases**

323 In conjunction with helium, O₂ and CO₂ were measured by CF-MIMS at several
 324 distances from the injection site. Measurements were externally calibrated using
 325 micro-gas chromatograph (μGC) measurements, in the same way as for helium. In
 326 both streams, the helium enrichment due to the injection was less than 1 μmol L⁻¹,
 327 so it did not induce significant degassing of O₂ or CO₂. In stream B, O₂ and CO₂
 328 measurements failed because of a calibration error of the μGC.

329 CO₂ evasion was calculated using the measured CO₂ concentrations and the gas
 330 exchange rate coefficient derived from the helium injection. Gas exchange rate
 331 coefficients were first converted from He to CO₂ based on the ratio of their Schmidt
 332 numbers (equation 4). The Schmidt number for CO₂ is given in table 1. The CO₂
 333 evasion rate at the stream-atmosphere interface (mol m⁻² s⁻¹) was then calculated
 334 using the flux equation first developed for reaeration by Young and Huryn (1998)
 335 and later derived for CO₂ evasion (Billett et al. 2004; Hope et al. 2001; Öquist et al.
 336 2009; Wallin et al. 2011) :

$$CO_{2\ evasion} = (CO_{2\ stream} - CO_{2\ eq}) \times k_{CO_2} \times \frac{q}{U \times w} \quad (6)$$

337 where $CO_{2\ stream}$ is the measured CO_2 concentration ($mol\ L^{-1}$), $CO_{2\ eq}$ is the
 338 concentration at equilibrium with the atmosphere ($mol\ L^{-1}$), k_{CO_2} is the gas exchange
 339 rate coefficient for CO_2 (s^{-1}), Q is the stream discharge ($L\ s^{-1}$), U is the mean velocity
 340 of the water ($m\ s^{-1}$) and w is the stream width (m).

341 2.7. List of the parameters

342 The parameters used in the paper are listed in table 3.

Table 3. List of parameters used in the paper.

| Symbol | Variable | Unit |
|-----------------|---|---------------|
| C_{Cl} | concentration of chloride | $mol\ L^{-1}$ |
| C_{Cl}^{down} | downstream concentration of chloride | $mol\ L^{-1}$ |
| C_{Cl}^{up} | upstream concentration of chloride | $mol\ L^{-1}$ |
| C_{He} | concentration of helium | $mol\ L^{-1}$ |
| C_{He}^{eq} | concentration of helium at equilibrium with the atmosphere | $mol\ L^{-1}$ |
| C_{He}^{down} | downstream concentration of helium | $mol\ L^{-1}$ |
| C_{He}^{up} | upstream concentration of helium | $mol\ L^{-1}$ |
| D_x | longitudinal dispersion coefficient | $m^2\ s^{-1}$ |
| E | Aeration efficiency | [-] |
| Fr | Froude number | [-] |
| g | standard acceleration due to gravity | $m\ s^{-2}$ |
| h | water depth | m |
| i | slope | [-] |
| k | gas exchange rate coefficient | s^{-1} |
| k_2 | gas exchange rate coefficient for O_2 at 20°C (also called reaeration rate coefficient) | s^{-1} |

| | | |
|-------------|--|--------------|
| k_{He} | gas exchange rate coefficient for He at the stream temperature | s^{-1} |
| L | stream length | m |
| Q | stream discharge | $m^3 s^{-1}$ |
| Re | Reynolds number | [] |
| R_{m-t} | mass transfer Reynolds number (fitted with data) | [] |
| Sc_{CO_2} | Schmidt number for CO_2 | [] |
| Sc_{He} | Schmidt number for He | [] |
| Sc_{O_2} | Schmidt number for O_2 | [] |
| T | stream temperature | $^{\circ}C$ |
| t | time | s |
| U | Stream velocity | $m s^{-1}$ |
| x | Distance | m |
| w | Stream width | m |
| λ | Dimensionless gas exchange factor | [] |
| ν | kinematic viscosity | $m^2 s^{-1}$ |

343 3. RESULTS

344 3.1. Gas exchange mapping

345 In both streams (A and B), measurements at several distances from the injection
346 site show a decrease in helium concentrations from upstream to downstream
347 (figure 3). In stream A, the helium concentrations decrease from 140 nmol L^{-1} at
348 14 m from the injection site to 84 nmol L^{-1} at 52 m downstream. A light rain event
349 occurred at the end of the experiment, just before the pump was set up at the most
350 upstream measurement location (9 m). The rain increased the gas exchanges at the
351 stream surface (Ho et al. 2000), leading to lower helium concentrations at 9 m (130

352 nmol L⁻¹) than at 14 m (140 nmol L⁻¹). In stream B, helium concentrations decrease
353 from 820 nmol L⁻¹ at 15 m from the injection site to 650 nmol L⁻¹ at 98 m
354 downstream. The CF-MIMS semi-continuous measurements allowed visualization
355 and quantification of the uncertainty in helium concentration estimates. The relative
356 standard deviation (RSD) of the 60 to 70 measurements available at each distance
357 was comprised between 1.7 and 4.5% in stream A, and between 0.9 and 1.5% in
358 stream B, attesting the stability of helium concentrations at each location. The lower
359 RSD in stream B is probably due to the higher helium injection rate. The large
360 number of measurements allows to perform a trend analysis on each plateau. It
361 reveals the absence of systematic decrease or increase of the helium concentration
362 upon a plateau (Supplementary data, Table A.2). In stream A, 4 plateaus have a slight
363 increasing trend and 3 plateaus have a slight decreasing trend. In stream B, 3 plateaus
364 have a slight increasing trend and one plateau has a slight decreasing trend. This
365 suggest an overall stability of the injection rate. Electrical conductivity can be
366 considered as stable along the streams, since its variation from upstream to
367 downstream is lower than the instrumental relative standard deviation. EC stability
368 thus shows the absence of major groundwater inputs prone to modify the helium
369 signal. In stream A, where measurements of O₂ and CO₂ are available, the
370 consistency in the variations of He, O₂ and CO₂ further confirms the absence of
371 disturbance of the gas content by groundwater inputs. CO₂ concentrations in
372 groundwater, as measured at a small spring located 20 meters upstream from the
373 injection site, reach 650 μmol L⁻¹, that is 30 times the atmospheric equilibrium.

374 Inputs of such concentrated groundwater along the studied reach would have
375 induced a sharp increase in CO₂ concentrations in the stream. However, CO₂
376 concentrations follow a general decreasing trend, from at 299 μmol L⁻¹ at 14 m to
377 288 μmol L⁻¹ at 52 m, suggesting that there are no major inputs of groundwater along
378 the studied reach. Salt injections had to be stopped before the end of the experiments
379 because of a deficit in salt injection solution. It is unlikely to bias the conclusions
380 reached here, as EC does not change between the downstream and upstream ends of
381 each studied reach (figure 3).

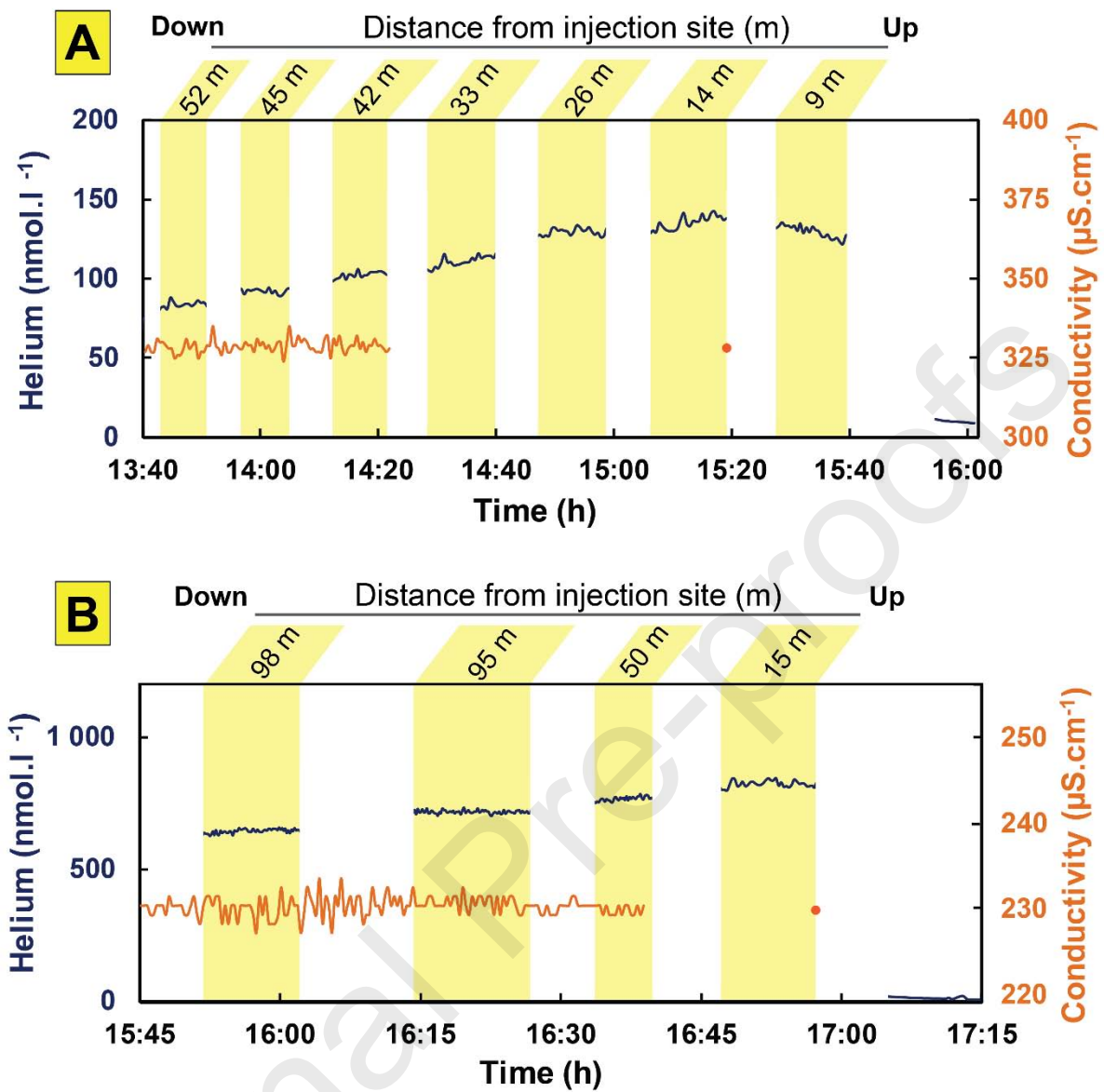


Figure 3. Monitoring of helium in stream A (up) and B (down). Blue lines represent the calibrated helium concentration, orange lines represent the electrical conductivity. Each plateau, highlighted by a yellow band, corresponds to a measurement location. Salt injection was stopped at 14:20 in stream A and at 16:40 in stream B. In stream A, it rained at the end of the experiment, when the pump was at 9 m from the injection site. Rain increased gas exchanges between stream and atmosphere thus lowering helium concentrations. The complete helium time series, including the measurements during the changes of measurement location, are presented in the Supplementary data, Figure A.2.

382 Global gas exchange rate coefficients in each stream were calculated using the
383 concentration difference between the most upstream and downstream locations
384 (equation 3). Since EC does not vary along each stream, the ratio between upstream
385 and downstream chloride concentrations is equal to 1 and can be simplified in
386 equation 3. The gas exchange rate coefficient for helium, k_{He} , was 196 d^{-1} in stream
387 A and 99 d^{-1} in stream B, corresponding to a reaeration rate coefficient, k_2 , of
388 respectively 130 d^{-1} and 60 d^{-1} (equation 4). These k_2 are in the range of values found
389 by other gas tracer release experiments in headwater streams (table 4). The
390 reaeration rate coefficient is significantly higher in the 1st order stream (A) than in
391 the 2nd order stream (B). It is consistent with the observations of Wallin et al. (2011)
392 showing an increase in the rate of CO_2 degassing with lower stream order.

Table 4. Reaeration rate coefficients measured in this study are in the range of reaeration rate coefficients from other gas tracer release experiments performed in headwater streams ($Q < 100 \text{ L s}^{-1}$).

| Reference | Gaseous tracer | Non-volatile tracer | k_2 (d^{-1}) |
|-----------------------------|----------------------|-------------------------------|---------------------------|
| This study, stream A | He | chloride | 130 |
| This study, stream B | He | chloride | 60 |
| Wanninkhof et al. (1990) | SF ₆ | ³ H ₂ O | 119 |
| Genereux and Hemond (1992) | propane, ethane | chloride | 118 – 139 |
| Soares et al. (2013) | propane | rhodamine WT | 27 – 367 |
| Benson et al. (2014) | SF ₆ , Xe | - | 47 – 66 |
| Knapp et al. (2019) | propane, krypton | fluorescein | 15 – 134 |

393 For each sub-reach, reaeration rate coefficients were calculated in the same way as
 394 for the full stream reaches. Helium concentrations and reaeration rate coefficients
 395 were then reported as a function of the distance from injection site (figure 4).
 396 Uncertainties in the helium concentrations were estimated by the standard deviations
 397 of the 60 to 70 CF-MIMS measurements available for each plateau. Standard
 398 deviations are small (figure 4), demonstrating the robustness of the measurements.
 399 Uncertainties in the gas exchange rate coefficients were estimated by randomly
 400 subsampling each plateau of helium concentration. The gas exchange rate coefficient
 401 was calculated using a randomly chosen value of the upstream plateau and a

402 randomly chosen value of the downstream plateau. The random sampling was
403 reiterated 1000 times for each sub-reach, leading to 1000 k_2 values. The standard
404 deviation of the 1000 k_2 values indicated the uncertainty due to helium measurement
405 (figure 4). The uncertainty is smaller in stream B than in stream A, due to the lower
406 noise level in stream B. A big advantage of the continuous measurements with in-
407 situ CF-MIMS is that it produces a significant number of measurements, which
408 allows to visualize and quantify the uncertainties. For the sub-reaches where EC was
409 available, the uncertainty due to EC measurements was quantified in the same way,
410 by sub-sampling EC values from each plateau. Taking into account the uncertainty
411 due to EC measurements increased the standard deviation by 50% in sub-reach A₅,
412 by 8% in sub-reach A₆ and by 10% in sub-reach B₃. Thus, the uncertainty due to EC
413 measurements is lower than the uncertainty due to helium measurements, but is not
414 negligible. When possible, we recommend using a fluorescent dye as conservative
415 tracer, rather than NaCl. The measurement accuracy of fluorescent dyes is usually
416 higher, and fluorescent dyes are not present naturally in water, which lowers the
417 overall uncertainty on gas exchange rate coefficients.

418 The gas exchanges are heterogeneously distributed along the streams. In stream A,
419 k_2 increases by a factor of 6 from the less turbulent zones ($k_2(A_2) = 50 \text{ d}^{-1}$;
420 $k_2(A_4) = 70 \text{ d}^{-1}$) to the highest cascade ($k_2(A_5) = 360 \text{ d}^{-1}$). Intermediary values are
421 found in the sub-reach displaying three successive small cascades ($k_2(A_3) = 220 \text{ d}^{-1}$)
422 and in the agitated sub-reach with no identifiable cascade ($k_2(A_6) = 140 \text{ d}^{-1}$). Thus,
423 reaeration rate coefficients are ranked according to the level of turbulence. In stream

424 B, the range of reaeration rate coefficients is larger. The reaeration rate coefficient
425 is 40 times higher in the cascade ($k_2(B_3) = 1030 \text{ d}^{-1}$) than in the flat area
426 ($k_2(B_1) = k_2(B_2) = 25 \text{ d}^{-1}$). Note that the first two sub-reaches B_1 and B_2 , presenting
427 visually the same morphological characteristics, have the same k_2 values, which
428 supports the reliability of the method. This mapping of gas exchanges evidences a
429 high heterogeneity of degassing along the streams. Exchanges are strongly focused
430 in cascades: a 35 cm high cascade loses as much gas as an 80 m long low-turbulent
431 reach.

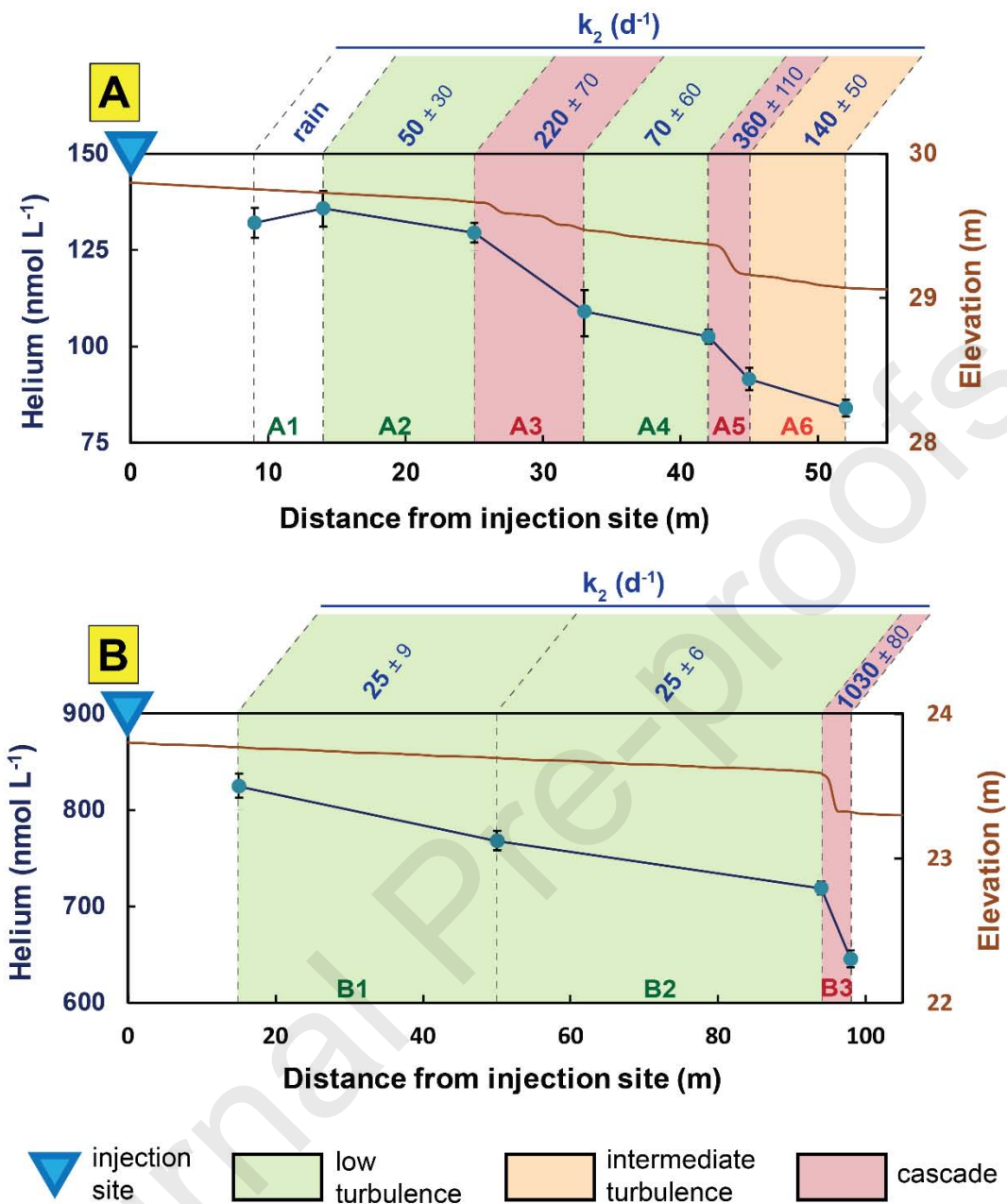


Figure 4. Helium loss along stream A (top) and stream B (bottom) as a function of the distance from the injection site. Helium concentrations were calculated at each location as the average of the plateau highlighted in figure 3. In stream A, it rained at the end of the injection, inducing higher gas exchanges between stream and atmosphere that lowered helium concentrations measured at 9 m from injection site. Error bars in the helium concentration represent $\pm \sigma$. On top of each graph, reaeration rate coefficients are given (k_2). The confidence intervals of the reaeration rate coefficient, determined by a subsampling of each plateau of helium concentration, represent $\pm \sigma$.

432 3.2. Suitability of predictive equations

433 The ten predictive equations given in table 2 were applied to the streams A and B
434 using the hydraulic parameters given in table A.1. At the reach scale, the ten
435 predictive equations systematically underestimate reaeration rate coefficients, by a
436 factor comprised between 1.2 and 2.2 (figure 5). Reaeration rate coefficients were
437 also calculated for each sub-reach using the local hydraulic parameters. The mean
438 and standard deviation of the ten predicted k_2 values (obtained with the ten equations
439 of table 2) are given in table 5. On average, predictive equations strongly
440 underestimate gas exchanges in the cascade sub-reaches, while they are consistent
441 in low-turbulent zones. The spread of the k_2 values given by the different equations,
442 indicated by their standard deviation, is also significantly higher in cascades than in
443 low-turbulent zones. Elevated differences between predicted and measured k_2 values

444 in cascades are due to the fact that physically, predictive equations are non-reliable
 445 in high-turbulent zones (section 2.5). They are based on parameters that are highly
 446 difficult to measure in cascades such as the stream depth. The underestimation of
 447 predicted reaeration rate coefficients in cascades significantly biases the predictions
 448 at the full-reach scale, leading to a systematic underestimation of global gas
 449 exchanges.

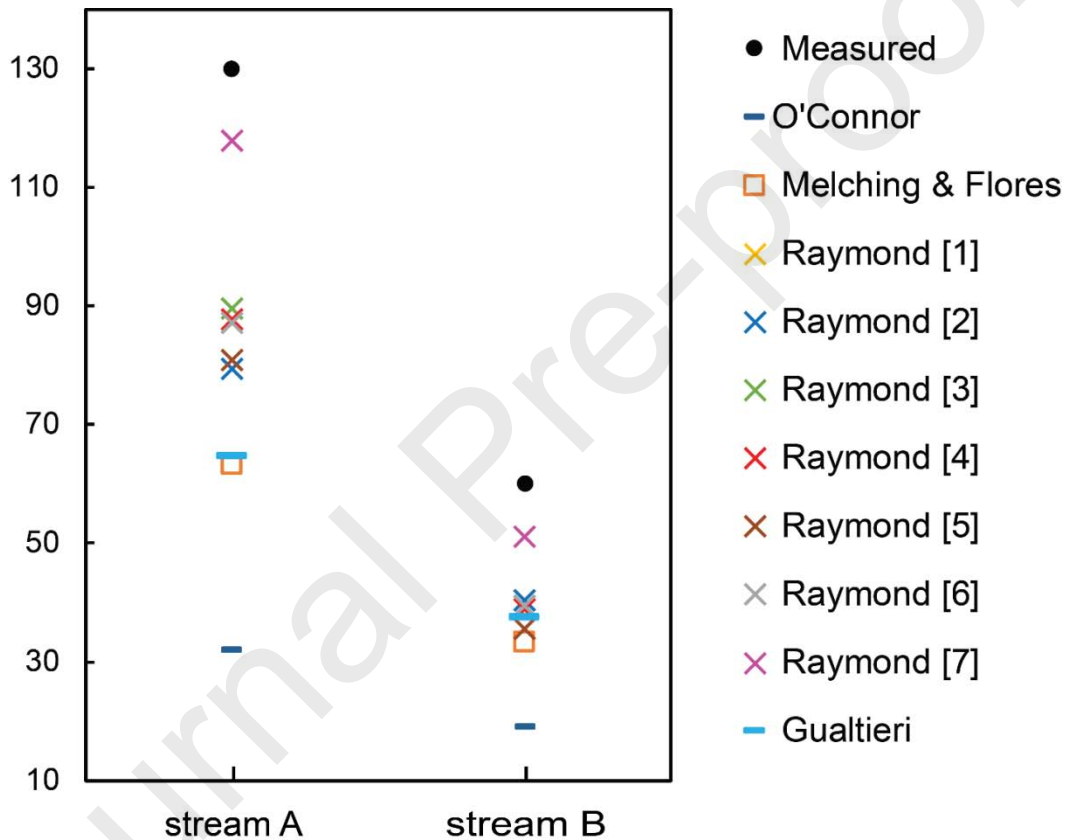


Figure 5. Predictive equations systematically underestimate the reaeration rate coefficient measured at the full-reach scale.

Table 5. Comparison of predicted and measured reaeration rate coefficients in each sub-reach. The mean and standard deviation of the predicted k_2 derive from the statistics of the values obtained with the ten equations of table 2.

| Stream | Sub-reach | Agitation level | Measured k_2 (d ⁻¹) | Mean of the predicted k_2 (d ⁻¹) | Standard deviation of the predicted k_2 (d ⁻¹) |
|-----------|-----------|-----------------|-----------------------------------|--|--|
| A | A2 | calm | 50 | 47 | 8 |
| | A3 | cascade | 220 | 111 | 38 |
| | A4 | calm | 70 | 61 | 13 |
| | A5 | cascade | 360 | 189 | 81 |
| | A6 | intermediate | 140 | 86 | 26 |
| | B | B1 | calm | 25 | 22 |
| B2 | | calm | 25 | 22 | 3 |
| B3 | | cascade | 1030 | 679 | 441 |

450 3.3. Impacts on reactive gases

451 With a mean concentration of around 290 $\mu\text{mol L}^{-1}$, stream A is oversaturated in
 452 CO_2 , in the sense that it contains 10 times more CO_2 than it would at equilibrium
 453 with the atmosphere (figure 6). CO_2 oversaturation is frequent in headwater streams,
 454 because of inputs of groundwater that are highly concentrated in CO_2 due to the
 455 aerobic degradation of organic matter (Cole et al. 2007). Water-rock interaction can
 456 also be a source of CO_2 in streams, especially in karst regions (Chen et al. 2004).
 457 The large excess of CO_2 in stream A originates from a small spring that flows 20
 458 meters upstream from the injection site. The spring water has a CO_2 concentration

459 reaching $650 \mu\text{mol L}^{-1}$, which is 30 times higher than the atmospheric equilibrium.
460 Contrariwise, stream A shows an undersaturation in O_2 (figure 6). Its O_2
461 concentration is comprised between 280 and $300 \mu\text{mol L}^{-1}$, while at equilibrium with
462 the atmosphere it would be $344 \mu\text{mol L}^{-1}$. Undersaturation in O_2 is common in
463 headwater streams because they are mostly net heterotrophs (Knapp et al. 2015;
464 Riley and Dodds 2012; Young and Huryn 1999). In cascades, the state of the stream
465 is rapidly modified by strong exchanges of gas following partial pressure gradients.
466 CO_2 oversaturation induces significant drops in CO_2 in cascades, while O_2
467 undersaturation induces gains in O_2 (figure 6). Release of CO_2 to the atmosphere, as
468 well as stream oxygenation, mainly occurs in the cascades. Note that the rain event
469 that occurred when the pump was at 9 m from the injection site increased gas

470 exchanges, leading to a drop in CO₂ concentration and an increase in O₂
 471 concentration.

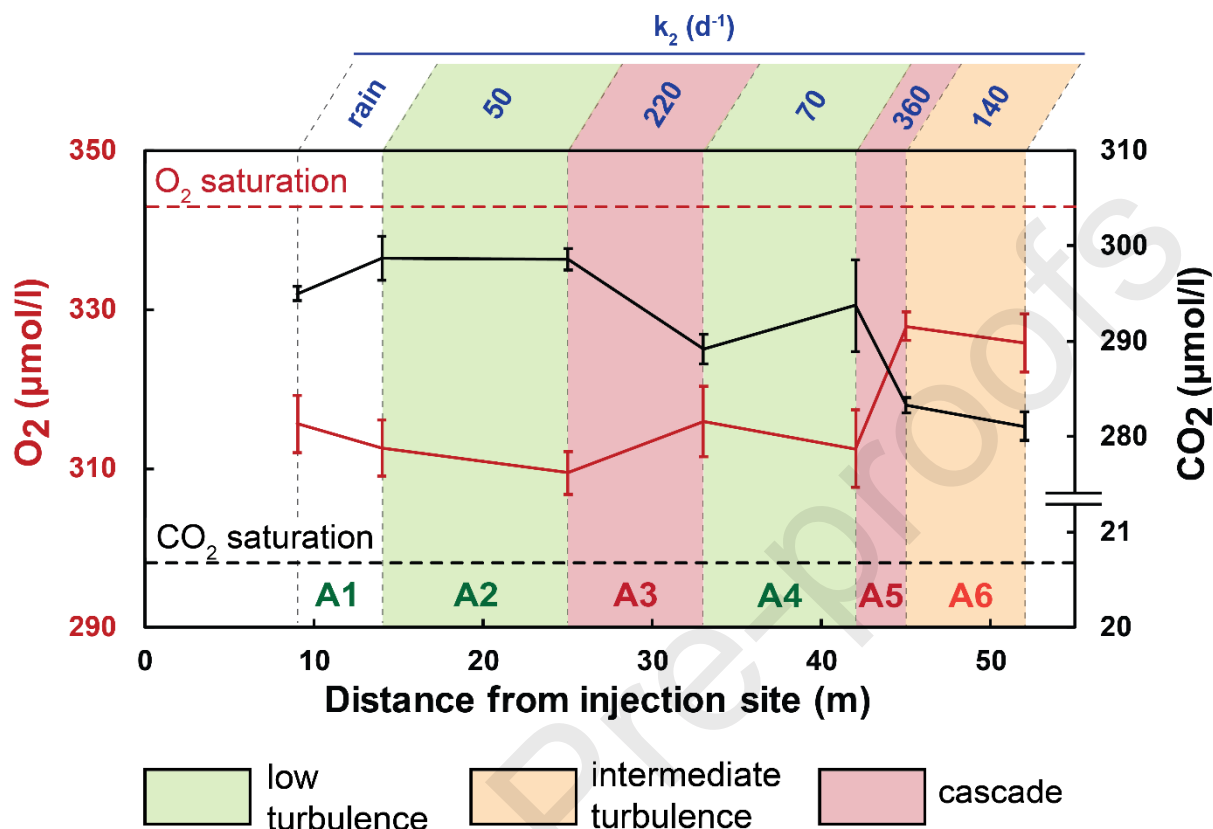


Figure 6. Cascades induce a rapid gain of O₂ (red) and release of CO₂ (black) along stream A. Errors bars represent $\pm \sigma$. Dashed lines indicate O₂ (red) and CO₂ (black) equilibrium with the atmosphere. k_2 values obtained by helium injection are recalled on the top of the graph and area colors indicate the visually-determined level of turbulence.

472 Based on the mean CO₂ concentration of stream A and the gas exchange rate
 473 coefficient measured with helium and converted to CO₂ (equation 4), we estimated
 474 the global CO₂ evasion rate of stream A at 47 $\mu\text{mol m}^{-2} \text{s}^{-1}$ (equation 6). This
 475 corresponds to 48 $\text{gC m}^{-2} \text{d}^{-1}$, which is close to the evasion rate of 56 $\text{gC m}^{-2} \text{d}^{-1}$ that

476 was measured in a Canadian steep headwater stream by direct CO₂ injections
477 (McDowell and Johnson 2018). The CO₂ evasion rate of stream A was also
478 calculated using the gas exchange rate coefficients predicted by the empirical
479 equations of table 2. It yielded systematically lower CO₂ evasion rates, comprised
480 between 16 and 44 gC m⁻² d⁻¹ (table 6). Thus, the underestimation of gas exchange
481 rate coefficients by empirical equations (section 3.2.) leads to a significant
482 underestimation of the CO₂ flux from headwater streams.

483 If CO₂ concentrations in the stream were modified solely by gas exchanges
484 with the atmosphere, the calculated evasion rate of 48 gC m⁻² d⁻¹ would imply a
485 decrease of 50 μmol L⁻¹ in the CO₂ concentration between the upstream and the
486 downstream end of the reach A. This is higher than the measured net loss of CO₂,
487 close to 20 μmol L⁻¹ (Figure 6), showing that other processes, such as oxygenic
488 respiration, partly counterbalance the loss of CO₂ to the atmosphere. It highlights
489 that the CO₂ evasion rates cannot be derived directly from the changes in CO₂
490 concentration along the streams.

Table 6. CO₂ evasion rate in stream A derived from the gas exchange rate coefficients obtained with the equations of table 2. Predictive equations of gas exchange rate coefficients lead to an underestimation of CO₂ evasion rate.

| Gas exchange coefficient based on | CO ₂ evasion rate (gC m ⁻² d ⁻¹) |
|---|--|
| This experiment | 48 |
| O'Connor and Dobbins (1958) | 16 |
| Melching and Flores (1999) | 24 |
| Gualtieri and Gualtieri (2000) Gualtieri et al. (2002) | 23 |
| | [1] 29 |
| | [2] 29 |
| | [3] 33 |
| Raymond et al. (2012) | [4] 33 |
| | [5] 30 |
| | [6] 32 |
| | [7] 44 |

491 **4. DISCUSSION**

492 **4.1. Predictions of gas exchanges**

493 Comparison between measured and predicted k_2 values demonstrates that the
 494 presence of a few cascades along a stream significantly biases global predictions of
 495 gas exchange, leading to a systematic underestimation of reaeration rate coefficients.
 496 This is consistent with the study of Ulseth et al. (2019), showing, at stream scale,

497 that empirical models underestimate gas exchanges in high-channel slope streams.
498 McDowell and Johnson (2018) also highlighted, when studying a headwater stream,
499 that models underestimate gas exchange rate coefficients for high k values.

500 Processes governing gas exchanges in cascades fundamentally differ from those in
501 flowing sections (section 2.5). In cascades, air bubbles have a strong control over
502 gas exchanges (Chanson 1995; Chanson and Toombes 2002; Cirpka et al. 1993).
503 Overlooking specific processes occurring in cascades leads to an underestimation of
504 gas exchanges in headwater catchments, where shallow streams often display natural
505 cascades. Increasing the reliability of predictions would require separate
506 consideration of low-turbulent zones and cascades. For low-turbulent stream
507 sections, our study confirms the predictive capacities of the empirical and semi-
508 empirical equations of table 2. For cascades, predictions are more challenging and
509 require additional morphological characterization or field experiments. Studies
510 focused on spillways in flumes (Baylar et al. 2006; Essery et al. 1978; Gameson
511 1957; Gulliver et al. 1998; Khdhiri et al. 2014; Tebbutt 1972; Toombes and Chanson
512 2005) and on dams (Caplow et al. 2004; Gamlin et al. 2001) or cascades (Cirpka et
513 al. 1993) in rivers, use the aeration efficiency E instead of the gas exchange rate
514 coefficient k . Aeration efficiency was defined by Gameson (1957) and represents
515 the total change in gas concentration occurring in the cascade, normalized by the air-
516 water concentration gradient:

$$E = \frac{C_{down} - C_{up}}{C_{eq} - C_{up}} \quad (7)$$

517 where C_{up} (mol L⁻¹) is the upstream concentration, C_{down} (mol L⁻¹) is the
518 downstream concentration and C_{eq} (mol L⁻¹) is the dissolved gas concentration at
519 equilibrium with the atmosphere. Equations derived from lab experiments predict
520 aeration efficiency as a function of cascade total height and, if applicable, of
521 additional morphological parameters of the cascade such as the height of
522 intermediate steps, or the angle of the weir (Baylar and Bagatur 2006; Baylar et al.
523 2006; Baylar et al. 2011; Essery et al. 1978; Khdhiri et al. 2014). The morphological
524 characteristics of the hydraulic structure seem to be more reliable to predict aeration
525 in cascades than the depth of the water layer. However, if these morphological
526 characteristics are well-defined in flumes, they are much harder to describe properly
527 in natural streams, where cascades are made up of heterogeneous stones and pieces
528 of wood. For more accurate gas exchange quantification, direct measurements
529 remain necessary in cascades.

530 **4.2. Impact of cascades on groundwater discharge estimates**

531 Groundwater discharge in streams is commonly quantified using the natural gas
532 tracer ²²²Rn. Some authors like Gilfedder et al. (2019) and Cartwright et al. (2014)
533 raised the question of the impact of the variability of turbulence on ²²²Rn degassing
534 rate and thus on groundwater discharge estimation. Our study points out that
535 cascades, by generating a fast equilibration between the stream and the atmosphere,
536 erase an important part of the gaseous groundwater signal in the stream (e.g. Rn, He,
537 Ar, CO₂, CH₄, N₂, N₂O). A cascade that is a few tens of centimeters high can lose as
538 much gas as a hundred meter long stream. Since such cascades are very common in

539 low-order streams, this is prone to yield an underestimation of the groundwater
540 discharge calculated by ^{222}Rn mass balances. The location of the cascades should be
541 taken into account when defining the ^{222}Rn sampling strategy and their number and
542 size between the up and down ^{222}Rn sampling locations minimized. Our results
543 suggest that in reaches without notable cascades, one can reasonably calculate the
544 ^{222}Rn degassing rate with empirical equations. In reaches displaying notable
545 cascades, however, direct gas tracer experiments appear to be necessary.

546 **4.3. Hot spots of reaeration**

547 Studies based on flume experiments recommend the use of dams in rivers subject
548 to eutrophication to enhance water reaeration (Tebbutt 1972). Our study shows that
549 natural cascades significantly increase the oxygenation of headwater streams. In this
550 way, they might strongly help sustaining aerobic metabolism, and thus provide a
551 crucial ecosystem service in headwater catchment subject to eutrophication (Dodds
552 and Smith 2016; Garnier and Billen 2007). Considered as reaeration hot spots, small
553 cascades have the potential to enhance measurably the ecological conditions of
554 eutrophic streams and might thus be considered in management and restoration
555 strategies (Palmer et al. 2005).

556 **4.4. Hot spots of CO₂ emission**

557 Most headwater streams are net sources of atmospheric CO₂ (Cole et al. 2007;
558 Marx et al. 2017). Indeed, organic matter respiration occurring in the contributing
559 compartments (aquifer, hyporheic zone, soil) and in the stream network itself is often
560 responsible for an oversaturation in CO₂ (Cole et al. 2007) compared to the

561 equilibrium with the atmosphere. Drops in CO₂ partial pressure in water after
562 cascades and highly turbulent zones have been evidenced in headwater
563 streams (Duvert et al. 2018; Leibowitz et al. 2017; Natchimuthu et al. 2017). In karst
564 systems, these drops have been linked to water softening (Chen et al. 2004). At a
565 much bigger scale, Liu et al. (2017) showed that CO₂ outgassing from low-gradient
566 large rivers was strongly controlled by the geomorphology. Here, by simultaneously
567 mapping the loss of a gas tracer and the changes in CO₂ concentration along a
568 headwater stream, we establish a direct link between streambed morphology, gas
569 exchanges, and CO₂ release to the atmosphere. We show that cascades significantly
570 enhance gas exchanges, leading to a fast CO₂ release to the atmosphere. In a study
571 focused on the temporal variability of gas exchanges, McDowell and Johnson (2018)
572 showed that 84% of CO₂ emissions from a steep headwater stream occurred when
573 discharge was higher than the median. They suggested that high flow events, because
574 they increase turbulence, can be seen as “hot moments” of CO₂ emission in
575 headwater streams (McClain et al. 2003). Here, we highlight the spatial variability
576 of CO₂ emissions and show that similarly, by increasing gas exchanges, cascades
577 can be viewed as “hot spots” of CO₂ emission in headwater streams.

578 If we assume the 19 km-long first order stream network of our 35 km² catchment
579 has the same CO₂ emission rate as the studied stream A, a rough estimate of the total
580 evasion of CO₂ over all first-order streams of the catchment can be calculated. We
581 limit the upscaling to the first-order stream network of a small catchment, in which
582 we assume that on average, cascades have the frequency and the size of those of

583 stream A. Predictive equations from table 2 would lead to a total CO₂ emission
584 comprised between 150 and 300 tC year⁻¹ with the mean of the outputs from the ten
585 equations being 220 tC year⁻¹, while the measured gas exchange rate leads to a CO₂
586 emission of 330 tC year⁻¹. Such a rough, first-order estimation indicates that the
587 prediction of gas exchange rate coefficients at a large-scale with empirical equations
588 is likely to induce a general underestimation of CO₂ emission from headwater
589 catchments. Similarly, empirical equations probably lead to an underestimation of
590 the emission of other greenhouse gases such as CH₄.

591 **5. CONCLUSION**

592 Using continuous helium injection, we mapped gas exchanges along two low-slope
593 headwater streams in a temperate catchment in Brittany (France). Our experimental
594 set-up took advantage of the real-time data visualization allowed by the *in-situ* CF-
595 MIMS. It highlights the new opportunities offered by this technology, in terms of
596 spatial as well as temporal characterization of gas exchange processes. The semi-
597 continuous measurements allow to visualize and to quantify the uncertainties.

598 We evidenced a high spatial variability of gas exchanges, related to the small-scale
599 heterogeneity of the streambed morphology, which is a characteristic feature of
600 headwater streams. During one of our tracer tests, a small cascade was responsible
601 for almost half of the helium loss, while it occupied less than 4% of the total stream
602 length. Nevertheless, the equations predicting the gas exchange rate coefficients in
603 headwater streams do not account for the specific processes governing gas

604 exchanges in natural cascades. As a result, while empirical relationships perform
605 well in low-turbulent zones, they systematically underestimate gas exchange rate
606 coefficients as soon as small cascades are present. This highlights the necessity of
607 performing direct measurements of gas exchange rate coefficients in reaches
608 displaying cascades while low-turbulent zones can be efficiently characterized by
609 empirical equations.

610 Additional CO₂ and O₂ measurements highlighted that small cascades strongly
611 modify the chemical state of headwater streams. High gas exchange rate coefficients
612 allow a fast incorporation of O₂ in the water and a fast release of CO₂ to the
613 atmosphere. Thus, cascades sustain respiration by rebalancing O₂ concentrations in
614 the stream. At the same time, they promote the evasion of the oversaturated CO₂ to
615 the atmosphere. Finally, small natural cascades are hot spots for both stream
616 oxygenation and greenhouse gas emission. Rough calculations of CO₂ emissions
617 showed that the use of empirical equations leads to an underestimation of global CO₂
618 emissions from headwater streams. Since the small-scale morphological
619 heterogeneity is a characteristic feature of headwater streams, the upscaling effort
620 could be helped by a distinct consideration of cascades and low-turbulent sections.
621 The first step would be to separately characterize gas exchange processes in these
622 totally different hydrodynamic regimes. The second step would be to estimate the
623 proportion of these two regimes in the stream network. This could be helped by
624 innovative technologies such as LIDAR, allowing a fine-scale characterization of
625 the topography.

626 **ACKNOWLEDGMENTS**

627 PhD of Camille Vautier is funded by the French Ministry for Higher Education,
628 Research and Innovation. Most of the equipment, especially the CF-MIMS, was
629 funded by the CRITEX project (ANR-11-EQPX-0011). Analysis with μ GC were
630 performed within the CONDATE-EAU analytical platform in Rennes. Field work
631 was performed in the Long-Term Socio-Ecological Research (LTSER) site “Zone
632 Atelier Armorique”. The authors thank Christophe Petton and Virginie Vergnaud for
633 their precious involvement in the field experiments and in the laboratory analysis.
634 We also greatly thank Madeleine Nicolas for the proof-reading of the manuscript.
635 We thank the four reviewers, including Jordan F. Clark, for constructive comments
636 and suggestions.

APPENDIX A: supplementary data

- 637 - Figure A.1: Photograph of the bubbling system
- 638 - Figure A.2: Entire time series of the monitoring of helium
- 639 - Table A.1: Hydraulic and morphologic characteristics of reaches A and B
- 640 - Table A.2: Test of the stability of the plateaus of helium concentration

641 **REFERENCES**

- 642 Aristegi, L., O. Izagirre & A. Elosegi, 2009. Comparison of several methods to
 643 calculate reaeration in streams, and their effects on estimation of metabolism.
 644 *Hydrobiologia* 635(1):113-124 doi:10.1007/s10750-009-9904-8.
- 645 Avery, E., R. Bibby, A. Visser, B. Esser & J. Moran, 2018. Quantification of
 646 Groundwater Discharge in a Subalpine Stream Using Radon-222. *Water* 10(2)
 647 doi:10.3390/w10020100.
- 648 Baird, M. H. I. & J. F. Davidson, 1962. Annular jets—II: Gas absorption. *Chemical*
 649 *Engineering Science* 17(6):473-480 doi:[https://doi.org/10.1016/0009-](https://doi.org/10.1016/0009-2509(62)85016-7)
 650 [2509\(62\)85016-7](https://doi.org/10.1016/0009-2509(62)85016-7).
- 651 Baylar, A. & T. Bagatur, 2006. Experimental studies on air entrainment and oxygen
 652 content downstream of sharp-crested weirs. *Water and Environment Journal*
 653 20(4):210-216 doi:10.1111/j.1747-6593.2005.00002.x.
- 654 Baylar, A., M. E. Emiroglu & T. Bagatur, 2006. An experimental investigation of
 655 aeration performance in stepped spillways. *Water and Environment Journal*
 656 20(1):35-42 doi:10.1111/j.1747-6593.2005.00009.x.
- 657 Baylar, A., M. Unsal & F. Ozkan, 2011. GEP modeling of oxygen transfer efficiency
 658 prediction in aeration cascades. *KSCE Journal of Civil Engineering*
 659 15(5):799-804 doi:10.1007/s12205-011-1282-x.
- 660 Benson, A., M. Zane, T. Becker, A. Visser, S. Uriostegui, E. DeRubeis, J. Moran,
 661 B. Esser & J. Clark, 2014. Quantifying Reaeration Rates in Alpine Streams
 662 Using Deliberate Gas Tracer Experiments. *Water* 6(4):1013-1027
 663 doi:10.3390/w6041013.
- 664 Bernot, M. J., D. J. Sobota, R. O. Hall Jr, P. J. Mulholland, W. K. Dodds, J. R.
 665 Webster, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V.
 666 Gregory, N. B. Grimm, S. K. Hamilton, S. L. Johnson, W. H. McDowell, J. L.
 667 Meyer, B. Peterson, G. C. Poole, H. M. Valett, C. Arango, J. J. Beaulieu, A.
 668 J. Burgin, C. Crenshaw, A. M. Helton, L. Johnson, J. Merriam, B. R.
 669 Niederlehner, J. M. O'brien, J. D. Potter, R. W. Sheibley, S. M. Thomas & K.
 670 Wilson, 2010. Inter-regional comparison of land-use effects on stream
 671 metabolism. *Freshwater Biology* 55(9):1874-1890 doi:doi:10.1111/j.1365-
 672 2427.2010.02422.x.
- 673 Billett, M. F., S. M. Palmer, D. Hope, C. Deacon, R. Storeton-West, K. J.
 674 Hargreaves, C. Flechard & D. Fowler, 2004. Linking land-atmosphere-stream
 675 carbon fluxes in a lowland peatland system. *Global Biogeochemical Cycles*
 676 18(1) doi:10.1029/2003gb002058.
- 677 Bishop, K., I. Buffam, M. Erlandsson, J. Fölster, H. Laudon, J. Seibert & J.
 678 Temnerud, 2008. *Aqua Incognita: the unknown headwaters*. *Hydrological*
 679 *Processes* 22(8):1239-1242 doi:10.1002/hyp.7049.

- 680 Bott, T. L., D. S. Montgomery, J. D. Newbold, D. B. Arscott, C. L. Dow, A. K.
681 Aufdenkampe, J. K. Jackson & L. A. Kaplan, 2006. Ecosystem metabolism in
682 streams of the Catskill Mountains (Delaware and Hudson River watersheds)
683 and Lower Hudson Valley. *J N Am Benthol Soc* 25(4):1018-1044
684 doi:10.1899/0887-3593(2006)025[1018:Emisot]2.0.Co;2.
- 685 Caplow, T., P. Schlosser & T. Ho David, 2004. Tracer Study of Mixing and
686 Transport in the Upper Hudson River with Multiple Dams. *Journal of*
687 *Environmental Engineering* 130(12):1498-1506 doi:10.1061/(ASCE)0733-
688 9372(2004)130:12(1498).
- 689 Carlson, T., 1911. The diffusion of oxygen in water. *Journal of the American*
690 *Chemical Society* 33(7):1027-1032 doi:10.1021/ja02220a002.
- 691 Cartwright, I., H. Hofmann, B. Gilfedder & B. Smyth, 2014. Understanding
692 parafluvial exchange and degassing to better quantify groundwater inflows
693 using ^{222}Rn : The King River, southeast Australia. *Chemical Geology* 380:48-
694 60 doi:10.1016/j.chemgeo.2014.04.009.
- 695 Chanson, H., 1995. Air-water gas transfer at hydraulic jump with partially developed
696 inflow. *Water Research* 29(10):2247-2254 doi:[https://doi.org/10.1016/0043-
697 1354\(95\)00056-Q](https://doi.org/10.1016/0043-1354(95)00056-Q).
- 698 Chanson, H. & L. Toombes, 2002. Air–water flows down stepped chutes: turbulence
699 and flow structure observations. *International Journal of Multiphase Flow*
700 28(11):1737-1761 doi:[https://doi.org/10.1016/S0301-9322\(02\)00089-7](https://doi.org/10.1016/S0301-9322(02)00089-7).
- 701 Chatton, E., T. Labasque, J. de La Bernardie, N. Guiheneuf, O. Bour & L. Aquilina,
702 2017. Field Continuous Measurement of Dissolved Gases with a CF-MIMS:
703 Applications to the Physics and Biogeochemistry of Groundwater Flow.
704 *Environ Sci Technol* 51(2):846-854 doi:10.1021/acs.est.6b03706.
- 705 Chen, J., D. D. Zhang, S. J. Wang & T. F. Xiao, 2004. Water self-softening processes
706 at waterfall sites. *Acta Geol Sin-Engl Ed* 78(5):1154-1161.
- 707 Churchill, M. A., H. L. Elmore & R. A. Buckingham, 1964. The prediction of stream
708 reaeration rates. In Southgate, B. A. (ed) *Advances in Water Pollution*
709 *Research*. Pergamon, 89-136.
- 710 Cirpka, O., P. Reichert, O. Wanner, S. R. Mueller & R. P. Schwarzenbach, 1993.
711 Gas exchange at river cascades: field experiments and model calculations.
712 *Environ Sci Technol* 27(10):2086-2097 doi:10.1021/es00047a014.
- 713 Cole, J. J., Y. T. Prairie, N. F. Caraco, W. H. McDowell, L. J. Tranvik, R. G. Striegl,
714 C. M. Duarte, P. Kortelainen, J. A. Downing, J. J. Middelburg & J. Melack,
715 2007. Plumbing the Global Carbon Cycle: Integrating Inland Waters into the
716 Terrestrial Carbon Budget. *Ecosystems* 10(1):172-185 doi:10.1007/s10021-
717 006-9013-8.
- 718 Cook, P. G., G. Favreau, J. C. Dighton & S. Tickell, 2003. Determining natural
719 groundwater influx to a tropical river using radon, chlorofluorocarbons and
720 ionic environmental tracers. *Journal of Hydrology* 277(1-2):74-88
721 doi:10.1016/s0022-1694(03)00087-8.

- 722 Crawford, J. T., N. R. Lottig, E. H. Stanley, J. F. Walker, P. C. Hanson, J. C. Finlay
723 & R. G. Striegl, 2014. CO₂ and CH₄ emissions from streams in a lake-rich
724 landscape: Patterns, controls, and regional significance. *Global*
725 *Biogeochemical Cycles* 28(3):197-210 doi:10.1002/2013gb004661.
- 726 Dodds, W. & V. Smith, 2016. Nitrogen, phosphorus, and eutrophication in streams.
727 *Inland Waters* 6(2):155-164 doi:10.5268/iw-6.2.909.
- 728 Duvert, C., D. E. Butman, A. Marx, O. Ribolzi & L. B. Hutley, 2018. CO₂ evasion
729 along streams driven by groundwater inputs and geomorphic controls. *Nature*
730 *Geoscience* 11(11):813-818 doi:10.1038/s41561-018-0245-y.
- 731 Essery, I. T. S., T. H. Y. Tebbutt & S. K. Rajaratnam, 1978. Design of Spillways for
732 Reaeration of Polluted Waters. CIRIA Report No 72, Jan London, UK:36.
- 733 Gameson, A. L. H., 1957. Weirs and aeration of rivers. *J Inst Water Eng* 11:477-
734 490.
- 735 Gamlin, J. D., J. F. Clark, G. Woodside & R. Herndon, 2001. Large-Scale Tracing
736 of Ground Water with Sulfur Hexafluoride. *Journal of Environmental*
737 *Engineering* 127(2):171-174 doi:doi:10.1061/(ASCE)0733-
738 9372(2001)127:2(171).
- 739 Garnier, J. & G. Billen, 2007. Production vs. respiration in river systems: an
740 indicator of an "ecological status". *The Science of the total environment*
741 375(1-3):110-24 doi:10.1016/j.scitotenv.2006.12.006.
- 742 Genereux, D. P. & H. F. Hemond, 1990. Naturally Occurring Radon 222 as a Tracer
743 for Streamflow Generation: Steady State Methodology and Field Example.
744 *Water Resources Research* 26(12):3065-3075
745 doi:doi:10.1029/WR026i012p03065.
- 746 Genereux, D. P. & H. F. Hemond, 1992. Determination of gas exchange rate
747 constants for a small stream on Walker Branch Watershed, Tennessee. *Water*
748 *Resources Research* 28(9):2365-2374 doi:doi:10.1029/92WR01083.
- 749 Gilfedder, B. S., I. Cartwright, H. Hofmann & S. Frei, 2019. Explicit Modeling of
750 Radon-222 in HydroGeoSphere During Steady State and Dynamic Transient
751 Storage. *Groundwater* 57(1):36-47 doi:10.1111/gwat.12847.
- 752 Gleeson, T., A. H. Manning, A. Popp, M. Zane & J. F. Clark, 2018. The suitability
753 of using dissolved gases to determine groundwater discharge to high gradient
754 streams. *Journal of Hydrology* 557:561-572
755 doi:10.1016/j.jhydrol.2017.12.022.
- 756 Goncalves, J., A. Silveira, G. B. Lopes, M. S. da Luz & A. L. A. Simoes, 2017.
757 Reaeration Coefficient Estimate: New Parameter for Predictive Equations.
758 *Water Air Soil Pollut* 228(8):10 doi:10.1007/s11270-017-3491-5.
- 759 Gualtieri, C. & P. Gualtieri, 2000. Field verification for a reaeration model in
760 streams. Paper presented at the 4th International Conference On Hydrosience
761 & Engineering, Seoul, Korea.
- 762 Gualtieri, C., P. Gualtieri & G. P. Doria, 2002. Dimensional analysis of reaeration
763 rate in streams. *Journal of Environmental Engineering-Asce* 128(1):12-18
764 doi:10.1061/(asce)0733-9372(2002)128:1(12).

- 765 Gulliver, J., S., S. Wilhelms, C. & K. Parkhill, L., 1998. Predictive Capabilities in
766 Oxygen Transfer at Hydraulic Structures. *Journal of Hydraulic Engineering*
767 124(7):664-671 doi:10.1061/(ASCE)0733-9429(1998)124:7(664).
- 768 Haider, H., W. Ali & S. Haydar, 2013. Evaluation of various relationships of
769 reaeration rate coefficient for modeling dissolved oxygen in a river with
770 extreme flow variations in Pakistan. *Hydrological Processes* 27(26):3949-
771 3963 doi:10.1002/hyp.9528.
- 772 Hall, R. O. & H. L. Madinger, 2018. Use of argon to measure gas exchange in
773 turbulent mountain streams. *Biogeosciences* 15(9):3085-3092
774 doi:10.5194/bg-15-3085-2018.
- 775 Ho, D. T., W. E. Asher, L. F. Bliven, P. Schlosser & E. L. Gordan, 2000. On
776 mechanisms of rain-induced air-water gas exchange. *Journal of Geophysical*
777 *Research: Oceans* 105(C10):24045-24057 doi:10.1029/1999jc000280.
- 778 Hope, D., S. M. Palmer, M. F. Billett & J. J. C. Dawson, 2001. Carbon dioxide and
779 methane evasion from a temperate peatland stream. *Limnology and*
780 *Oceanography* 46(4):847-857 doi:doi:10.4319/lo.2001.46.4.0847.
- 781 Jähne, B., G. Heinz & W. Dietrich, 1987a. Measurement of the diffusion coefficients
782 of sparingly soluble gases in water. *Journal of Geophysical Research*
783 92(C10):10767 doi:10.1029/JC092iC10p10767.
- 784 Jähne, B., K. O. Münnich, R. Börsinger, A. Dutzi, W. Huber & P. Libner, 1987b. On
785 the parameters influencing air-water gas exchange. *Journal of Geophysical*
786 *Research: Oceans* 92(C2):1937-1949 doi:doi:10.1029/JC092iC02p01937.
- 787 Khdhiri, H., O. Potier & J. P. Leclerc, 2014. Aeration efficiency over stepped
788 cascades: better predictions from flow regimes. *Water Res* 55:194-202
789 doi:10.1016/j.watres.2014.02.022.
- 790 Kilpatrick, F. A., R. E. Rathbun, N. Yotsukura, G. W. Parker & L. L. DeLong, 1987.
791 Determination of stream reaeration coefficients by use of tracers Open-File
792 Report.
- 793 Knapp, J. L., K. Osenbruck & O. A. Cirpka, 2015. Impact of non-idealities in gas-
794 tracer tests on the estimation of reaeration, respiration, and photosynthesis
795 rates in streams. *Water Res* 83:205-16 doi:10.1016/j.watres.2015.06.032.
- 796 Knapp, J. L. A., K. Osenbrück, M. S. Brennwald & O. A. Cirpka, 2019. In-situ mass
797 spectrometry improves the estimation of stream reaeration from gas-tracer
798 tests. *Science of The Total Environment* 655:1062-1070
799 doi:<https://doi.org/10.1016/j.scitotenv.2018.11.300>.
- 800 Kolbe, T., J. Marcais, Z. Thomas, B. W. Abbott, J. R. de Dreuzy, P. Rousseau-
801 Gueutin, L. Aquilina, T. Labasque & G. Pinay, 2016. Coupling 3D
802 groundwater modeling with CFC-based age dating to classify local
803 groundwater circulation in an unconfined crystalline aquifer. *Journal of*
804 *Hydrology* 543:31-46 doi:10.1016/j.jhydrol.2016.05.020.
- 805 Lauerwald, R., G. G. Laruelle, J. Hartmann, P. Ciais & P. A. G. Regnier, 2015.
806 Spatial patterns in CO₂ evasion from the global river network. *Global*
807 *Biogeochemical Cycles* 29(5):534-554 doi:10.1002/2014gb004941.

- 808 Leibowitz, Z. W., L. A. F. Brito, P. V. De Lima, E. M. Eskinazi-Sant'Anna & N. O.
809 Barros, 2017. Significant changes in water pCO₂ caused by turbulence from
810 waterfalls. *Limnologia* 62:1-4 doi:10.1016/j.limno.2016.09.008.
- 811 Liu, S., X. X. Lu, X. Xia, X. Yang & L. Ran, 2017. Hydrological and
812 geomorphological control on CO₂ outgassing from low-gradient large rivers:
813 An example of the Yangtze River system. *Journal of Hydrology* 550:26-41
814 doi:10.1016/j.jhydrol.2017.04.044.
- 815 Marx, A., J. Dusek, J. Jankovec, M. Sanda, T. Vogel, R. van Geldern, J. Hartmann
816 & J. A. C. Barth, 2017. A review of CO₂ and associated carbon dynamics in
817 headwater streams: A global perspective. *Rev Geophys* 55(2):560-585
818 doi:10.1002/2016rg000547.
- 819 McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M.
820 Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H.
821 McDowell & G. Pinay, 2003. Biogeochemical Hot Spots and Hot Moments
822 at the Interface of Terrestrial and Aquatic Ecosystems. *Ecosystems* 6(4):301-
823 312 doi:10.1007/s10021-003-0161-9.
- 824 McDowell, M. J. & M. S. Johnson, 2018. Gas Transfer Velocities Evaluated Using
825 Carbon Dioxide as a Tracer Show High Streamflow to Be a Major Driver of
826 Total CO₂ Evasion Flux for a Headwater Stream. *Journal of Geophysical*
827 *Research: Biogeosciences* 123(7):2183-2197 doi:10.1029/2018jg004388.
- 828 Melching, C. S. & H. E. Flores, 1999. Reaeration equations derived from US
829 geological survey database. *Journal of Environmental Engineering-Asce*
830 125(5):407-414 doi:10.1061/(asce)0733-9372(1999)125:5(407).
- 831 Mulholland, P. J., C. S. Fellows, J. L. Tank, N. B. Grimm, J. R. Webster, S. K.
832 Hamilton, E. Martí, L. Ashkenas, W. B. Bowden, W. K. Dodds, W. H.
833 McDowell, M. J. Paul & B. J. Peterson, 2001. Inter-biome comparison of
834 factors controlling stream metabolism. *Freshwater Biology* 46(11):1503-1517
835 doi:doi:10.1046/j.1365-2427.2001.00773.x.
- 836 Natchimuthu, S., M. B. Wallin, L. Klemetsson & D. Bastviken, 2017. Spatio-
837 temporal patterns of stream methane and carbon dioxide emissions in a
838 hemiboreal catchment in Southwest Sweden. *Sci Rep* 7:39729
839 doi:10.1038/srep39729.
- 840 O'Connor, D. J. & W. E. Dobbins, 1958. Mechanism of Reaeration in Natural
841 Streams. *Transactions of the American Society of Civil Engineers*
842 123(1):641-666.
- 843 Öquist, M. G., M. Wallin, J. Seibert, K. Bishop & H. Laudon, 2009. Dissolved
844 Inorganic Carbon Export Across the Soil/Stream Interface and Its Fate in a
845 Boreal Headwater Stream. *Environ Sci Technol* 43(19):7364-7369
846 doi:10.1021/es900416h.
- 847 Palmer, M. A., E. S. Bernhardt, J. D. Allan, P. S. Lake, G. Alexander, S. Brooks, J.
848 Carr, S. Clayton, C. N. Dahm, J. Follstad Shah, D. L. Galat, S. G. Loss, P.
849 Goodwin, D. D. Hart, B. Hassett, R. Jenkinson, G. M. Kondolf, R. Lave, J. L.
850 Meyer, T. K. O'Donnell, L. Pagano & E. Sudduth, 2005. Standards for

- 851 ecologically successful river restoration. *Journal of Applied Ecology*
852 42(2):208-217 doi:10.1111/j.1365-2664.2005.01004.x.
- 853 Palumbo, J. E. & L. C. Brown, 2014. Assessing the Performance of Reaeration
854 Prediction Equations. *Journal of Environmental Engineering* 140(3):7
855 doi:10.1061/(asce)ee.1943-7870.0000799.
- 856 Raymond, P. A., C. J. Zappa, D. Butman, T. L. Bott, J. Potter, P. Mulholland, A. E.
857 Laursen, W. H. McDowell & D. Newbold, 2012. Scaling the gas transfer
858 velocity and hydraulic geometry in streams and small rivers. *Limnology and*
859 *Oceanography: Fluids and Environments* 2(1):41-53 doi:10.1215/21573689-
860 1597669.
- 861 Riley, A. J. & W. K. Dodds, 2012. Whole-stream metabolism: strategies for
862 measuring and modeling diel trends of dissolved oxygen. *Freshwater Science*
863 32(1):56-69, 14.
- 864 Ritz, S., K. Dähnke & H. Fischer, 2017. Open-channel measurement of
865 denitrification in a large lowland river. *Aquatic Sciences* 80(1)
866 doi:10.1007/s00027-017-0560-1.
- 867 Soares, P. A., G. Faht, A. Pinheiro, M. R. da Silva & E. Zucco, 2013. Determination
868 of reaeration-rate coefficient by modified tracer gas technique. *Hydrological*
869 *Processes* 27(19):2710-2720 doi:10.1002/hyp.9371.
- 870 Tebbutt, T. H. Y., 1972. Some studies on reaeration in cascades. *Water Research*
871 6(3):297-304 doi:[https://doi.org/10.1016/0043-1354\(72\)90007-3](https://doi.org/10.1016/0043-1354(72)90007-3).
- 872 Tobias, C. R., J. K. Bohlke, J. W. Harvey & E. Busenberg, 2009. A simple technique
873 for continuous measurement of time-variable gas transfer in surface waters.
874 *Limnol Oceanogr Meth* 7:185-195 doi:10.4319/lom.2009.7.185.
- 875 Toombes, L. & H. Chanson, 2005. Air-Water Mass Transfer on a Stepped
876 Waterway. *Journal of Environmental Engineering* 131(10):1377-1386
877 doi:doi:10.1061/(ASCE)0733-9372(2005)131:10(1377).
- 878 Tranvik, L. J., J. A. Downing, J. B. Cotner, S. A. Loiselle, R. G. Striegl, T. J.
879 Ballatore, P. Dillon, K. Finlay, K. Fortino, L. B. Knoll, P. L. Kortelainen, T.
880 Kutser, S. Larsen, I. Laurion, D. M. Leech, S. L. McCallister, D. M.
881 McKnight, J. M. Melack, E. Overholt, J. A. Porter, Y. Prairie, W. H. Renwick,
882 F. Roland, B. S. Sherman, D. W. Schindler, S. Sobek, A. Tremblay, M. J.
883 Vanni, A. M. Verschoor, E. von Wachenfeldt & G. A. Weyhenmeyer, 2009.
884 Lakes and reservoirs as regulators of carbon cycling and climate. *Limnology*
885 *and Oceanography* 54(6, part 2):2298-2314
886 doi:doi:10.4319/lo.2009.54.6_part_2.2298.
- 887 Tsivoglou, E. C. & L. A. Neal, 1976. Tracer Measurement of Reaeration: III.
888 Predicting the Reaeration Capacity of Inland Streams. *Journal (Water*
889 *Pollution Control Federation)* 48(12):2669-2689.
- 890 Ulseth, A. J., R. O. Hall, M. Boix Canadell, H. L. Madinger, A. Niayifar & T. J.
891 Battin, 2019. Distinct air–water gas exchange regimes in low- and high-
892 energy streams. *Nature Geoscience* 12(4):259-263 doi:10.1038/s41561-019-
893 0324-8.

- 894 Wallin, M. B., M. G. Öquist, I. Buffam, M. F. Billett, J. Nisell & K. H. Bishop, 2011.
895 Spatiotemporal variability of the gas transfer coefficient (KCO₂) in boreal
896 streams: Implications for large scale estimates of CO₂ evasion. *Global*
897 *Biogeochemical Cycles* 25(3) doi:10.1029/2010gb003975.
- 898 Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the
899 ocean. *Journal of Geophysical Research* 97(C5):7373 doi:10.1029/92jc00188.
- 900 Wanninkhof, R., P. J. Mulholland & J. W. Elwood, 1990. Gas exchange rates for a
901 first-order stream determined with deliberate and natural tracers. *Water*
902 *Resources Research* 26(7):1621-1630 doi:doi:10.1029/WR026i007p01621.
- 903 Weber, U. W., P. G. Cook, M. S. Brennwald, R. Kipfer & T. C. Stieglitz, 2019. A
904 Novel Approach To Quantify Air-Water Gas Exchange in Shallow Surface
905 Waters Using High-Resolution Time Series of Dissolved Atmospheric Gases.
906 *Environ Sci Technol* 53(3):1463-1470 doi:10.1021/acs.est.8b05318.
- 907 Wise, D. L. & G. Houghton, 1966. The diffusion coefficients of ten slightly soluble
908 gases in water at 10–60°C. *Chemical Engineering Science* 21(11):999-1010
909 doi:[https://doi.org/10.1016/0009-2509\(66\)85096-0](https://doi.org/10.1016/0009-2509(66)85096-0).
- 910 Young, R. G. & A. D. Huryn, 1998. Comment: Improvements to the diurnal
911 upstream-downstream dissolved oxygen change technique for determining
912 whole-stream metabolism in small streams. *Canadian Journal of Fisheries and*
913 *Aquatic Sciences* 55(7):1784-1785 doi:10.1139/f98-052.
- 914 Young, R. G. & A. D. Huryn, 1999. Effects of land use on stream metabolism and
915 organic matter turnover. *Ecological Applications* 9(4):1359-1376
916 doi:10.1890/1051-0761(1999)009[1359:Eoluos]2.0.Co;2.

917

918 **Camille Vautier:** Conceptualization, Methodology, Investigation, Visualization,
919 Writing - Original Draft. **Ronan Abhervé:** Conceptualization, Methodology,
920 Investigation, Visualization. **Thierry Labasque:** Conceptualization, Methodology,
921 Investigation. **Anniel M. Laverman:** Writing - Review & Editing. **Aurélie Guillou:**
922 Investigation. **Eliot Chatton:** Methodology, Investigation. **Pascal Dupont:**
923 Conceptualization. **Luc Aquilina:** Conceptualization, Writing - Review & Editing.
924 **Jean-Raynald de Dreuzy:** Conceptualization, Writing - Review & Editing,
925 Supervision.

926 **Declaration of interests**

927

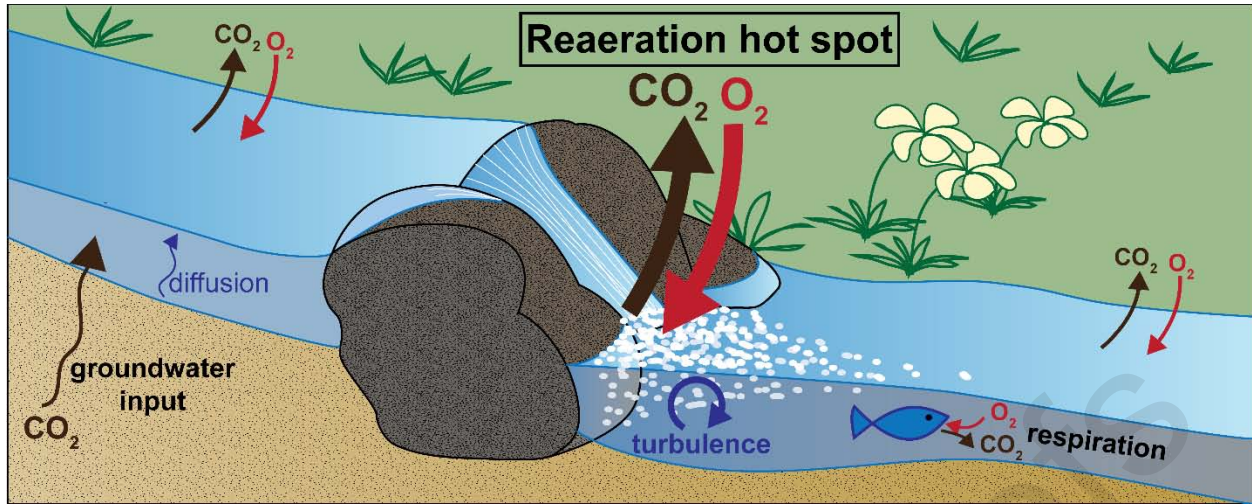
928 The authors declare that they have no known competing financial interests or
929 personal relationships that could have appeared to influence the work reported in
930 this paper.

931

932 The authors declare the following financial interests/personal relationships which
933 may be considered as potential competing interests:

934

935



Journal Pre-proofs