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Technical Note: Cost-efficient approaches to measure carbon dioxide (CO₂) fluxes and concentrations in terrestrial and aquatic environments using mini loggers

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Abstract

Fluxes of CO₂ are important for our understanding of the global carbon cycle and greenhouse gas balances. Several significant CO₂ fluxes in nature may still be neglected as illustrated by recent findings of high CO₂ emissions from aquatic environments, previously not recognized in global carbon balances. Therefore it is important to develop convenient and affordable ways to measure CO₂ in many types of environments. At present, direct measurements of CO₂ fluxes from soils or waters, or CO₂ concentrations in surface water, are typically labour intensive or require costly equipment. We here present an approach with measurement units based on small inexpensive CO₂ loggers, originally made for indoor air quality monitoring, that were tested and adapted for field use.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 CO₂ 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 CO₂ flux and $p\text{CO}_{2\text{aq}}$ in terrestrial and aquatic environments.

1 Introduction

The carbon dioxide (CO₂) 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 exchange of carbon (Denman et al., 2007). Inland waters, including lakes, reservoirs and rivers/streams are often showing a net emission of CO₂ from degradation or weathering processes in surrounding soils, sediments and water columns (e.g. Battin et al., 2009; Aufdenkampe et al., 2011). The inland water emissions has been estimated to 2.1 Pg yr⁻¹ (Raymond et al., 2013) which is in the same

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order of magnitude as the estimated land carbon sink (2.6 Pgyr^{-1}) (Denman et al., 2007).

Direct measurements of CO_2 fluxes across the soil–atmosphere and water–atmosphere surface often rely on flux chamber (FC) measurements, representing a conceptually straight-forward technique where the system in focus is covered by a chamber and the change in CO_2 over time in the chamber headspace is used to calculate the flux. Because of potentially rapid equilibration between the chamber headspace and the system covered by the chamber, it is usually recommended to use short-term deployments with repeated samplings during each deployment (e.g. sampling every 6th minute for 30 min). For replicated and robust measurements it is also desired to perform repeated deployments over extended periods. At the same time it is necessary to have multiple measurement units to account for spatial variability. Therefore measurements accounting for both spatial and temporal variability tend to be laborious if relying on manual sampling or costly in terms of equipment if automated chamber systems are used.

Because direct flux measurements are time consuming, simpler alternatives have been tried. For aquatic environments the CO_2 flux is often estimated from surface water concentrations (usually expressed as equivalent partial pressure of CO_2 according to Henry's Law; $p\text{CO}_{2\text{aq}}$) and the piston velocity (k) according to

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

where F is flux (e.g. $\text{mol m}^{-2} \text{d}^{-1}$), k is the piston velocity (e.g. m d^{-1} ; linked to the water turbulence and can be seen as the part of the water column exchanging gas with the atmosphere per time unit), K_{H} is the Henry's Law constant (e.g. $\text{mol m}^{-3} \text{atm}^{-1}$), and $p\text{CO}_{2\text{air}}$ is the partial pressure of CO_2 in the air above the water surface ($p\text{CO}_{2\text{aq}}$ and $p\text{CO}_{2\text{air}}$ in units of atm) (Cole and Caraco, 1998). Several ways to estimate k from e.g. wind speed and various ways to measure water turbulence (for water bodies), or slope (for running waters) have been used (e.g. Cole and Caraco, 1998; Gålfalk et al., 2013; Wallin et al., 2011), but although models may work well in the systems where

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they were developed, extrapolations to other systems are uncertain (Schilder et al., 2013). $p\text{CO}_{2\text{aq}}$ is typically either estimated from pH and alkalinity or measured directly. The estimation of $p\text{CO}_{2\text{aq}}$ from pH and alkalinity measurements is most common because of the large amounts of pH and alkalinity data available from national monitoring (Raymond et al., 2013) but such indirect $p\text{CO}_{2\text{aq}}$ estimates becomes unreliable at low alkalinity, at pH below 6, or at high levels of organic acids (e.g. in humic waters) so direct measurements are desirable (Abril et al., 2015; Hunt et al., 2011). Therefore direct measurements of fluxes and $p\text{CO}_{2\text{aq}}$ are needed to constrain the present estimates of CO_2 fluxes (Abril et al., 2015).

The most common way to directly measure $p\text{CO}_{2\text{aq}}$ manually is by filling a large bottle (1–2 L) completely with water, thereafter introducing a small headspace which is equilibrated with the water by shaking, and then the headspace CO_2 concentration is measured (Cole et al., 1994). Considering both indirect and direct approaches, there are presently data from approximately 7900 water bodies and 6700 running water locations (Raymond et al., 2013). However, these values typically represent snapshots in time for each system as monitoring of temporal dynamics is demanding in terms of time or equipment. Daytime measurements predominate in spite of expectations of higher $p\text{CO}_{2\text{aq}}$ during night when respiration dominates over photosynthesis.

Due to the importance of CO_2 fluxes and concentrations, and the need to cover temporal variability, a number of automated techniques have been developed. Apart from the eddy covariance technique for large scale net fluxes, commercial automated flux chamber systems to measure CO_2 flux from soil environments are available (e.g. www.li-cor.com). For $p\text{CO}_{2\text{aq}}$, an increasing number of commercial systems have recently become available (e.g. SAMI-CO₂; http://sunburstsensors.com). The costly components in those systems are typically the instrumentation to measure and log CO_2 levels. For monitoring $p\text{CO}_{2\text{aq}}$ recent method developments showed the possibility to have a near infrared CO_2 gas sensor (e.g. VAISALA GMT220) under water by protecting it with a waterproof but gas permeable membrane (Johnson et al., 2010). This technique is increasingly used and represents important progress, while still being relatively ex-

pensive, accounting for both the CO₂ sensor and the separate logger unit needed, and power consuming, requiring large and heavy batteries for long-term remote use.

A high cost of the measuring equipment means that only a few measurement units can be afforded for simultaneous use, and thereby that information of spatial variability have to be sacrificed. This is a severe limitation for constraining present estimates of CO₂ exchange across land or water surfaces and the atmosphere. Low-cost equipment that can measure this exchange over time at multiple well-constrained locations would be highly valuable. The aim of this study was to test if low-cost CO₂ loggers developed for e.g. monitoring indoor air quality and regulate ventilation in buildings, can also be used efficiently in environmental research. These types of sensors typically do not have the same high performance and sensitivity as the present commercial instruments for CO₂ measurements in environmental science (e.g. by companies such as Los Gatos Research, Picarro, Li-Cor, and Quantek Instruments). However, if they are good enough for some environmental applications, the lower cost, allowing for simultaneous deployment of a large number of measurement units, would make such loggers highly beneficial.

We here present approaches to measure CO₂ fluxes and concentrations in nature using a small CO₂ logger that is positioned inside a chamber headspace. The cost of this type of CO₂ logger system is estimated to be < 1–20% of the alternative systems presently available and used for environmental studies. Apart from testing logger performance under different environmental conditions we provide examples of the following types of measurements:

- Fluxes between soil and atmosphere.
- Fluxes between lake surface water and the atmosphere.
- Measurements of surface water concentrations ($p\text{CO}_{2\text{aq}}$) by monitoring CO₂ in the headspace of floating chambers in which the headspace CO₂ concentration was allowed to be equilibrated with the water. This represents a new type of in situ $p\text{CO}_{2\text{aq}}$ measurement supplementing the previous approaches having

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submerged sensors and where the issue of biofilm formation around submerged sensors is avoided. These types of $p\text{CO}_{2\text{aq}}$ measurements were made in a lake and in a stream network.

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

2 The material and methods

2.1 Logger description

We used the ELG CO_2 logger made by SenseAir (www.senseair.se). It was chosen because of promising specifications, including:

- CO_2 detection by non-dispersive infrared (NDIR) spectroscopy over a guaranteed range of 0–5000 ppm (we discovered an actual linear range of 0–10 000 ppm; see below).
- Simultaneous logging of CO_2 , temperature, and relative humidity.
- Operating temperature range of 0–50 °C with temperature compensated CO_2 values.
- Full function at high humidity – from 0–99 % (non-condensing conditions).
- Includes an internal logger (5400 logging events), and adjustable measurement intervals from 30 s to 0.5 years.
- Operated with 5.5–12 VDC and has low power consumption (a small standard 9 V battery works fine for extended periods as long as the battery voltage is above 7.5 V).
- Convenient calibration.

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- Freely available user-friendly software for sensor control and data management (can be downloaded at www.senseair.se).
- Easily available documentation allowing supplementary modifications of the sensor for field use.
- Possibility to control one peripheral device connected to the logger (e.g. a pump).

More technical specifications and sensor documentation are available at the manufacturer's web page (www.senseair.se).

2.2 Sensor adaption for field use and initial calibration

The loggers are sold as electrical board modules that are vulnerable to corrosion and do not have suitable connectors for power supply, data communication, and calibration. Therefore adaptations for field use had to be made. First, suitable connectors (power cable, data communication cable, pins for calibration start/stop jumper, and pins for manual start/stop of logging by jumper) were soldered onto the board. An UART data communication cable was also made. Thereafter all parts of the board, except the connector pins, the temperature and RH sensors and the CO₂ sensor membrane surface, were covered with several layers of varnish for moisture protection. A detailed description on how to make all of this is available in the Supplement.

The loggers were connected to power (individual 9 V batteries for each logger) and calibrated batch-wise in N₂ (representing zero CO₂ gas) by connecting the calibration pins according to manufacturer instructions (zero calibration). Calibration is made repeatedly as long as the jumpers are connected with improved results over time. Our typical procedure was to run the zero calibration for approximately 3 h. Alternative ways of calibration are also possible as described in the Supplement, and were used when zero calibration was not possible (e.g. in the field).

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2.3 Sensor performance tests

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

2.3.1 Test of calibration and linear measurement range

After calibration, each sensor was tested by being set to log concentrations over time in a gas tight box connected to a Los Gatos Research greenhouse gas analyzer (LGR; DLT-100) so that the gas in the box with the batch of CO₂ loggers was continuously circulated through the LGR instrument. CO₂ levels in the box were changed over time either by injection of standard gases, or simply by breathing into the box to increase concentrations, or by putting an active plant in the box to reduce CO₂ concentrations over time (by its photosynthesis). Thereby the response of the loggers and the LGR to CO₂ levels ranging from 200 to 10 000 ppmv could be compared.

2.4 Field measurements

Three types of field measurements were tried and are presented here as examples of how the loggers can be used: (1) flux measurements from soil, (2) flux measurements from water, and (3) measurements of CO₂ concentration in water ($p\text{CO}_{2\text{aq}}$). The flux measurements were based on monitoring of concentration changes over time with loggers placed in static flux chambers. The $p\text{CO}_{2\text{aq}}$ measurements were also performed by measuring CO₂ concentrations inside a chamber but in this case the chamber headspace was allowed to reach equilibrium with the water, thereby making headspace CO₂ concentrations reflect surface water concentrations according to Henry's Law.

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area, and represented the measured fluxes. In our tests new measurement periods were started by simply lifting the chamber for a few minutes to vent the headspace and then replacing the chamber on the soil.

2.4.2 Aquatic CO₂ flux measurements

5 For aquatic flux measurements, floating chambers were put on a small boreal forest lake. In the examples presented here, CO₂ fluxes during morning and evening were measured over 4 days. The logger unit was started indoors before going to the lake and measurements were made every 6th minute throughout the whole 4 day period. Fluxes were calculated from the change in CO₂ content over time in the chamber headspace.

10 To start a new measurement the chamber was lifted, vented for five minutes, and then replaced on the water. This venting procedure was made morning and evening generating two flux estimates per day valid for the period right after venting and restarting the measurements. After the 4 day period the chambers were taken from the lake and data was downloaded from the logger when back in the laboratory. We also performed
15 additional flux measurements on a pond at the Linköping University Campus using both data from the CO₂ logger inside a chamber, and from manual samples taken by syringe from the same chamber which were analyzed by gas chromatography. This comparison was made to verify that the change in headspace CO₂ content over time measured with loggers corresponded to traditional manual measurements.

2.4.3 Surface water pCO_{2aq} measurements

20 Our pCO_{2aq} measurements are based on the principle that after a floating chamber headspace has equilibrated with the water, the measured partial pressure of CO₂ in the chamber headspace will represent this surface water pCO_{2aq}. In this way pCO_{2aq} can be measured in a chamber headspace without any submerged sensors being in
25 risk of damage from water intrusions or resulting in bias from biofilms on the submerged sensor surface. On the other hand the pCO_{2aq} response in a chamber headspace will

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be delayed due to the equilibration time which will depend on the piston velocity (k) and chamber dimensions. The response time can potentially be shortened by mixing of the headspace or the surface water under the chamber by installing fans or by pumping. We here focused on exploring the use of the $p\text{CO}_{2\text{aq}}$ chamber units without any fans/pumps because we wanted to first try the simplest and most power-efficient approach. As peripheral devices can conveniently be connected and controlled by the loggers, addition of fans or pumps is practically easy to explore further in cases when needed based on specific research questions. In general the tests and examples provided here represent a start and we expect that future users will develop additional ways to use the loggers presented.

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

1. Test of spatio-temporal variability in a large shallow lake (Tämnaren, Uppsala, Sweden). Here seven units were deployed for approximately 2 days with a logging interval of 5 min, near the North and South shores and at the center of the lake, respectively (Fig. 1).
2. Test of a 20 day deployment with a 1 h logging interval at a small shallow boreal lake (in the Skogaryd Reserach Catchment, Vänersborg, Sweden).
3. Test of measuring stream $p\text{CO}_{2\text{aq}}$ at 14 locations in a stream network (Skogaryd, Vänersborg, Sweden) over a 24 h period with a logging interval of 1 min.

3 Results and discussion

3.1 Test of calibration, linear response range, and influence of temperature and humidity

The results of the sensors were always well correlated with LGR results (Fig. 2). Above 7000 ppmv the LGR response started to become non-linear but the CO_2 loggers kept

a linear response up to 10 000 ppmv (confirmed also by additional analyses using gas chromatography). The combined influence of temperature and humidity was found to be small, causing an error < 7.6% (see Supplement). Based on our tests this error could be compensated for as described in the Supplement. Given the linear response up to 10 000 ppmv and this temperature-humidity correction the logger was found suitable. Logger drift over time was not notable in the tests and examples provided here but is expected during long-term use (the manufacturer estimate a drift of 50 ppmv year⁻¹ under indoor conditions). It is therefore recommended to collect occasional manual samples for drift check and correction (see Supplement).

3.2 Flux measurements

Examples of results from the flux measurements are shown in Fig. 3. Clear and consistent linear responses of CO₂ concentrations over time in the chambers, being suitable for calculation of fluxes, were collected with very limited effort in both terrestrial and aquatic environments. The work primarily consisted of starting the units, deploying chambers, flushing the chamber headspace at desired time intervals to restart measurements, making a few manual measurements before flushing the chamber for sensor validation and drift correction (no drift correction was needed for the data presented in this study), and downloading the data. The same work effort normally needed for manual flux measurements (including not only sampling but also sample preservation and manual sample analyses) with one chamber could now yield flux measurements from more than 10 chambers with logger units inside.

The fluxes obtained for the soils were 2534–2954 mg C m⁻² d⁻¹ (Fig. 3a), which corresponds well with the previous range found for soil fluxes in corresponding environments (Raich and Schlesinger, 1992). The lake fluxes measured were 216–666 and 364–427 mg C m⁻² d⁻¹ (Fig. 3b and c, respectively), which also is well within the expected range (Selvam et al., 2014; Trolle et al., 2012). The flux data from the logger inside the chamber were also identical with data from manual sampling and gas chromatography analysis (Fig. 3c). Thus, given their low price and suitable sensitivity, these

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chamber-logger units seem highly useful in most types of flux chamber measurements and have the potential to substantially increase the data generation per work effort.

3.3 $p\text{CO}_{2\text{aq}}$ measurements

The $p\text{CO}_{2\text{aq}}$ measurements from chambers with equilibrated headspace revealed large spatial differences with synchronous temporal variability on the big lake (Fig. 4). Data from a long-term deployment (20 days) showed a consistent diel pattern with increasing $p\text{CO}_{2\text{aq}}$ during night and decreasing levels during the day as expected. However, it should be noted that the diel amplitude of these measurements is underestimated because of the delay depending on k and the chamber area and volume which together determines how fast the equilibration between the headspace and the water occur. Thus the $p\text{CO}_{2\text{aq}}$ values should be seen as a moving average. The response time of the presented chamber based system may under some conditions be relatively slow but provides integrated mean values over a few hours, and avoids potential bias from biofilms developing on submerged sensors. One way to speed up the response time would be to let the logger control a pump that draws air from the logger box and releases it just below the water surface under the chamber, resulting in surface water purging favouring rapid equilibration. This adaption could easily be made but requires a larger battery for long-term use.

The long-term tests showed that our passive approach with a protective box to avoid condensation in the logger measurement cell worked well for 1–2 weeks. Over time moisture seemed to accumulate in the sensor protection box and consequently unrealistic high peaks caused by water condensation inside the measurement cell, often reaching the maximum value (10 000 ppm; Fig. 5a), were noted more frequently with time. This effect disappeared once conditions in the chamber favored drying of the sensor and the sensors survived occasional condensation with maintained performance. The occurrence of condensation events increased with increasing temperature difference between day and nighttime temperatures and therefore the condensation events were more common on the sunlit lake surfaces than on waters in the shadow (e.g. the

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streams describe below). To remove the condensation data peaks we adopted a simple data filtering routine that removed data points that were more than 10 % higher than the ± 4 h median relative to the data point (Fig. 5b). This filtering procedure to remove condensation events becomes inefficient if condensation events are too frequent. We therefore suggest to routinely dry the logger indoors overnight every 7–14 days (depending on the local conditions) of deployment. Given the low price, the loggers can simply be replaced with a separate set of dry units to avoid losing data while the loggers are being taken indoor for drying. For longer deployments where weekly or biweekly visits are not possible, more advanced measures to prevent condensation should be considered. As the loggers can control one peripheral unit it would be possible to equip the system with a larger battery and a pump that draws air to the sensor through a desiccant removing water vapor. Another potential alternative to prevent condensation is to heat the measurement cell a few degrees above the surrounding air if there is enough power.

The logger units were also found highly suitable for logging $p\text{CO}_{2\text{aq}}$ in streams (Fig. 6). By tethering the units on the streams, equilibrium time is reduced by the turbulence induced around the chamber edges. (While this is a problem for stream flux measurements, it is beneficial for $p\text{CO}_{2\text{aq}}$ measurements with our approach.) Further, the low price of our units allows the use of a greater number of units compared to other approaches, which is an advantage for monitoring $p\text{CO}_{2\text{aq}}$ at multiple points in e.g. a stream network for doing CO_2 mass balances and for studying the regulation of $p\text{CO}_{2\text{aq}}$ over large scales. Figure 6 provides an example where 14 units were used simultaneously in a stream network and where spatio-temporal variability over 24 h revealed (1) significant spatial differences between locations in the catchment, providing indications of different CO_2 export from soils and also of local hot spots for CO_2 emissions, and (2) how a rain event and an associated change in discharge influenced the temporal dynamics of $p\text{CO}_{2\text{aq}}$.

The $p\text{CO}_{2\text{aq}}$ values in all the examples are in the expected range of 200 to $> 10\,000$ found in various types of waters (Marotta et al., 2009; Raymond et al., 2013; Selvam

et al., 2014). The chamber headspace equilibration method used here adheres better than bottle headspace analysis to the ideal conditions of having an infinitely small headspace and an infinitely large water volume. In the bottle there is a limited water volume that can supply CO₂ to the headspace and bottle headspace extraction may therefore underestimate $p\text{CO}_{2\text{aq}}$ compared to an equilibrated chamber.

4 Conclusions

We conclude that the approach to measure and log CO₂ fluxes and $p\text{CO}_{2\text{aq}}$ presented here can be an important supplement to previously presented approaches. When focusing on high temporal resolution of $p\text{CO}_{2\text{aq}}$ (response time of minutes), the previous approaches with submersible sensors (e.g. Johnson et al., 2010) are probably preferred. However, our approach provides a cost- and labor-efficient multi-measurement point alternative for (i) easy flux measurements and (ii) $p\text{CO}_{2\text{aq}}$ measurements which are not biased by potential biofilms on submersed equipment, and where delayed response times for $p\text{CO}_{2\text{aq}}$ are acceptable (the delay is shorter at higher turbulence/piston velocity and can be estimated from the data obtained from the initial part of the deployment showing how quickly headspace-water equilibrium is reached).

While well constrained CO₂ fluxes are critical for the global carbon balance, the previous estimates are uncertain in terms of spatio-temporal variability and flux regulation, and are for aquatic environments often based on indirect measurements recently suggested to frequently be highly biased (Abril et al., 2015). Hence there is a need to rapidly improve the situation and increase the global availability of high quality data based on direct CO₂ measurements. We believe the presented measurement approaches with small logger units are affordable, efficient, user friendly, and suitable for widespread use – thereby having potential to be important tools in future CO₂ studies.

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Associated content

Supplement including a manual on how to build and use the described CO₂ logger units, details about some of our tests, and advice on the practical use of the loggers are available.

5 **The Supplement related to this article is available online at doi:10.5194/bgd-12-2357-2015-supplement.**

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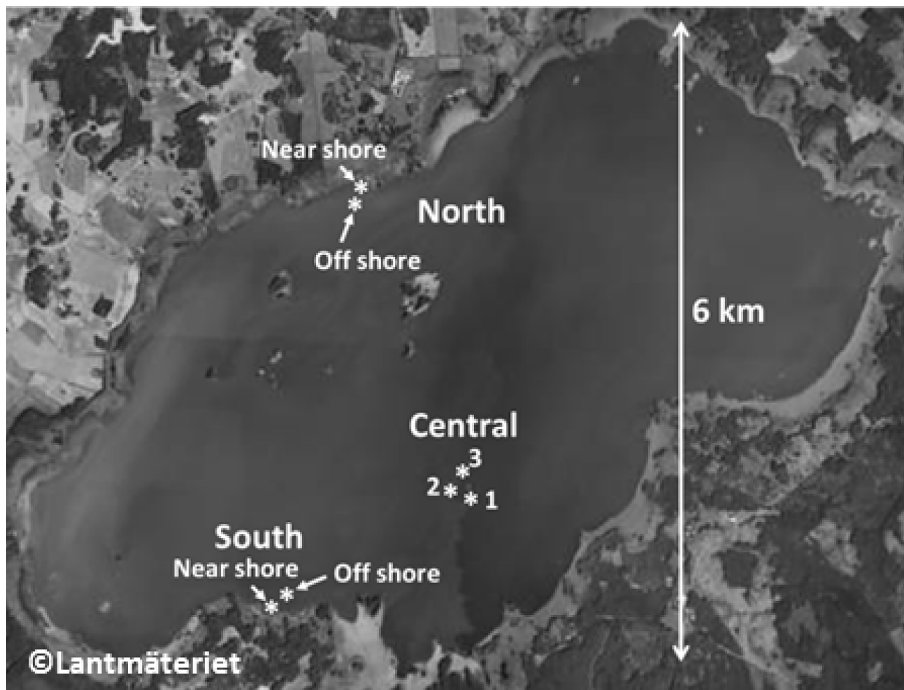


Figure 1. Map indicating the locations of the chambers on the lake Tämnaaren. The map is published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with Linköping University.

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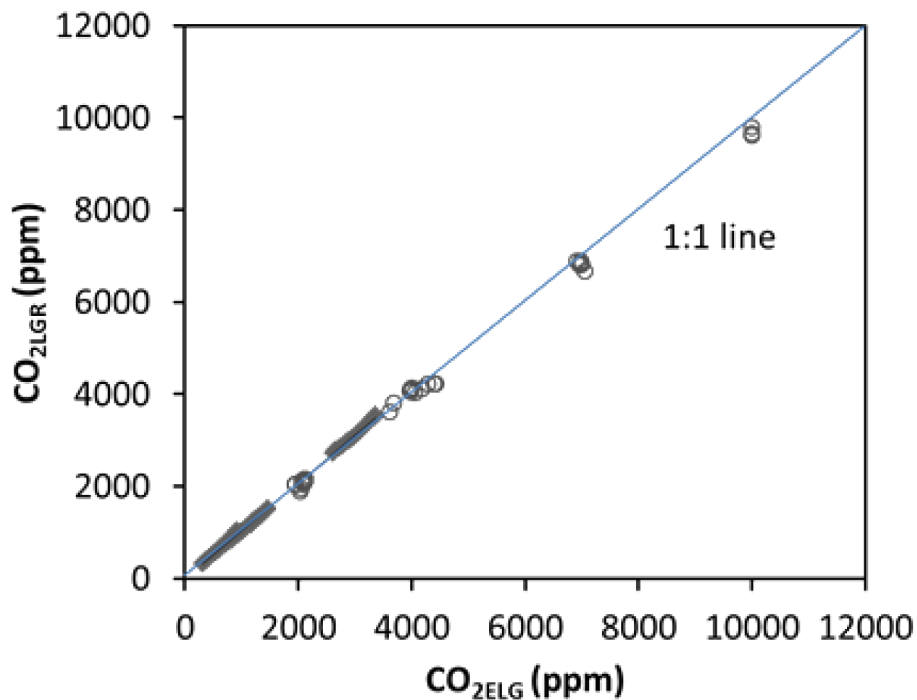


Figure 2. Comparison of CO₂ mixing ratio (ppm) measured with a Los Gatos Research greenhouse gas analyzer (LGR; DLT100) and the CO₂ logger by Senseair (ELG). Measurements were made with ELG loggers from two different batches at two separate occasions (diamonds forming bold lines and circles, respectively). The ELG have a maximum limit at 10 000 ppm in its present configuration. The LGR is affected by saturation/quenching effects in the measurement cell starting at 6000 ppm explaining the slight offset compared to the 1 : 1 line.

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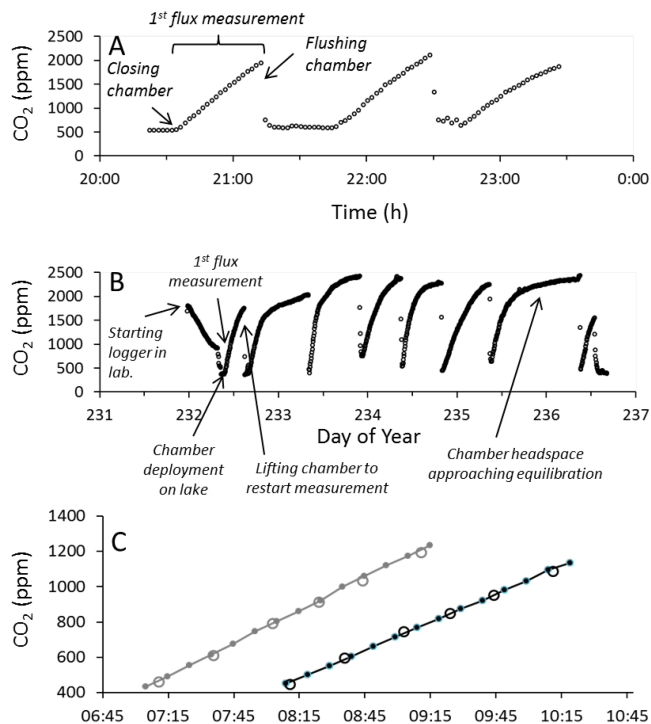


Figure 3. Examples of CO₂ flux measurements by a logger unit inside a flux chamber. Panel (a) shows three repeated soil CO₂ efflux (soil respiration) measurements. Panel (b) shows logger raw data from eight repeated flux measurement on a small wind sheltered boreal lake using a floating chamber. The different work steps in this example are indicated in the figure. In this example chamber deployments were restarted manually but the CO₂ logger can also be used in automatic chambers (Duc et al., 2010). Panel (c) shows a comparison between flux measurements on a pond with CO₂ loggers inside two floating chambers (solid lines with dots) and manual samples taken from the same chambers and analyzed by gas chromatography (circles). Gray and black symbols denote the two different flux measurements.

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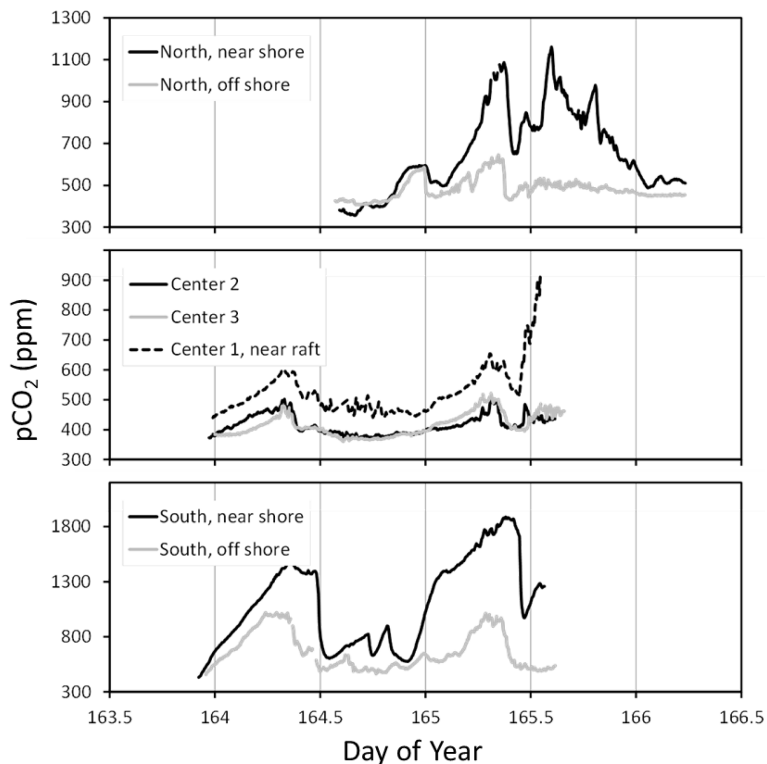


Figure 4. Illustration of spatial variability of $p\text{CO}_{2\text{aq}}$ (expressed as mixing ratio – ppm) in a large shallow (mean depth 2 m) lake revealed by seven CO_2 logger-chamber units. The locations of each chamber are indicated in Fig. 1. See text for details. Note different y axis scales and that this lake was wind exposed with variable wind conditions during the measurement period.

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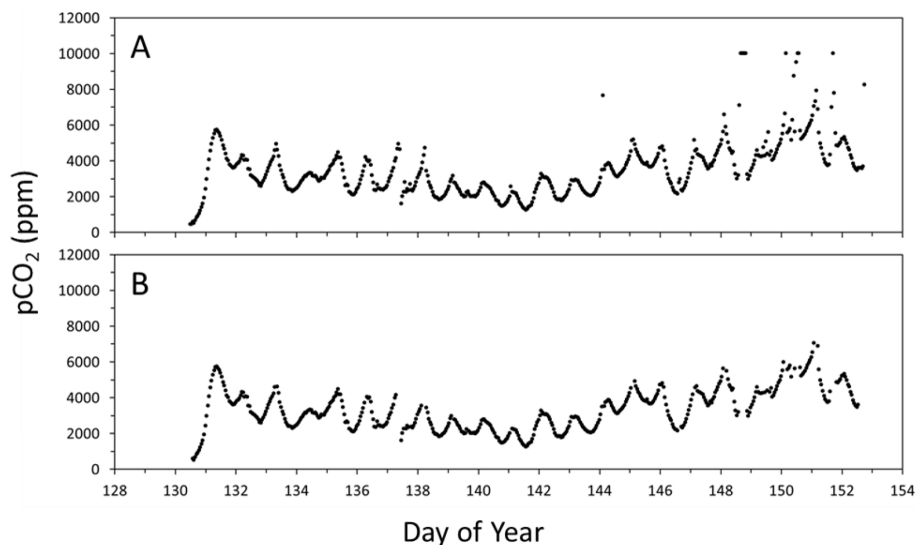


Figure 5. Example of long-term monitoring of $p\text{CO}_{2\text{aq}}$ at 1 h intervals in a small shallow boreal wetland pond (mean depth 1 m). Panel (a) shows raw data indicating spikes in the data most likely due to condensation events (or possibly related with animals temporary visiting the chambers;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

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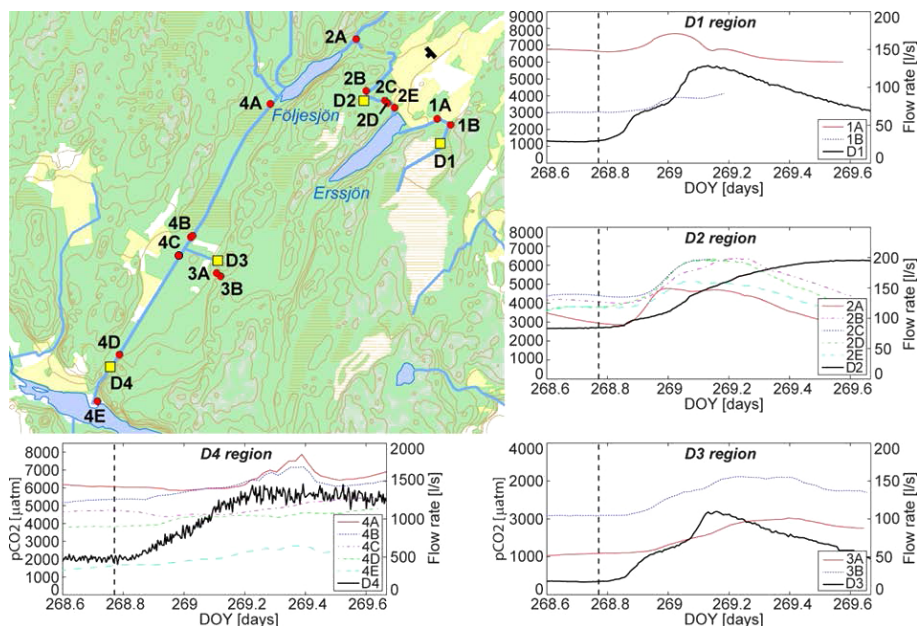


Figure 6. Example of 24 h of data from 14 CO₂ logger-chamber units placed on the main streams in a catchment stream network to log stream $p\text{CO}_{2\text{aq}}$. Yellow squares (D1–D4) denote water discharge stations representing stream regions and the water flows from D1 to D4 with the D3 stream being a tributary entering the main stream upstream of D4. The red dots represent the CO₂ logger-chamber units. Data (with the initial time of chamber equilibration removed) are displayed region-wise in the sub-panels together with the measured discharge. A rain event caused an increase in the discharge half way during the measurement period which seems related with increased $p\text{CO}_{2\text{aq}}$ in most locations. DOY denotes day or the year. The map is published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with Linköping University.

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