

# Technical Note: Cost-efficient approaches to measure carbon dioxide (CO<sub>2</sub>) fluxes and concentrations in terrestrial and aquatic environments using mini loggers

D. Bastviken<sup>1</sup>, I. Sundgren<sup>1</sup>, S. Natchimuthu<sup>1</sup>, H. Reyier<sup>1</sup>, M. Gålfalk<sup>1</sup>

<sup>1</sup>Department of Thematic Studies – Environmental Change, Linköping University, Linköping, Sweden.

Correspondence to: D. Bastviken (david.bastviken@liu.se)

## Abstract

Fluxes of CO<sub>2</sub> are important for our understanding of the global carbon cycle and greenhouse gas balances. Several significant CO<sub>2</sub> fluxes in nature may still be neglected as illustrated by recent findings of high CO<sub>2</sub> emissions from aquatic environments, previously not recognized in global carbon balances. Therefore it is important to develop convenient and affordable ways to measure CO<sub>2</sub> in many types of environments. At present, direct measurements of CO<sub>2</sub> fluxes from soils or waters, or CO<sub>2</sub> concentrations in surface water, are typically labour intensive or require costly equipment. We here present an approach with measurement units based on small inexpensive CO<sub>2</sub> loggers, originally made for indoor air quality monitoring, that were tested and adapted for field use. Measurements of soil-atmosphere and lake-atmosphere fluxes, as well as of spatio-temporal dynamics of water CO<sub>2</sub> concentrations (expressed as the equivalent partial pressure,  $p\text{CO}_{2\text{aq}}$ ) in lakes and a stream network are provided as examples. Results from all these examples indicate that this approach can provide a cost- and labor efficient alternative for direct measurements and monitoring of CO<sub>2</sub> flux and  $p\text{CO}_{2\text{aq}}$  in terrestrial and aquatic environments.

## 1 Introduction

The carbon dioxide (CO<sub>2</sub>) exchange across soil-atmosphere or water-atmosphere interfaces is of fundamental importance for the global carbon cycle. Soil respiration returns substantial amounts of the carbon fixed by plants to the atmosphere and contributes to the net ecosystem

1 exchange of carbon (Denman et al., 2007). Inland waters, including lakes, reservoirs and  
2 rivers/streams are often showing a net emission of CO<sub>2</sub> from degradation or weathering  
3 processes in surrounding soils, sediments and water columns (Aufdenkampe et al., 2011;  
4 Battin et al., 2009). The inland water emissions has been estimated to 2.1 Pg yr<sup>-1</sup> (Raymond et  
5 al., 2013) which is in the same order of magnitude as the estimated land carbon sink (2.6 Pg  
6 yr<sup>-1</sup>) (Denman et al., 2007).

7 Direct measurements of CO<sub>2</sub> fluxes across the soil-atmosphere and water-atmosphere  
8 surface often rely on flux chamber (FC) measurements, representing a conceptually straight-  
9 forward technique where the system in focus is covered by a chamber and the change in CO<sub>2</sub>  
10 over time in the chamber headspace is used to calculate the flux (Davidson et al., 2002).  
11 Because of potentially rapid equilibration between the chamber headspace and the system  
12 covered by the chamber, it is usually recommended to use short-term deployments with  
13 repeated samplings during each deployment (e.g. sampling every 5<sup>th</sup> minute for 30 minutes).  
14 For replicated and robust measurements it is also desired to perform repeated deployments  
15 over extended periods. At the same time it is necessary to have multiple measurement units to  
16 account for spatial variability. Therefore measurements accounting for both spatial and  
17 temporal variability tend to be laborious if relying on manual sampling or costly in terms of  
18 equipment if automated chamber systems are used.

19 Because direct flux measurements are time consuming, simpler alternatives have been  
20 tried. For aquatic environments the CO<sub>2</sub> flux is often estimated from surface water  
21 concentrations (usually expressed as equivalent partial pressure of CO<sub>2</sub> according to Henry's  
22 Law;  $p\text{CO}_{2\text{aq}}$ ) and the piston velocity ( $k$ ) according to

$$23 \quad F = k \cdot K_{\text{H}} \cdot (p\text{CO}_{2\text{aq}} - p\text{CO}_{2\text{air}}) \quad (1)$$

24 where  $F$  is the flux between the water and the atmosphere (e.g. mol m<sup>-2</sup> d<sup>-1</sup>),  $k$  is the piston  
25 velocity (e.g. m d<sup>-1</sup>; linked to the water turbulence and can be seen as the part of the water  
26 column exchanging gas with the atmosphere per time unit),  $K_{\text{H}}$  is the Henry's Law constant  
27 (e.g. mol m<sup>-3</sup> atm<sup>-1</sup>), and  $p\text{CO}_{2\text{air}}$  is the partial pressure of CO<sub>2</sub> in the air above the water  
28 surface ( $p\text{CO}_{2\text{aq}}$  and  $p\text{CO}_{2\text{air}}$  in units of atm) (Liss and Slater, 1974). Several ways to estimate  
29  $k$  from e.g. wind speed and various ways to measure water turbulence (for water bodies), or  
30 slope (for running waters) have been used (Abril et al., 2009; Cole and Caraco, 1998; Gålfalk  
31 et al., 2013; Raymond et al., 2013; Wallin et al., 2011), but although models may work well in  
32 the systems where they were developed, extrapolations to other systems are uncertain

1 (Schilder et al., 2013).  $p\text{CO}_{2\text{aq}}$  is typically either estimated from pH and alkalinity or  
2 measured directly. The estimation of  $p\text{CO}_{2\text{aq}}$  from pH and alkalinity measurements is most  
3 common because of the large amounts of pH and alkalinity data available from national  
4 monitoring (Raymond et al., 2013) but such indirect  $p\text{CO}_{2\text{aq}}$  estimates becomes unreliable at  
5 low alkalinity, at pH below 6, or at high levels of organic acids (e.g. in humic waters) so  
6 direct measurements are desirable (Abril et al., 2015; Hunt et al., 2011). Therefore direct  
7 measurements of fluxes and  $p\text{CO}_{2\text{aq}}$  are needed to constrain the present estimates of  $\text{CO}_2$   
8 fluxes (Abril et al., 2015). It should also be noted that  $p\text{CO}_{2\text{aq}}$  is not solely used for flux  
9 calculations - it a useful variable in itself for biogeochemical studies of aquatic ecosystems,  
10 e.g. in assessments of ecosystem carbon metabolism.

11 The most common way to directly measure  $p\text{CO}_{2\text{aq}}$  manually is by filling a large bottle  
12 (1-2 L) completely with water, thereafter introducing a small headspace which is equilibrated  
13 with the water by shaking, and then the headspace  $\text{CO}_2$  concentration is measured (Cole et al.,  
14 1994). Considering both indirect and direct approaches, there are presently data from  
15 approximately 7900 water bodies and 6700 running water locations (Raymond et al., 2013).  
16 However, these values typically represent snapshots in time for each system as monitoring of  
17 temporal dynamics is demanding in terms of time or equipment. Daytime measurements  
18 predominate in spite of expectations of higher  $p\text{CO}_{2\text{aq}}$  during night when respiration  
19 dominates over photosynthesis.

20 Due to the importance of  $\text{CO}_2$  fluxes and concentrations, and the need to cover  
21 temporal variability, a number of automated techniques have been developed. Apart from the  
22 eddy covariance technique for large scale net fluxes, commercial automated flux chamber  
23 systems to measure  $\text{CO}_2$  flux from soil environments are available (e.g. [www.li-cor.com](http://www.li-cor.com)). For  
24  $p\text{CO}_{2\text{aq}}$ , an increasing number of commercial systems have recently become available (e.g.  
25 SAMI-CO<sub>2</sub>, <http://sunburstsensors.com>, measures  $\text{CO}_2$  indirectly via pH measurements in a  
26 reagent solution; ProOceanus Mini-Pro  $\text{CO}_2$ , <http://www.pro-oceanus.com>; Contros HydroC-  
27  $\text{CO}_2$ , <http://www.contros.eu>). The costly components in those systems are typically the  
28 instrumentation to measure and log  $\text{CO}_2$  levels. For monitoring  $p\text{CO}_{2\text{aq}}$  recent method  
29 developments showed the possibility to have a near infrared  $\text{CO}_2$  gas sensor (e.g. VAISALA  
30 GMT220) under water by protecting it with a waterproof but gas permeable membrane  
31 (Johnson et al., 2010). This technique is increasingly used and represents important progress,  
32 while still being relatively expensive, accounting for both the  $\text{CO}_2$  sensor and the separate

1 logger unit needed, and power consuming, requiring large and heavy batteries for long-term  
2 remote use.

3 Recently flow-through equilibrators, has become increasingly used for  $p\text{CO}_{2\text{aq}}$   
4 measurements in various designs allowing remote or long term use (e.g. Abril et al., 2015;  
5 Abril et al., 2006; Sutton et al., 2014). Water and air are pumped through the equilibrator  
6 system and in some designs the gas is exchanged across a membrane surface while other  
7 types of equilibrators are based on rapid direct gas exchange to an equilibrator headspace by  
8 e.g. purging (Santos et al., 2012). A related approach is to pump air through gas permeable  
9 tubing in the water (Hari et al., 2008). The air can be sampled by syringe or circulated through  
10 an external infra-red gas analyzer.

11 A high cost of the measuring equipment means that only a few measurement units can  
12 be afforded for simultaneous use, and thereby that information of spatial variability have to be  
13 sacrificed. This is a severe limitation for constraining present estimates of  $\text{CO}_2$  exchange  
14 across land or water surfaces and the atmosphere. Low-cost equipment that can measure this  
15 exchange over time at multiple well-constrained locations would be highly valuable. The aim  
16 of this study was to test if low-cost  $\text{CO}_2$  loggers developed for e.g. monitoring indoor air  
17 quality and regulate ventilation in buildings, can also be used efficiently in environmental  
18 research. These types of sensors typically do not have the same high performance and  
19 sensitivity as the present commercial instruments for  $\text{CO}_2$  measurements in environmental  
20 science (e.g. by companies such as Los Gatos Research, Picarro, LI-COR, PP Systems, and  
21 Quantek Instruments). However, if they are good enough for some environmental  
22 applications, the lower cost, allowing for simultaneous deployment of a large number of  
23 measurement units, would make such loggers highly beneficial.

24 We here present approaches to measure  $\text{CO}_2$  fluxes and concentrations in nature using  
25 small  $\text{CO}_2$  logger that is positioned inside a chamber headspace. The cost of this type of  $\text{CO}_2$   
26 logger system is estimated to be <1-20 % of the alternative systems presently available and  
27 used for environmental studies. Apart from testing logger performance under different  
28 environmental conditions we provide examples of the following types of measurements:

- 29 – Fluxes between soil and atmosphere.
- 30 – Fluxes between lake surface water and the atmosphere.

- 1 – Measurements of surface water concentrations ( $p\text{CO}_{2\text{aq}}$ ) by monitoring  $\text{CO}_2$  in the  
2 headspace of floating chambers in which the headspace  $\text{CO}_2$  concentration was allowed  
3 to be equilibrated with the water. This represents a new type of *in-situ*  $p\text{CO}_{2\text{aq}}$   
4 measurement supplementing the previous approaches having submerged sensors or  
5 equilibrators, and where the issue of biofilm formation around submerged sensors is  
6 avoided. These types of  $p\text{CO}_{2\text{aq}}$  measurements were illustrated by measurements in a  
7 lake and in a stream network.

8 We also provide detailed information on how to prepare loggers and on how to use them  
9 under different conditions in the Supplement.

10

## 11 **2 The Material and methods**

### 12 **2.1 Logger description**

13 We used the ELG  $\text{CO}_2$  logger made by SenseAir ([www.senseair.se](http://www.senseair.se)). It was chosen because of  
14 promising specifications, including:

- 15 –  $\text{CO}_2$  detection by non-dispersive infrared (NDIR) spectroscopy over a guaranteed range  
16 of 0 - 5000 ppm (we discovered an actual linear range of 0 - 10 000 ppm; see below).
- 17 – Simultaneous logging of  $\text{CO}_2$ , temperature, and relative humidity.
- 18 – Operating temperature range of 0 - 50 °C with temperature compensated  $\text{CO}_2$  values.
- 19 – Full function at high humidity – from 0 - 99 % (non-condensing conditions).
- 20 – Includes an internal logger (5400 logging events), and adjustable measurement intervals  
21 from 30 seconds to 0.5 years.
- 22 – Operated with 5.5 - 12 VDC (a small standard 9 V battery worked fine for extended  
23 periods as long as the battery voltage is above 7.5 V) and has low power consumption  
24 (depends on the measurement frequency,  $\sim 250\mu\text{A}$  if 1 measurement/hour,  $\sim 50\mu\text{A}$  in  
25 sleep,  $\sim 60\text{ mA}$  average during active measurement sequence ( $\sim 12\text{s}$ ), see detailed  
26 information at [www.senseair.com](http://www.senseair.com)).
- 27 – Quick and easy calibration by the user (see Supplement).

- 1 – Freely available user-friendly software for sensor control and data management (can be  
2 downloaded at [www.senseair.se](http://www.senseair.se)).
  - 3 – Easily available documentation allowing supplementary modifications of the sensor for  
4 field use.
  - 5 – Possibility to control one peripheral device connected to the logger (e.g. a pump).
- 6 More technical specifications and sensor documentation are available at the manufacturer's  
7 web page ([www.senseair.se](http://www.senseair.se)).

## 8 **2.2 Sensor adaption for field use and initial calibration**

9 The loggers are sold as electrical board modules that are vulnerable to corrosion and do not  
10 have suitable connectors for power supply, data communication, and calibration. Therefore  
11 adaptations for field use had to be made. First, suitable connectors (power cable, data  
12 communication cable, pins for calibration start/stop jumper, and pins for manual start/stop of  
13 logging by jumper) were soldered onto the board. An UART data communication cable was  
14 also made. Thereafter all parts of the board, except the connector pins, the temperature and  
15 RH sensors and the CO<sub>2</sub> sensor membrane surface, were covered with several layers of  
16 varnish for moisture protection. A detailed description on how to make all of this is available  
17 in the Supplement.

18 The loggers were connected to power (individual 9V batteries for each logger) and  
19 calibrated batch-wise in N<sub>2</sub> (representing zero CO<sub>2</sub> gas) by connecting the calibration pins  
20 according to manufacturer instructions (zero calibration). Calibration is made repeatedly as  
21 long as the jumpers are connected with improved results over time. Our typical procedure was  
22 to run the zero calibration for approximately 3 hours. Alternative ways of calibration are also  
23 possible as described in the Supplement, and were used when zero calibration was not  
24 possible (e.g. in the field).

## 25 **2.3 Sensor performance tests**

26 Adequate sensor performance is a prerequisite for successful field use. Therefore we first  
27 performed tests of calibration and linear measurement range (described below), and tests of  
28 the influence of temperature and humidity on the measurements (explained in detail in the  
29 Supplement).

### 1 **2.3.1 Test of calibration and linear measurement range**

2 After calibration, each sensor was tested by being set to log concentrations over time in a gas  
3 tight box connected to a Los Gatos Research greenhouse gas analyzer (LGR; DLT-100) so  
4 that the gas in the box with the batch of CO<sub>2</sub> loggers was continuously circulated through the  
5 LGR instrument. CO<sub>2</sub> levels in the box were changed over time either by injection of standard  
6 gases, or simply by breathing into the box to increase concentrations, or by putting an active  
7 plant in the box to reduce CO<sub>2</sub> concentrations over time (by its photosynthesis). Thereby the  
8 response of the loggers and the LGR to CO<sub>2</sub> levels ranging from 200 to 10 000 ppmv could be  
9 compared.

### 10 **2.4 Field measurements**

11 Three types of field measurements were tried and are presented here as examples of how the  
12 loggers can be used: (1) Flux measurements from soil, (2) flux measurements from water, and  
13 (3) measurements of CO<sub>2</sub> concentration in water ( $p\text{CO}_{2\text{aq}}$ ). The flux measurements were based  
14 on monitoring of concentration changes over time with loggers placed in static flux chambers.  
15 The  $p\text{CO}_{2\text{aq}}$  measurements were also performed by measuring CO<sub>2</sub> concentrations inside a  
16 chamber allowing the chamber headspace to reach equilibrium with the water, thereby making  
17 headspace CO<sub>2</sub> concentrations reflect surface water concentrations according to Henry's Law.

18 For all these measurements the chambers used were made of plastic buckets (7.5 L  
19 volume, 30 cm diameter) covered with reflective alumina tape to minimize internal heating.  
20 This type of chamber has been shown to provide unbiased measurements of water–  
21 atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013). The CO<sub>2</sub> loggers were  
22 attached inside the chamber as shown in the Supplement (Figure S5). The battery was  
23 protected by a gas tight plastic box. For the soil measurements the logger was left uncovered  
24 in the chamber, but for measurements on water, protection against direct water splash as well  
25 as condensation was needed. We tried the simplest possible approach by covering the sensor  
26 with a plastic box having multiple 7 mm diameter holes drilled on one side to allow exchange  
27 of air (see Figure S6). The air was forced to pass a plastic plate in the box before reaching the  
28 logger to make some of the expected condensation occur on the plastic plate instead of on the  
29 sensor itself. This way of protecting the sensor from condensation and splashing water could  
30 potentially delay the response time if the air exchange between the chamber headspace and  
31 the box is restricted, but a test described in the Supplement showed that this was not the case

1 in our type of measurements. The routines used for calibration and measurement validation,  
2 including taking manual samples to check for potential sensor drift over time, are described in  
3 the Supplement.

#### 4 **2.4.1 Soil CO<sub>2</sub> flux measurements**

5 The soil flux measurements represented a simple test of logger suitability. The chambers were  
6 put gently onto non-vegetated hardwood forest soil and the risk for extensive lateral gas  
7 leakage was reduced by packing soil against the outer walls of the chamber. This procedure  
8 does not correspond to common recommendations regarding soils chambers (e.g. having  
9 preinstalled frames going into the soils) but shows if the loggers *per se* are suitable for soil  
10 flux measurements regardless of what type of chamber is used. As traditional flux  
11 measurements in soil chambers can be biased by the gas sampling (which can induce pressure  
12 changes in the chamber disturbing the gas concentration gradients in the soil) (Davidson et al.,  
13 2002), it is also favorable with a logger inside the chambers eliminating the need for gas  
14 sampling during the flux measurement period. The headspace CO<sub>2</sub> concentrations were  
15 logged over time at 2 minute intervals throughout measurement periods of 40 minutes. The  
16 change in headspace CO<sub>2</sub> content over time was calculated by the common gas law  
17 considering chamber volume and area, and represented the measured fluxes. In our tests new  
18 measurement periods were started by simply lifting the chamber for a few minutes to vent the  
19 headspace and then replacing the chamber on the soil.

#### 20 **2.4.2 Aquatic CO<sub>2</sub> flux measurements**

21 For aquatic flux measurements, floating chambers were put on a small boreal forest  
22 lake. In the examples presented here, CO<sub>2</sub> fluxes during morning and evening were measured  
23 over 4 days. The logger unit was started indoors before going to the lake and measurements  
24 were made every 6<sup>th</sup> minute throughout the whole 4-day period. Fluxes were calculated from  
25 the change in CO<sub>2</sub> content over time in the chamber headspace. To start a new measurement  
26 the chamber was lifted, vented for five minutes, and then replaced on the water. This venting  
27 procedure was made morning and evening generating two flux estimates per day valid for the  
28 period right after venting and restarting the measurements. After the 4-day period the  
29 chambers were taken from the lake and data was downloaded from the logger when back in  
30 the laboratory. We also performed additional flux measurements on a pond at the Linköping  
31 University Campus using both data from the CO<sub>2</sub> logger inside a chamber, and from manual

1 samples taken by syringe from the same chamber which were analyzed by gas  
2 chromatography. This comparison was made to verify that the change in headspace CO<sub>2</sub>  
3 content over time measured with loggers corresponded to traditional manual measurements.

#### 4 **2.4.3 Surface water $p\text{CO}_{2\text{aq}}$ measurements**

5 Our  $p\text{CO}_{2\text{aq}}$  measurements are based on the principle that after a floating chamber headspace  
6 has equilibrated with the water, the measured partial pressure of CO<sub>2</sub> in the chamber  
7 headspace will represent this surface water  $p\text{CO}_{2\text{aq}}$ . In this way  $p\text{CO}_{2\text{aq}}$  can be measured in a  
8 chamber headspace without any submerged sensors being in risk of damage from water  
9 intrusions or resulting in bias from biofilms on the submerged sensor surface. On the other  
10 hand the  $p\text{CO}_{2\text{aq}}$  response in a chamber headspace will be delayed due to the equilibration  
11 time which will depend on the piston velocity ( $k$ ) and chamber dimensions. The response time  
12 can potentially be shortened by mixing of the headspace or the surface water under the  
13 chamber by installing fans or by pumping. We evaluated the effect of equilibration time  
14 during a diel measurement cycle with and without fans and pumps (no notable effect  
15 observed) and performed additional modeling accounting for a greater range of  $k$ -values and  
16 testing effects of reducing the chamber volume to area ratio. A comparison between  $p\text{CO}_{2\text{aq}}$   
17 from instantaneous chamber headspace measurements and bottle headspace extractions were  
18 also made. The details of the evaluation and comparison is presented in detail in the  
19 Supplement. Based on the outcome we here focused on exploring the use of the  $p\text{CO}_{2\text{aq}}$   
20 chamber units further without any fans/pumps because we wanted to first try the simplest and  
21 most power-efficient approach. As peripheral devices can conveniently be connected and  
22 controlled by the loggers, addition of fans or pumps is practically easy to explore further in  
23 cases when needed based on specific research questions. In general the tests and examples  
24 provided here represent a start and we expect that future users will develop additional ways to  
25 use the loggers presented.

26 We made environmental  $p\text{CO}_{2\text{aq}}$  measurements in several ways including:

- 27 (a) Test of spatio-temporal variability in a large shallow lake (Tämnaren, Uppsala,  
28 Sweden). Here seven units were deployed for approximately 2 days with a logging  
29 interval of 5 min, near the North and South shores and at the center of the lake,  
30 respectively (Fig. 1).

- 1 (b) Test of a 20 day deployment with a 1 h logging interval at a small shallow boreal lake  
2 (in the Skogaryd Researach Catchment, Vänersborg, Sweden).
- 3 (c) Test of measuring stream  $p\text{CO}_{2\text{aq}}$  at 14 locations in a stream network (Skogaryd,  
4 Vänersborg, Sweden) over a 24 h period with a logging interval of 1 min.

5

### 6 **3 Results and discussion**

#### 7 **3.1 Test of calibration, linear response range, and influence of temperature** 8 **and humidity**

9 The results of the sensors were always well correlated with LGR results (Fig. 2). Above 7000  
10 ppmv the LGR response started to become non-linear but the  $\text{CO}_2$  loggers kept a linear  
11 response up to 10 000 ppmv (confirmed also by additional analyses using gas  
12 chromatography). The combined influence of temperature and humidity was found to be  
13 small, causing an error  $< 7.6\%$  (see Supplement). Logger drift over time was not notable in  
14 the tests and examples provided here, but is expected during long-term use (the manufacturer  
15 estimate a drift of 50 ppmv per year under indoor conditions). It is therefore recommended to  
16 collect occasional manual samples for drift check and correction (see Supplement) and to  
17 recalibrate the loggers frequently.

#### 18 **3.2 Flux measurements**

19 Examples of results from the flux measurements are shown in Fig. 3. Clear and consistent  
20 linear responses of  $\text{CO}_2$  concentrations over time in the chambers, being suitable for  
21 calculation of fluxes, were collected with very limited effort in both terrestrial and aquatic  
22 environments. The work primarily consisted of starting the units, deploying chambers,  
23 flushing the chamber headspace at desired time intervals to restart measurements, and  
24 downloading the data. The calculation of the flux is based on the slope of the  $\text{CO}_2$  change in  
25 the chamber headspace during the deployment. Thus, a flux measurement is based on a  
26 relative  $\text{CO}_2$  change which is not sensitive to moderate drift or to exact absolute values.  
27 Nevertheless, as a part of our general measurement routines, occasional manual measurements  
28 were taken before flushing the chamber for sensor validation and drift correction (no drift  
29 correction was needed for any data presented in this study).

1 The approach to place a CO<sub>2</sub> logger inside each chamber leads to several new  
2 advantages for flux measurements including:

3 (1) It allows chambers to be individual units that can be distributed much more widely than  
4 a system where the chambers are connected by tubing to one single external analyzer.  
5 This is important for capturing spatial variability and not being restricted to a limited  
6 area around a gas analyzer.

7 (2) Substantial time is saved by eliminating the need for manual sampling and subsequent  
8 sample handling and analyses. This allows much more time to be spent on better  
9 coverage of spatial or temporal variability in the fluxes or on accessory measurements.

10 The low cost of each flux chamber unit together with the time saving per unit adds substantial  
11 value even for short term, non-automated flux measurement efforts. The same work effort  
12 normally needed for manual flux measurements (including not only sampling but also sample  
13 preservation and manual sample analyses) with one chamber could now yield flux  
14 measurements from more than 10 chambers with logger units inside.

15 The fluxes obtained for the soils were 2534-2954 mg C m<sup>-2</sup> d<sup>-1</sup> (Fig. 3a), which  
16 corresponds well with the previous range found for soil fluxes in corresponding environments  
17 (Raich and Schlesinger, 1992). The lake fluxes measured were 216-666 and 364-427 mg C m<sup>-2</sup>  
18 d<sup>-1</sup> (Fig. 3b and 3c, respectively), which also is well within the range previously found in  
19 aquatic ecosystems (Selvam et al., 2014; Trolle et al., 2012). The flux data from the logger  
20 inside the chamber were nearly identical with data from manual sampling and gas  
21 chromatography analysis (Fig. 3c). Thus, given their low price and suitable sensitivity, these  
22 chamber-logger units seem highly useful in most types of flux chamber measurements and  
23 have the potential to substantially increase the data generation per work effort.

### 24 **3.3 pCO<sub>2aq</sub> measurements**

25 The pCO<sub>2aq</sub> values in all the examples were in the expected range of 200 to >10 000 found in  
26 various types of waters (Marotta et al., 2009; Raymond et al., 2013; Selvam et al., 2014). The  
27 measurements from chambers with equilibrated headspace revealed large spatial differences  
28 in pCO<sub>2aq</sub> with synchronous temporal variability on the big lake (Fig. 4). Data from a long-  
29 term deployment (20 days) showed a consistent diel pattern with increasing pCO<sub>2aq</sub> during  
30 night and decreasing levels during the day as expected. However, it should be noted that the  
31 diel amplitude of these measurements may be underestimated because of the delay depending  
32 on *k* and the chamber area and volume which together determines how fast the equilibration

1 between the headspace and the water occur (Fig. S11). The response time of the presented  
2 chamber based system may under some conditions be relatively slow but provides integrated  
3 mean values over e.g. a day (see discussion in the Supplement), and avoids potential bias from  
4 biofilms developing on submerged sensors. Reducing the volume to area ratio of the  
5 chamber will make the chamber respond faster (Fig. S13). Another way to speed up the  
6 response time would be to let the logger control a pump that draws air from the logger box  
7 and releases it just below the water surface under the chamber, resulting in surface water  
8 purging favouring rapid equilibration. This adaptation could easily be made but requires a  
9 larger battery for long-term use.

10 The long-term tests showed that our passive approach with a protective box to avoid  
11 condensation in the logger measurement cell worked well for 1-2 weeks. Over time moisture  
12 seemed to accumulate in the sensor protection box and consequently unrealistic high peaks  
13 caused by water condensation inside the measurement cell, often reaching the maximum  
14 value (10 000 ppm; Fig. 5a), were noted more frequently with time. This effect disappeared  
15 once conditions in the chamber favored drying of the sensor and the sensors survived  
16 occasional condensation with maintained performance. The occurrence of condensation  
17 events increased with increasing temperature difference between day and nighttime  
18 temperatures and therefore the condensation events were more common on the sunlit lake  
19 surfaces than on waters in the shadow (e.g. the streams described below). To remove the  
20 condensation data peaks we adopted a simple data filtering routine that removed data points  
21 that were more than 10% higher than the  $\pm 4$  hour median relative to the data point (Fig. 5a).  
22 This filtering procedure to remove data influenced by condensation becomes inefficient if  
23 condensation events are too frequent. We therefore suggest to routinely drying the logger  
24 indoors overnight every 7-14 days (depending on the local conditions) of deployment. Given  
25 the low price, the loggers can simply be replaced with a separate set of dry units to avoid  
26 losing data while the loggers are drying. For longer deployments where weekly or biweekly  
27 visits are not possible, more advanced measures to prevent condensation should be  
28 considered. As the loggers can control one peripheral unit it would be possible to equip the  
29 system with a larger battery and a pump that draws air to the sensor through a desiccant  
30 removing water vapor. Another potential alternative to prevent condensation is to heat the  
31 measurement cell a few degrees above the surrounding air if there is enough power.

1           The logger units were also found highly suitable for logging  $p\text{CO}_{2\text{aq}}$  in streams (Fig.  
2 6). By tethering the units on the streams, equilibrium time is reduced by the turbulence  
3 induced around the chamber edges. (While this is a problem for stream flux measurements, it  
4 is beneficial for  $p\text{CO}_{2\text{aq}}$  measurements with our approach.) Further, the low price of our units  
5 allows the use of a greater number of units compared to other approaches, which is an  
6 advantage for monitoring  $p\text{CO}_{2\text{aq}}$  at multiple points in e.g. a stream network for doing  $\text{CO}_2$   
7 mass balances and for studying the regulation of  $p\text{CO}_{2\text{aq}}$  over large scales. Fig. 6 provides an  
8 example where 14 units were used simultaneously in a stream network and where spatio-  
9 temporal variability over 24 h revealed (1) significant spatial differences between locations in  
10 the catchment, providing indications of different  $\text{CO}_2$  export from soils and also of local hot  
11 spots for  $\text{CO}_2$  emissions, and (2) how a rain event and an associated change in discharge  
12 influenced the temporal dynamics of  $p\text{CO}_{2\text{aq}}$ .

#### 13 **4 Conclusions**

14 We conclude that the approach to measure and log  $\text{CO}_2$  fluxes and  $p\text{CO}_{2\text{aq}}$  presented here can  
15 be an important supplement to previously presented approaches. When focusing on high  
16 temporal resolution of  $p\text{CO}_{2\text{aq}}$  (response time of minutes), the previous approaches with  
17 submersible sensors (e.g. Johnson et al., 2010) or rapid equilibrator systems connected to  $\text{CO}_2$   
18 analyzers (e.g. Abril et al., 2006) are probably preferred. In such cases, the Senseair  $\text{CO}_2$   
19 logger may be suitable for use together with equilibrator systems. The chamber approach  
20 described here provides a cost- and labor-efficient multi-measurement point alternative for (i)  
21 easy flux measurements and (ii)  $p\text{CO}_{2\text{aq}}$  measurements which are not biased by potential  
22 biofilms on submersed equipment, and where delayed response times for  $p\text{CO}_{2\text{aq}}$  are  
23 acceptable (the delay is shorter at higher turbulence/piston velocity and can be estimated from  
24 the data obtained from the initial part of the deployment showing how quickly water-  
25 headspace equilibrium is reached).

26           While well constrained  $\text{CO}_2$  fluxes are critical for the global carbon balance, the previous  
27 estimates are uncertain in terms of spatio-temporal variability and flux regulation. For aquatic  
28 environments  $\text{CO}_2$  fluxes are often based on indirect measurements demonstrated to  
29 frequently be highly biased (Abril et al., 2015). Hence there is a need to rapidly improve the  
30 situation and increase the global availability of high quality data based on direct  $\text{CO}_2$   
31 measurements. We believe the presented measurement approaches with small logger units are

1 affordable, efficient, user friendly, and suitable for widespread use – thereby having potential  
2 to be important tools in future CO<sub>2</sub> studies.

### 3 **Associated content**

4 Supplementary material including a manual on how to build and use the described CO<sub>2</sub> logger  
5 units, details about some of our tests, and advice on the practical use of the loggers are  
6 available.

### 7 **Acknowledgements**

8 We thank Björn Österlund, Lars Nylund, and Brian Scown for valuable assistance regarding  
9 logger functions and adaptations. Leif Klemedtsson and David Allbrand provided valuable  
10 support allowing easy access to the Skogaryd Research Catchment, where some of the field  
11 work was performed, and supplied discharge data. We are also grateful to many colleagues  
12 around the world for their interest and engaged discussions on the approaches presented here.  
13 This work was supported by grants from Linköping University and from the Swedish  
14 Research Council VR to David Bastviken.

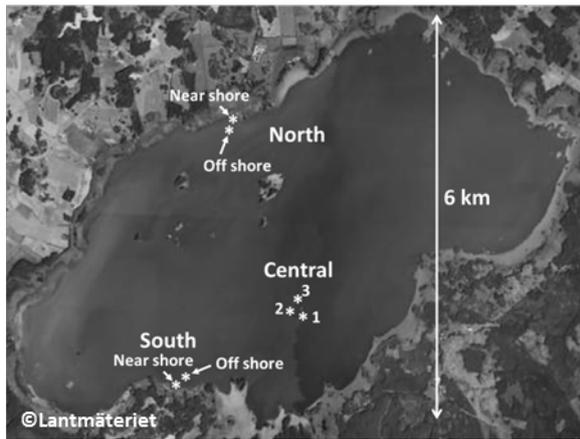
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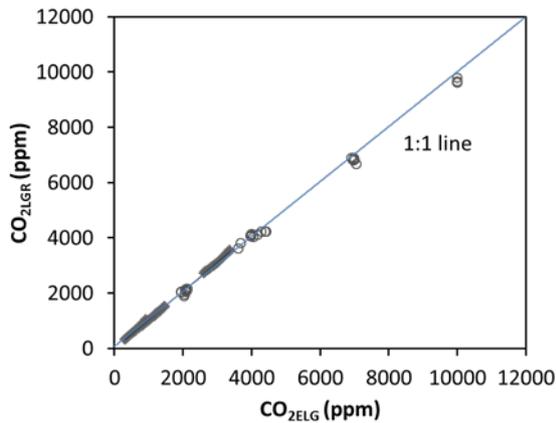
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1  
 2 Figure 1. Map indicating the locations of the chambers on the lake Tännaren. The map is  
 3 published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with  
 4 Linköping University.

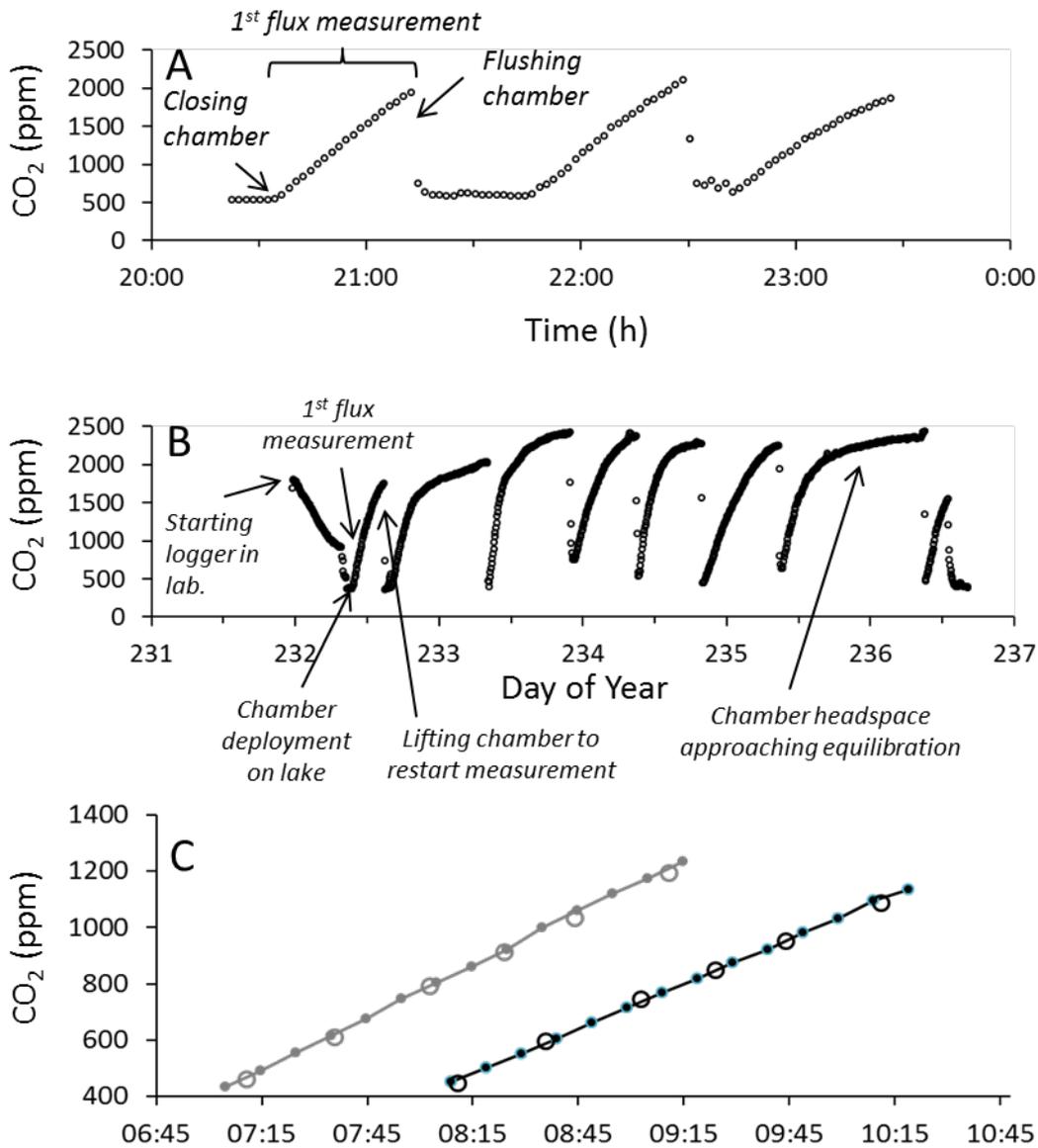
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6  
 7 Figure 2. Comparison of CO<sub>2</sub> mixing ratio (ppm) measured with a Los Gatos Research  
 8 greenhouse gas analyzer (LGR; DLT100) and the CO<sub>2</sub> logger by Senseair (ELG).  
 9 Measurements were made with ELG loggers from two different batches at two separate  
 10 occasions (diamonds forming bold lines and circles, respectively). The ELG have a maximum  
 11 limit at 10 000 ppm in its present configuration. The LGR is affected by saturation/quenching  
 12 effects in the measurement cell starting at 6000 ppm explaining the slight offset compared to  
 13 the 1:1 line.

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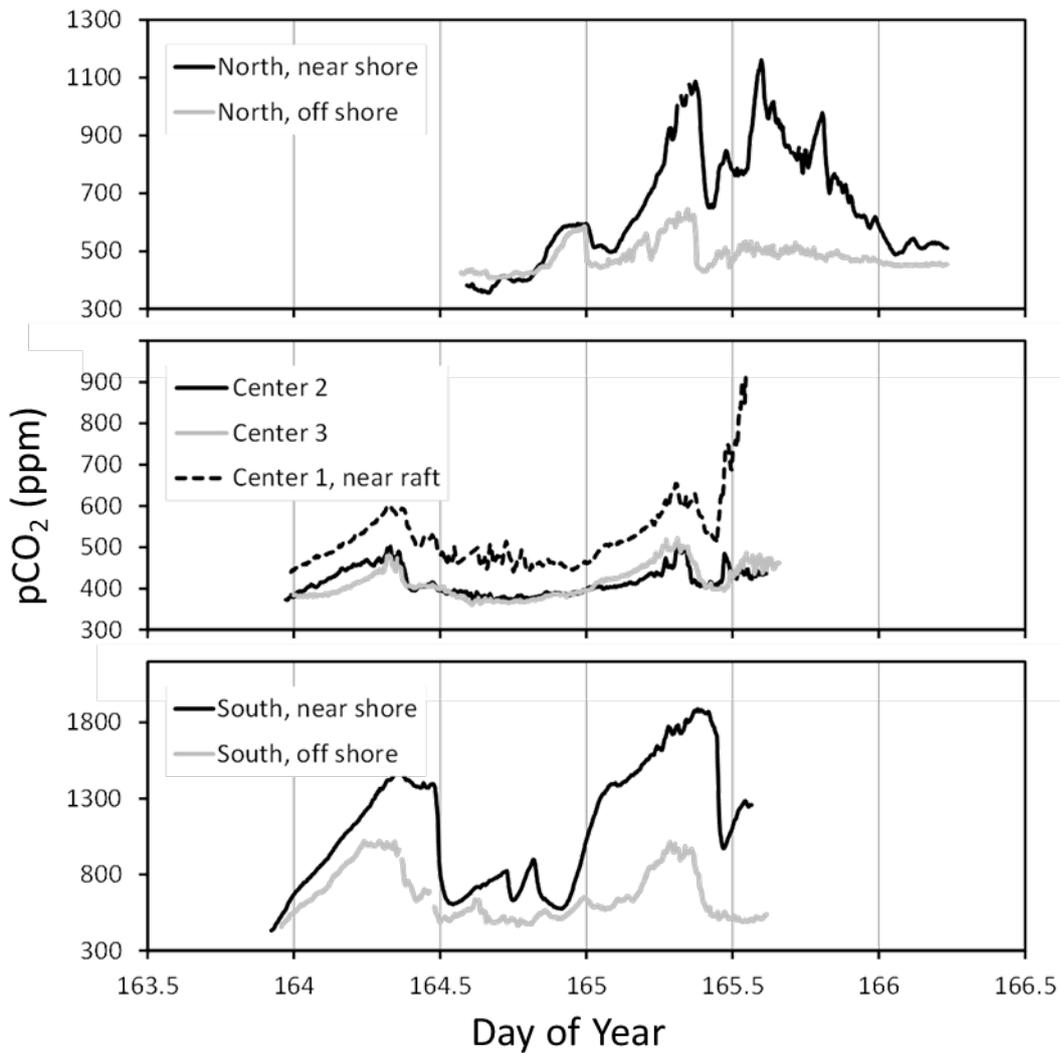
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1  
 2 Figure 3. Examples of CO<sub>2</sub> measurements by loggers inside flux chambers. Panel (a) shows  
 3 changes in CO<sub>2</sub> concentration with time inside a chamber (used to calculate fluxes) due to  
 4 soil CO<sub>2</sub> efflux in three repeated experiments. Panel (b) shows logger raw data from eight  
 5 repeated measurements on a small wind sheltered boreal lake using a floating chamber. The  
 6 different work steps in this example are indicated in the figure. In this example chamber  
 7 deployments were restarted manually at low temporal frequency due to additional parallel  
 8 field work and depending on priorities such measurements can be made at much higher  
 9 frequency. The CO<sub>2</sub> logger can also be used in automatic chambers (Duc et al., 2013). Panel  
 10 (c) shows a comparison between data from CO<sub>2</sub> loggers inside two floating chambers on a  
 11 pond (solid lines with dots) and manual samples taken from the same chambers and analyzed

1 by gas chromatography (circles). Gray and black symbols denote the two different  
2 measurements.

3

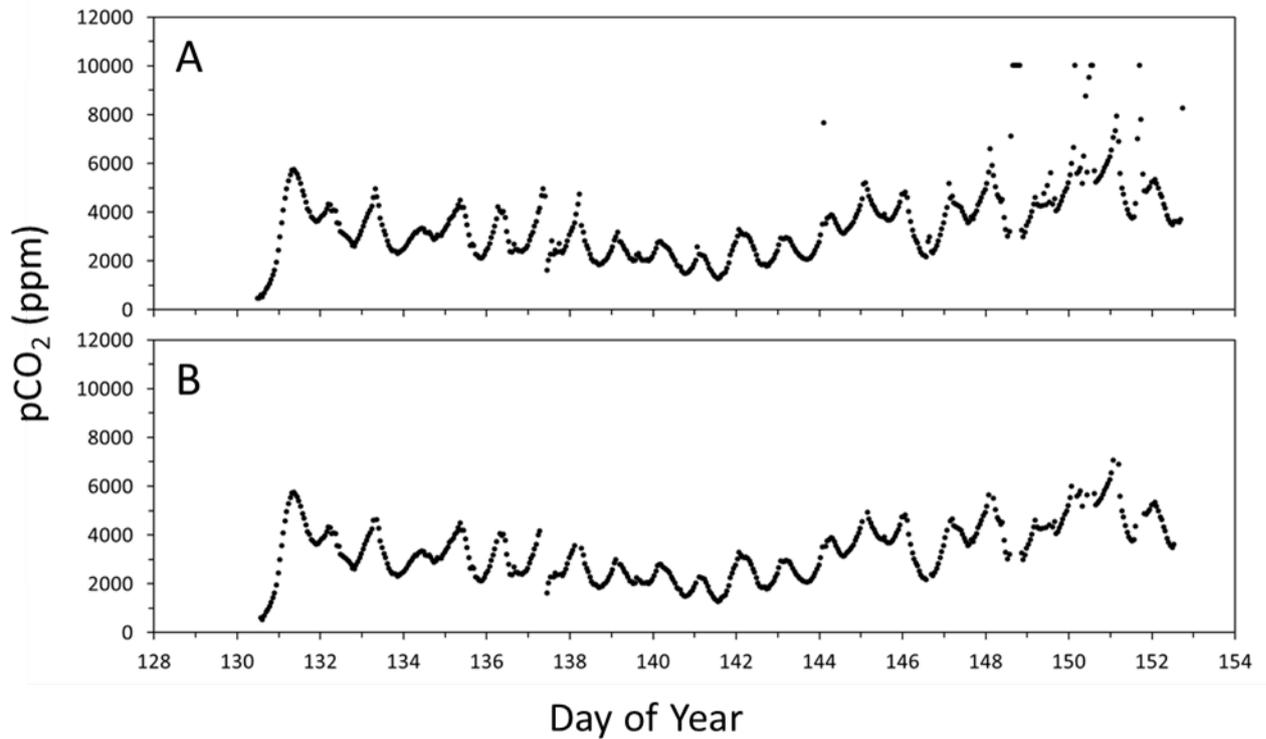


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5 Figure 4. Illustration of spatial variability of  $p\text{CO}_{2\text{aq}}$  (expressed as mixing ratio – ppm) in a  
6 large shallow (mean depth 2 m) lake revealed by seven CO<sub>2</sub> logger-chamber units. The  
7 locations of each chamber are indicated in Figure 1. See text for details. Note different y axis  
8 scales and that this lake was wind exposed with variable wind conditions during the  
9 measurement period.

10

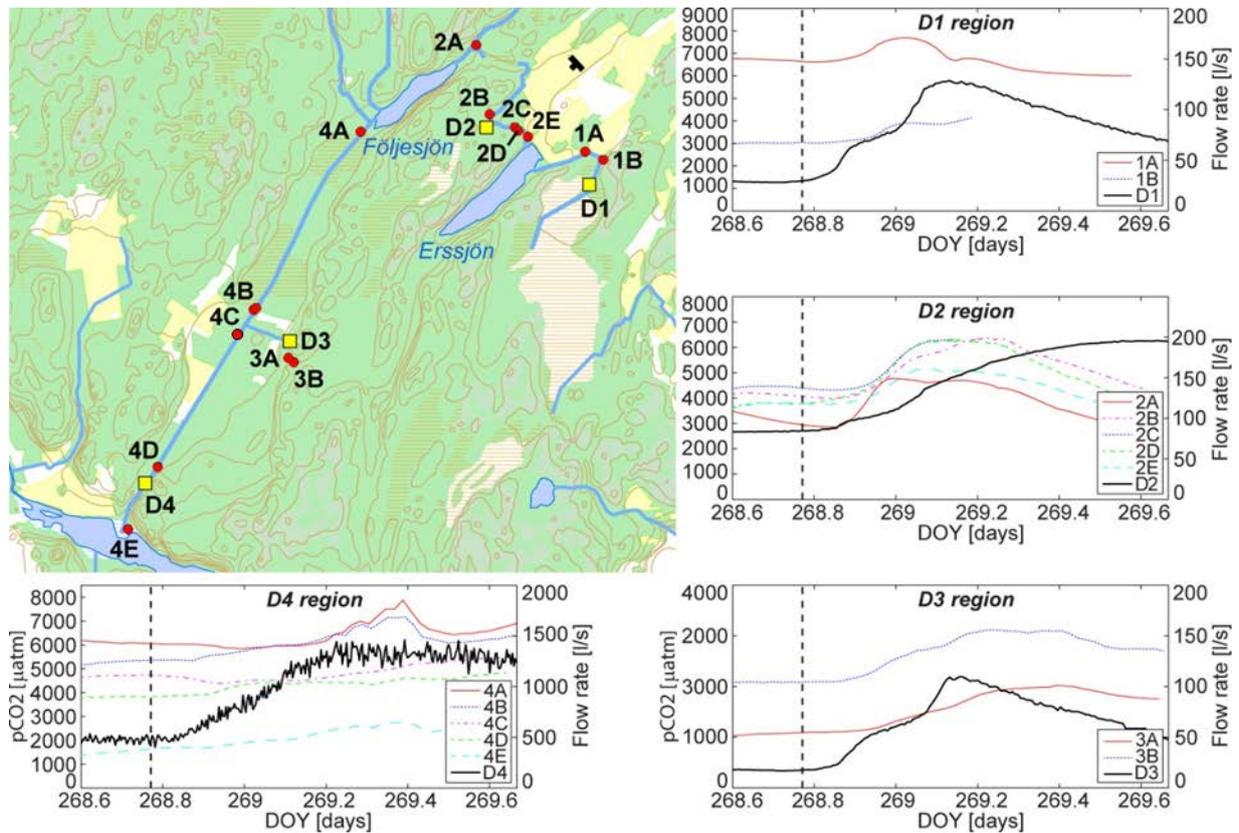
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1

2 Figure 5. Example of long-term monitoring of  $p\text{CO}_{2\text{aq}}$  at 1h intervals in a small shallow boreal  
 3 wetland pond (mean depth 1 m). Panel **A** shows raw data indicating spikes in the data most  
 4 likely due to condensation events (or possibly related with animals temporary visiting the  
 5 chambers; insects, frogs, etc), particularly towards the end of the deployment. Panel **B** shows  
 6 the same data as in **A** after a simple filtering procedure removing data points that were more  
 7 than 10% greater than the -4 to +4 h median of surrounding the data point.

8



1  
 2 Figure 6. Example of 24 h of data from 14 CO<sub>2</sub> logger-chamber units placed on the main  
 3 streams in a catchment stream network to log stream  $p\text{CO}_{2\text{aq}}$ . Yellow squares (D1 – D4)  
 4 denote water discharge stations representing stream regions and the water flows from D1 to  
 5 D4 with the D3 stream being a tributary entering the main stream upstream of D4. The red  
 6 dots represent the CO<sub>2</sub> logger-chamber units. Data (with the initial time of chamber  
 7 equilibration removed) are displayed region-wise in the sub-panels together with the  
 8 measured discharge. A rain event caused an increase in the discharge half way during the  
 9 measurement period which seems related with increased  $p\text{CO}_{2\text{aq}}$  in most locations. DOY  
 10 denotes day or the year. The map is published with permission from Lantmäteriet, Sweden  
 11 according to agreement i2012/898 with Linköping University.

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