Technical Note: Cost-efficient approaches to measure carbon dioxide (CO_2) fluxes and concentrations in terrestrial and aquatic environments using mini loggers

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Abstract

Fluxes of CO_2 are important for our understanding of the global carbon cycle and greenhouse gas balances. Several significant CO_2 fluxes in nature may still be neglected as illustrated by recent findings of high CO_2 emissions from aquatic environments, previously not recognized in global carbon balances. Therefore it is important to develop convenient and affordable ways to measure CO_2 in many types of environments. At present, direct measurements of CO_2 fluxes from soils or waters, or CO_2 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 We here present an approach with measurement units based on small inexpensive CO_2 loggers, originally made for indoor air quality monitoring, that were tested and adapted for field use.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_2 concentrations (expressed as the equivalent partial pressure, pCO_{2aq}) 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_2 flux and pCO_{2aq} in terrestrial and aquatic environments.

1 Introduction

The carbon dioxide (CO_2) 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 CO_2 from degradation or weathering processes in surrounding soils, sediments and water columns (Aufdenkampe et al., 2011; Battin et al., 2009). The inland water emissions has been estimated to 2.1 Pg yr^{-1} (Raymond et al., 2013) which is in the same order of magnitude as the estimated land carbon sink (2.6 Pg yr^{-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 (Davidson et al., 2002). Because of the heating inside soil chambers, and potentially rapid equilibration of the chamber headspace for chambers on water, it is usually recommended to use short-term deployments with repeated samplings during each deployment (e.g. sampling every 5^{th} minute for 30 minutes). 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; pCO_{2aq}) and the piston velocity (k) according to

$$F = k \cdot K_H \cdot (pCO_{2aq} - pCO_{2air}) \quad (1)$$

where F is the flux between the water and the atmosphere (e.g. mol m^{-2} 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. mol m^{-3} atm^{-1}), and pCO_{2air} is the partial pressure of CO_2 in the air above the water surface (pCO_{2aq} and pCO_{2air} in units of atm) (Liss and Slater, 1974). 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 (Abril et al., 2009; Cole and Caraco, 1998; Gålfalk et al., 2013; Raymond et al., 2013; Wallin et al., 2011), but although models may work well in the systems where they were developed, extrapolations to other systems are uncertain (Borges

et al., 2004; Schilder et al., 2013; Wanninkhof, 1992). pCO_{2aq} is typically either estimated from pH and alkalinity or measured directly. The estimation of pCO_{2aq} 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 pCO_{2aq} 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 pCO_{2aq} are needed to constrain the present estimates of CO_2 fluxes (Abril et al., 2015). It should also be noted that pCO_{2aq} is not solely used for flux calculations - it a useful variable in itself for biogeochemical studies of aquatic ecosystems, e.g. in assessments of ecosystem carbon metabolism.

The most common way to directly measure pCO_{2aq} 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 pCO_{2aq} during night when respiration dominates over photosynthesis in many types of systems.

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 pCO_{2aq}, an increasing number of commercial systems have recently become available (e.g. SAMI-CO2, http://sunburstsensors.com, measures CO_2 indirectly via pH measurements in a reagent solution; ProOceanus Mini-Pro CO_2, http://www.pro-oceanus.com; Contros HydroC-CO_2, http://www.contros.eu). The costly components in those systems are typically the instrumentation to measure and log CO_2 levels. For monitoring pCO_{2aq} 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 expensive, accounting for both the CO_2 sensor and the separate

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

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

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 CO_2 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 CO_2 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 CO_2 measurements in environmental science (e.g. by companies such as Los Gatos Research, Picarro, LI-COR, PP Systems, 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 CO_2 fluxes and concentrations in nature using small CO_2 logger that is positioned inside a chamber headspace. The cost of this type of CO_2 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 (pCO_{2aq}) by monitoring CO_2 in the headspace of floating chambers in which the headspace CO_2 concentration was allowed to be equilibrated with the water. This represents a new type of *in-situ* pCO_{2aq} measurement supplementing the previous approaches having submerged sensors or equilibrators, and where the issue of biofilm formation around submerged sensors is avoided. These types of pCO_{2aq} measurements were illustrated by measurements 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 seconds to 0.5 years.
- Operated with 5.5 - 12 VDC (a small standard 9 V battery worked fine for extended periods as long as the battery voltage is above 7.5 V) and has low power consumption (depends on the measurement frequency, ~250µA if 1 measurement/hour, ~50µA in sleep, ~60 mA average during active measurement sequence (~12s), see detailed information at www.senseair.com).
- Quick and easy calibration by the user (see Supplement).

- 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 adaptions 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 CO_2 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 9V batteries for each logger) and calibrated batch-wise in N_2 (representing zero CO_2 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 hours. 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).

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 CO_2 loggers was continuously circulated through the LGR instrument. CO_2 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 CO_2 concentrations over time (by its photosynthesis). Thereby the response of the loggers and the LGR to CO_2 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 CO_2 concentration in water (pCO_{2aq}). The flux measurements were based on monitoring of concentration changes over time with loggers placed in static flux chambers. The pCO_{2aq} measurements were also performed by measuring CO_2 concentrations inside a chamber allowing the chamber headspace to reach equilibrium with the water, thereby making headspace CO_2 concentrations reflect surface water concentrations according to Henry's Law.

For all these measurements the chambers used were made of plastic buckets (7.5 L volume, 30 cm diameter) covered with reflective alumina tape to minimize internal heating. This type of chamber has been shown to provide unbiased measurements of water–atmosphere gas exchange (Cole et al., 2010; Gålfalk et al., 2013). The CO_2 loggers were attached inside the chamber as shown in the Supplement (Figure S5). The battery was protected by a gas tight plastic box. For the soil measurements the logger was left uncovered in the chamber, but for measurements on water, protection against direct water splash as well as condensation was needed. We tried the simplest possible approach by covering the sensor with a plastic box having multiple 7 mm diameter holes drilled on one side to allow exchange of air (see Figure S6). The air was forced to pass a plastic plate in the box before reaching the logger to make some of the expected condensation occur on the plastic plate instead of on the sensor itself. This way of protecting the sensor from condensation and splashing water could potentially delay the response time if the air exchange between the chamber headspace and the box is restricted, but a test described in the Supplement showed that this was not the case

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

2.4.1 Soil CO_2 flux measurements

The soil flux measurements represented a simple test of logger suitability. The chambers were put gently onto non-vegetated hardwood forest soil and the risk for extensive lateral gas leakage was reduced by packing soil against the outer walls of the chamber. This procedure does not correspond to common recommendations regarding soils chambers (e.g. having preinstalled frames going into the soils) but shows if the loggers *per se* are suitable for soil flux measurements regardless of what type of chamber is used. As traditional flux measurements in soil chambers can be biased by the gas sampling (which can induce pressure changes in the chamber disturbing the gas concentration gradients in the soil) (Davidson et al., 2002), it is also favorable with a logger inside the chambers eliminating the need for gas sampling during the flux measurement period. The headspace CO_2 concentrations were logged over time at 2 minute intervals throughout measurement periods of 40 minutes. The change in headspace CO_2 content over time was calculated by the common gas law considering chamber volume and 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 CO_2 flux measurements

For aquatic flux measurements, floating chambers were put on a small boreal forest lake. In the examples presented here, CO_2 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 6^{th} minute throughout the whole 4-day period. Fluxes were calculated from the change in CO_2 content over time in the chamber headspace. 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 additional flux measurements on a pond at the Linköping University Campus using both data from the CO_2 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 CO_2 content over time measured with loggers corresponded to traditional manual measurements.

2.4.3 Surface water pCO_{2aq} measurements

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 CO_2 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 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 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 evaluated the effect of equilibration time during a diel measurement cycle with and without fans and pumps (no notable effect observed) and performed additional modeling accounting for a greater range of k-values and testing effects of reducing the chamber volume to area ratio. A comparison between pCO_{2aq} from instantaneous chamber headspace measurements and bottle headspace extractions were also made. The details of the evaluation and comparison is presented in detail in the Results and Discussion below and in the Supplement. Based on the outcome we here focused on exploring the use of the pCO_{2aq} chamber units further 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 pCO_{2aq} measurements in several ways including:

(a) 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).

(b) Test of a 20 day deployment with a 1 h logging interval at a small shallow boreal lake (in the Skogaryd Researach Catchment, Vänersborg, Sweden).

(c) Test of measuring stream pCO_{2aq} 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). 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 per year under indoor conditions). It is therefore recommended to collect occasional manual samples for drift check and correction (see Supplement) and to recalibrate the loggers frequently.

3.2 Flux measurements

Examples of results from the flux measurements are shown in Fig. 3. Clear and consistent linear responses of CO_2 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, and downloading the data. The calculation of the flux is based on the slope of the CO_2 change in the chamber headspace during the deployment. Thus, a flux measurement is based on a relative CO_2 change which is not sensitive to moderate drift or to exact absolute values. Nevertheless, as a part of our general measurement routines, occasional manual measurements were taken before flushing the chamber for sensor validation and drift correction (no drift correction was needed for any data presented in this study).

The approach to place a CO_2 logger inside each chamber leads to several new advantages for flux measurements including:

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

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

The low cost of each flux chamber unit together with the time saving per unit adds substantial value even for short term, non-automated flux measurement efforts. 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 3c, respectively), which also is well within the range previously found in aquatic ecosystems (Selvam et al., 2014; Trolle et al., 2012). The flux data from the logger inside the chamber were nearly identical with data from manual sampling and gas chromatography analysis (Fig. 3c). Thus, given their low price and suitable sensitivity, these 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 pCO_{2aq} measurements

The pCO_{2aq} values in all the examples were in the expected range of 200 to >10 000 found in various types of waters (Abril et al., 2014; Marotta et al., 2009; Raymond et al., 2013; Selvam et al., 2014). The most common traditional methods to measure pCO_{2aq} are the alkalinity-pH method and the bottle headspace equilibration technique (the latter from here on called the bottle method). The superiority of the bottle method compared to the alkalinity-pH method has already been thoroughly addressed (Abril et al., 2015). Therefore we here focus on comparing the bottle and the pCO_{2aq} chamber (i.e. chamber equilibrator) approaches.

The principle behind the pCO_{2aq} chamber approach is exactly the same as the principle for the bottle method and constitute the fundamental principle behind Henry's Law, e.g. that gas exchange between a confined gaseous headspace and a connected water volume will eventually approach an equilibrium at which the headspace concentration or partial pressure corresponds with the concentration in the water near the water-headspace interface. So in essence the methods are similar. There are however at least three reasons to believe that instantaneous pCO_{2aq} measurements from the common bottle headspace extraction and our pCO_{2aq} chamber technique are not always identical:

(1) The headspace to water volume ratio affects the measurements as the CO_2 transferred to the headspace could reduce the amount of CO_2 left in the water if the water volume is too small, resulting in underestimated pCO_{2aq} values. This can bias the bottle values depending on the headspace and water volumes and this is why it is often recommended to use a large bottle (1-2 L) and a small headspace (25-50 ml) in the bottle method. Even if following this recommendation, the headspace to water volume ratio is much smaller for the pCO_{2aq} chamber approach (e.g. a few L of headspace versus many m^3 or even large parts of the mixed water layer of a lake) which should therefore be more accurate in this regard. Fortunately, the bottle method bias is in most cases small (about 5 % for a 20 °C scenario with a 1 L bottle, a 50 ml headspace, and no available bicarbonate that can buffer the loss of CO_2 to the headspace) and can be corrected for but it is not always clear if such corrections are made.

(2) For the bottle approach, the transfer of water into large bottles without risk of losing volatile solutes is not trivial. Water pumping and transfer from water samplers can cause degassing. Hence the water sampling can result in loss of CO_2 causing underestimation of the real pCO_{2aq}. In the pCO_{2aq} chamber approach, there is no water sampling and the risk of water sampling bias is therefore removed.

(3) Another reason that numbers may not be identical is the potential delayed response of the pCO_{2aq} in the chamber while the bottle approach gives a snapshot value valid for the sampled water volume. This delay differs depending on the piston velocity (*k*; see Fig. 4) and means that day time CO_2 values in the pCO_{2aq} chambers may be influenced by the higher pCO_{2aq} from the previous night, thereby overestimating the instantaneous day-time pCO_{2aq}. Accordingly, night time CO_2 values in the chamber may underestimate the instantaneous night pCO_{2aq} by influence from lower daytime pCO_{2aq}.

Essentially, all the three points above show that single pCO_{2aq} chamber measurements, representing a longer time period, are not directly comparable with instantaneous bottle values, and makes it likely that chamber pCO_{2aq} values measured during day time should be slightly higher than corresponding bottle pCO_{2aq} measurements. This is also what we find when comparing single daytime pCO_{2aq} samples from chambers and bottles (Fig. 5). The difference seems to increase with pCO_{2aq} levels which is what would be expected if the bias is caused by loss from sampling (point 2 above) or by a strong diel cycling (point 3 above).

We find that while the principles behind both the bottle and the chamber approach are robust, there may be a delayed response of the pCO_{2aq} chamber depending on *k* (Fig. 4). Thus single snapshot measurements from the chambers during daytime can be overestimated (see Figure 5). However, the daily averages from the pCO_{2aq} chambers were representative under a wide range of *k* scenarios (in Fig. 4 the mean daily pCO_{2aq} chamber values were on an average 97% of the real values; range 92-99 %). There is also potential to speed up the temporal response of the pCO_{2aq} chambers by changing the chamber design (decreasing the volume and increasing the area; see also Fig. 6). Another 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 time of initial equilibration after deployment may be long at low *k* values (Figure 6). For example, in a water body at wind speeds below 0.6 m s^{-1} (corresponding to *k* values lower than 0.5 m d^{-1} using one common wind speed-*k* model; Cole and Caraco, 1998) the equilibration time is > 10 hours given the volume to area ratio of our chambers (Fig. 6). As stated above, this limits the use of the chamber pCO_{2aq} approach for diel variability, particularly during the first period after deployment. The delay in the chamber response when being near equilibrium levels is much shorter also at *k* values, making diel variability possible to distinguish although with a delay and hampered amplitude requiring careful consideration (Fig. 4).

The measurements from chambers with equilibrated headspace revealed large spatial differences in pCO_{2aq} with synchronous temporal variability on the big lake (Fig. 7). Data from a long-term deployment (20 days) showed a consistent diel pattern with increasing pCO_{2aq} during night and decreasing levels during the day as expected (Fig. 4 and above

discussion). 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. 8a), 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 streams described 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 hour median relative to the data point (Fig. 8b). This filtering procedure to remove data influenced by condensation becomes inefficient if condensation events are too frequent. We therefore suggest to routinely drying 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 drying. For longer deployments where weekly or biweekly visits are not possible, more advanced measures to prevent condensation should be considered. Potentially, silica gel in the sensor protection box could delay extensive influence of condensation events. As the loggers can control one peripheral unit it would also 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 pCO_{2aq} in streams (Fig. 9). 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 pCO_{2aq} 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 pCO_{2aq} at multiple points in e.g. a stream network for doing CO_2 mass balances and for studying the regulation of pCO_{2aq} over large scales. Fig. 9 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 pCO_{2aq}.

4 Conclusions

We conclude that the approach to measure and log CO_2 fluxes and pCO_{2aq} presented here can be an important supplement to previously presented approaches. When focusing on high temporal resolution of pCO_{2aq} (response time of minutes), the previous approaches with submersible sensors (e.g. (Johnson et al., 2010) or rapid equilibrator systems connected to CO_2 analyzers (e.g. Abril et al., 2006; Frankignoulle et al., 2001) are probably preferred. In such cases, the Senseair CO_2 logger may be suitable for use together with equilibrator systems. The chamber approach described here provides a cost- and labor-efficient multi-measurement point alternative for (*i*) easy flux measurements and (*ii*) pCO_{2aq} measurements which are not biased by potential biofilms on submersed equipment, and where delayed response times for pCO_{2aq} 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 water-headspace equilibrium is reached).

While well constrained CO_2 fluxes are critical for the global carbon balance, the previous estimates are uncertain in terms of spatio-temporal variability and flux regulation. For aquatic environments CO_2 fluxes are often based on indirect measurements demonstrated 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 CO_2 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 CO_2 studies.

Associated content

Supplementary material including a manual on how to build and use the described CO_2 logger units, details about some of our tests, and advice on the practical use of the loggers are available.

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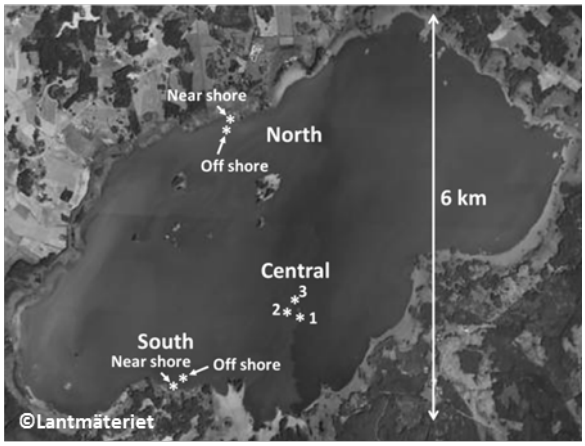

Figure 1. Map indicating the locations of the chambers on the lake Tämnaren. The map is published with permission from Lantmäteriet, Sweden according to agreement i2012/898 with Linköping University.

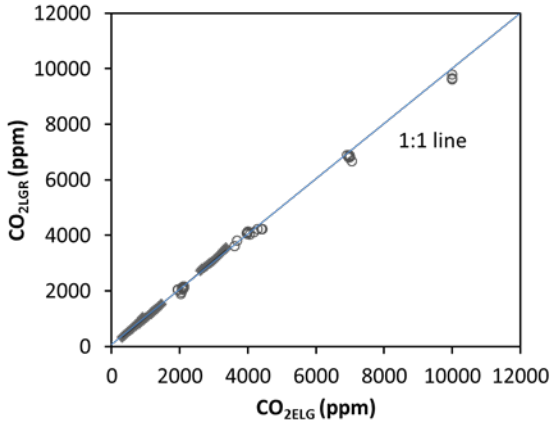

Figure 2. Comparison of CO_2 mixing ratio (ppm) measured with a Los Gatos Research greenhouse gas analyzer (LGR; DLT100) and the CO_2 logger by Senseair (ELG). Measurements were made with ELG loggers from two different batches at two separate occasions (diamonds forming bold lines and circles, respectively). 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.

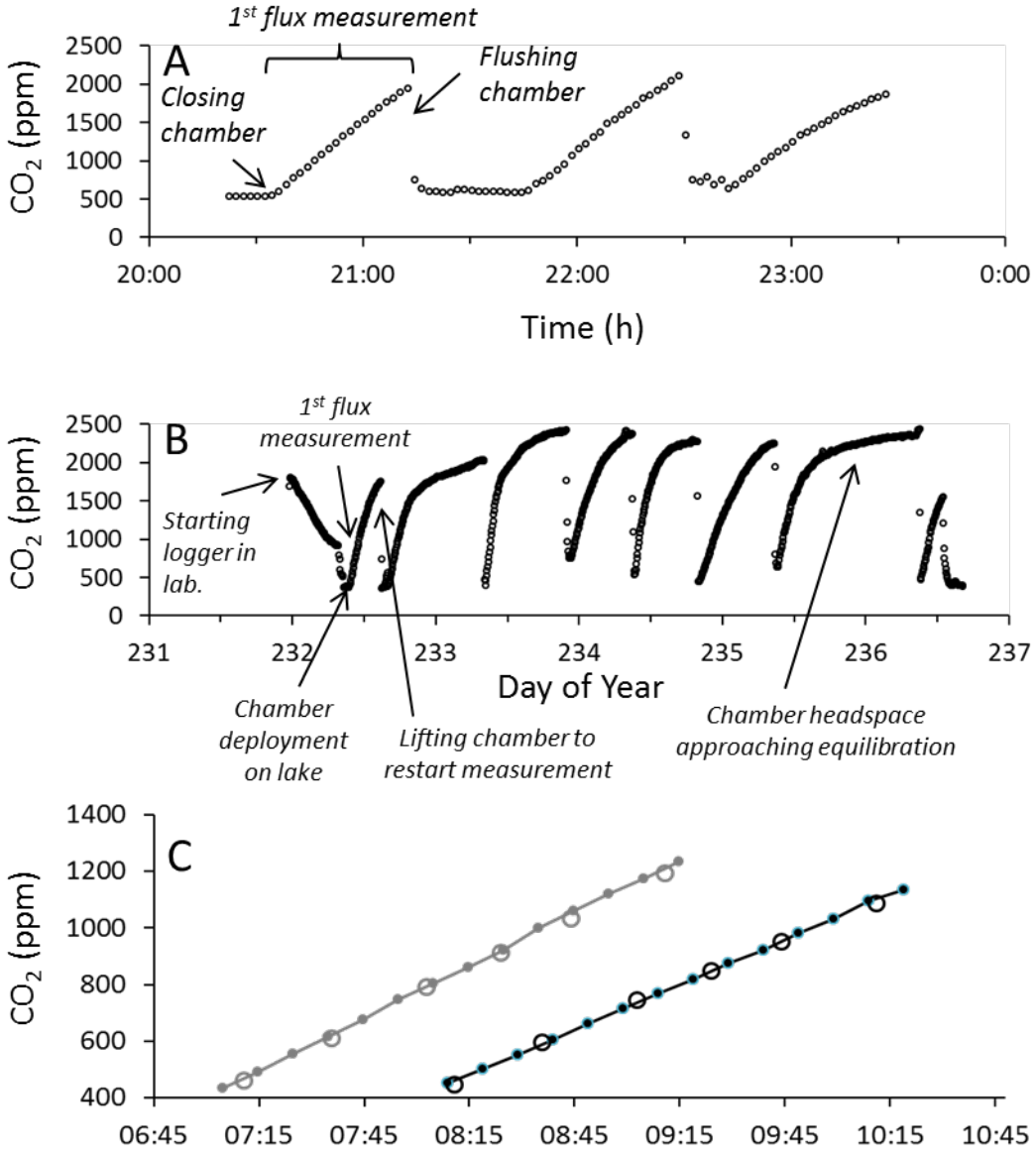

Figure 3. Examples of CO_2 measurements by loggers inside flux chambers. Panel (a) shows changes in CO_2 concentration with time inside a chamber (used to calculated fluxes) due to soil CO_2 efflux in three repeated experiments. Panel (b) shows logger raw data from eight repeated measurements on a small 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 at low temporal frequency due to additional parallel field work and depending on priorities such measurements can be made at much higher frequency. The CO_2 logger can also be used in automatic chambers (Duc et al., 2013). Panel (c) shows a comparison between data from CO_2 loggers inside two floating chambers on a pond (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 measurements.

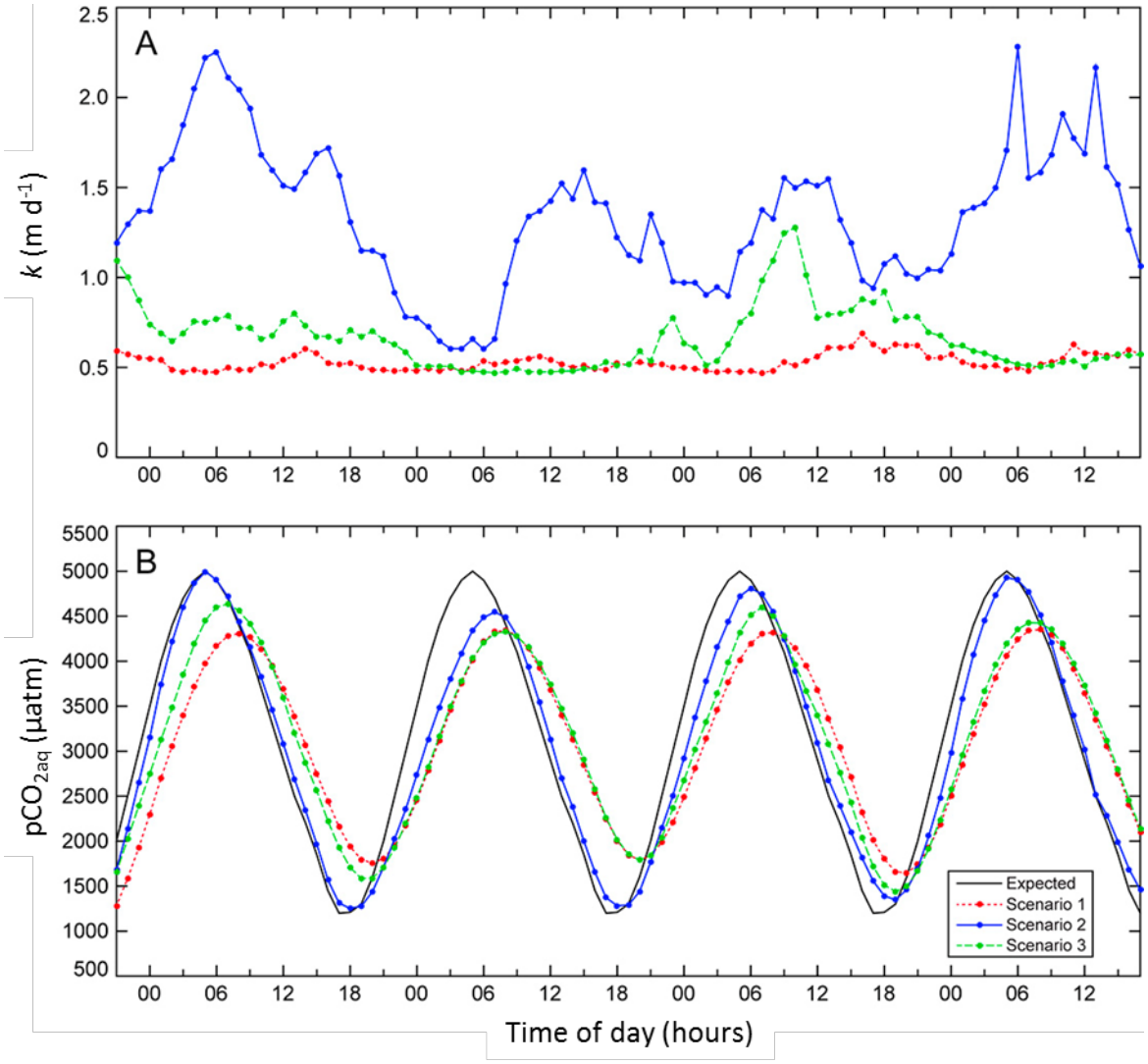

Figure 4. Example where *k* values (piston velocity; see text) were calculated from wind speed according to (Cole and Caraco, 1998) for three real scenarios with different diel variability (Panel A), and then used to model the diel pattern in pCO_{2aq} chambers of the type we used compared to the expected cases based on instantaneous pCO_{2aq} levels (Panel B). The expected case is fictive but inspired by levels found for a pond with large diel variability (Natchimuthu et al., 2014).

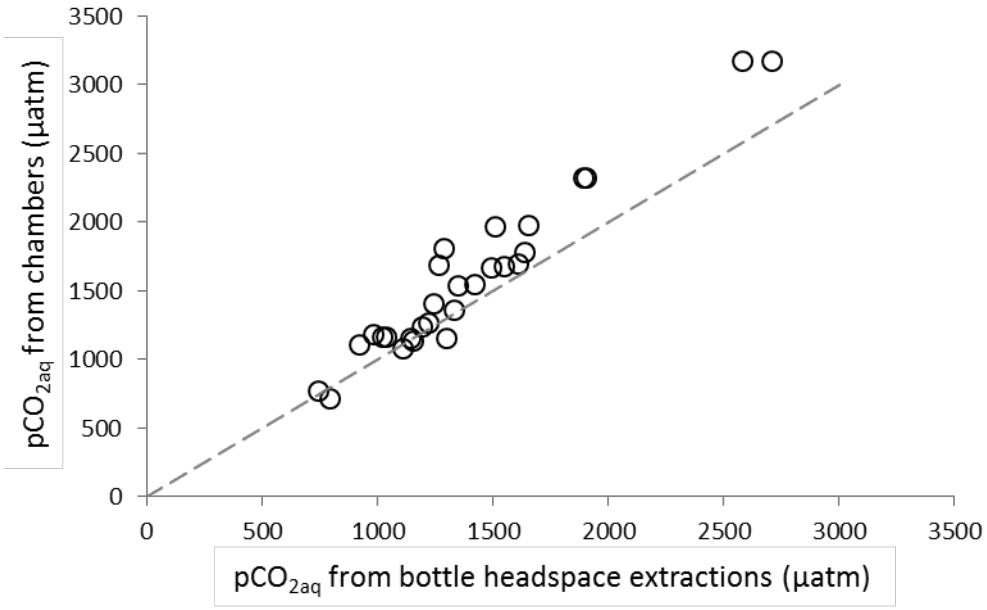

Figure 5. Comparison between instantaneous day-time measurements from pCO_{2aq} chambers (allowed to reach equilibrium) and traditional bottle headspace extractions (1025 ml total volume, 50 ml headspace, not corrected for the enclosing a limited amount of inorganic carbon in the bottle; see text). R^2 for a linear regression is 0.94. The dashed line is the 1:1 line (see above text for discussion of the deviation from this line).

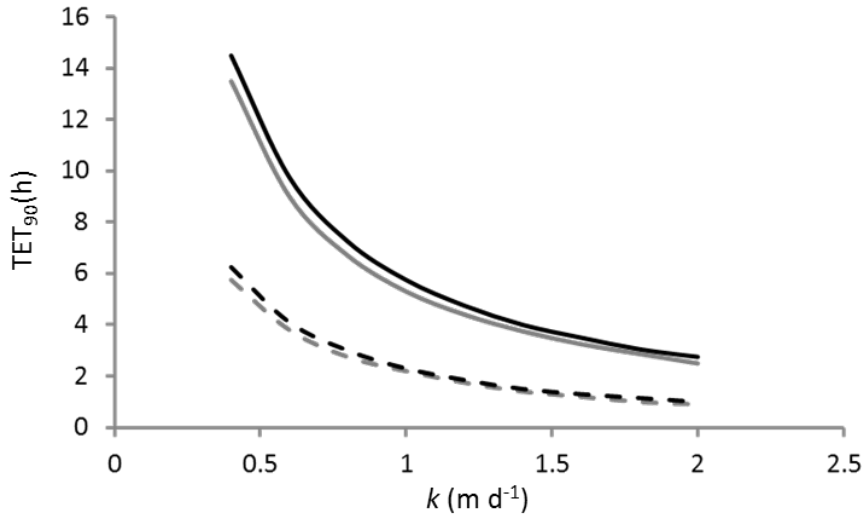

Figure 6. Theoretical equilibration time to within 90% (TET_{90}) of the true pCO_{2aq} after deploying the described chambers (solid lines) at different piston velocities (k), a temperature of 20 °C, and a pCO_{2aq} of 2000 µatm (grey) or 8000 µatm (black). The dashed lines show TET_{90} for chambers with a two times higher area to volume ratio compared to the chambers we used. Another way to speed up equilibration time is by mixing the water below the chambers (see text above).

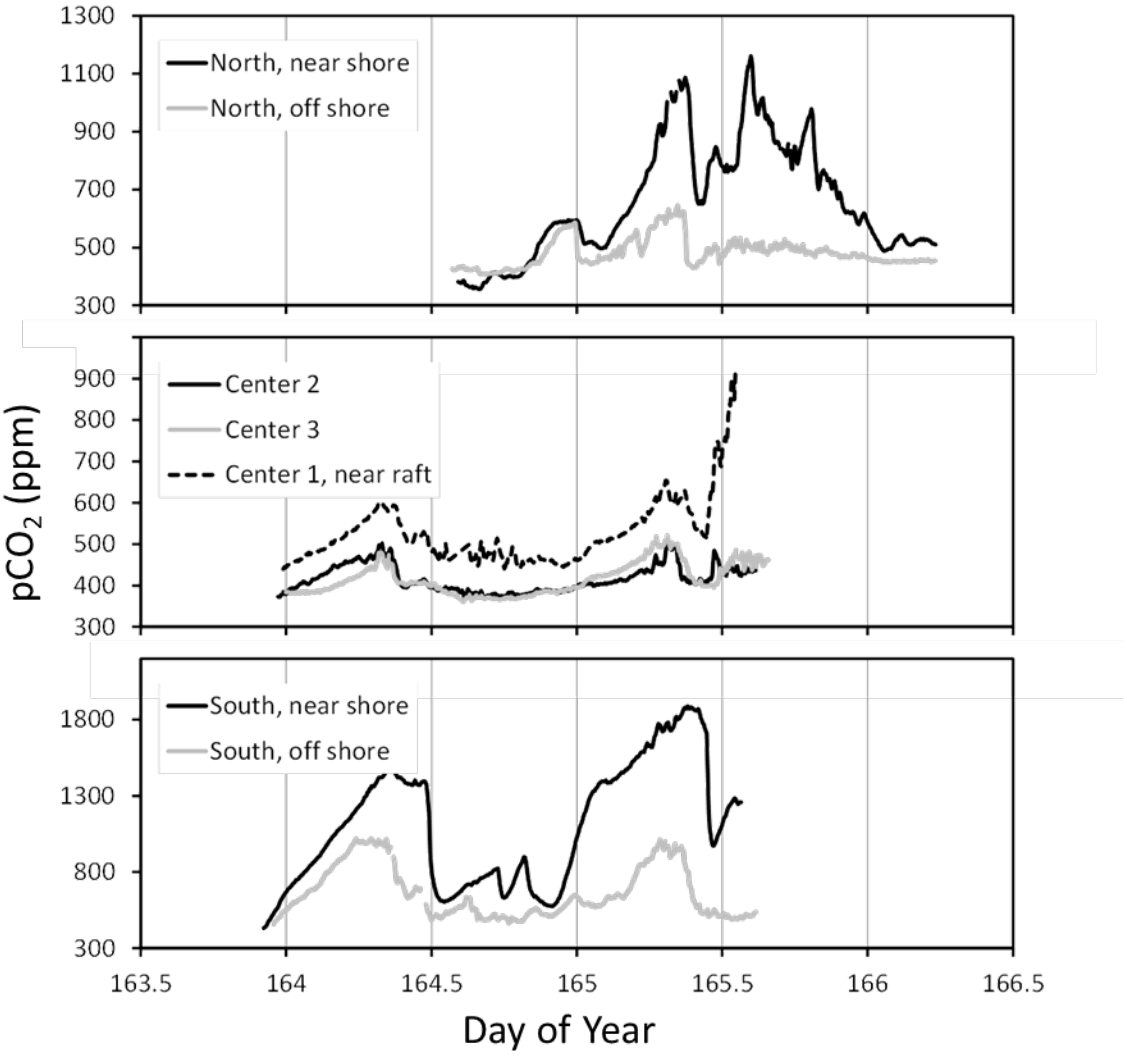

Figure 7. Illustration of spatial variability of pCO_{2aq} (expressed as mixing ratio – ppm) in a large shallow (mean depth 2 m) lake revealed by seven CO_2 logger-chamber units. The locations of each chamber are indicated in Figure 1. See text for details. Note different y axis scales and that this lake was wind exposed with variable wind conditions during the measurement period.

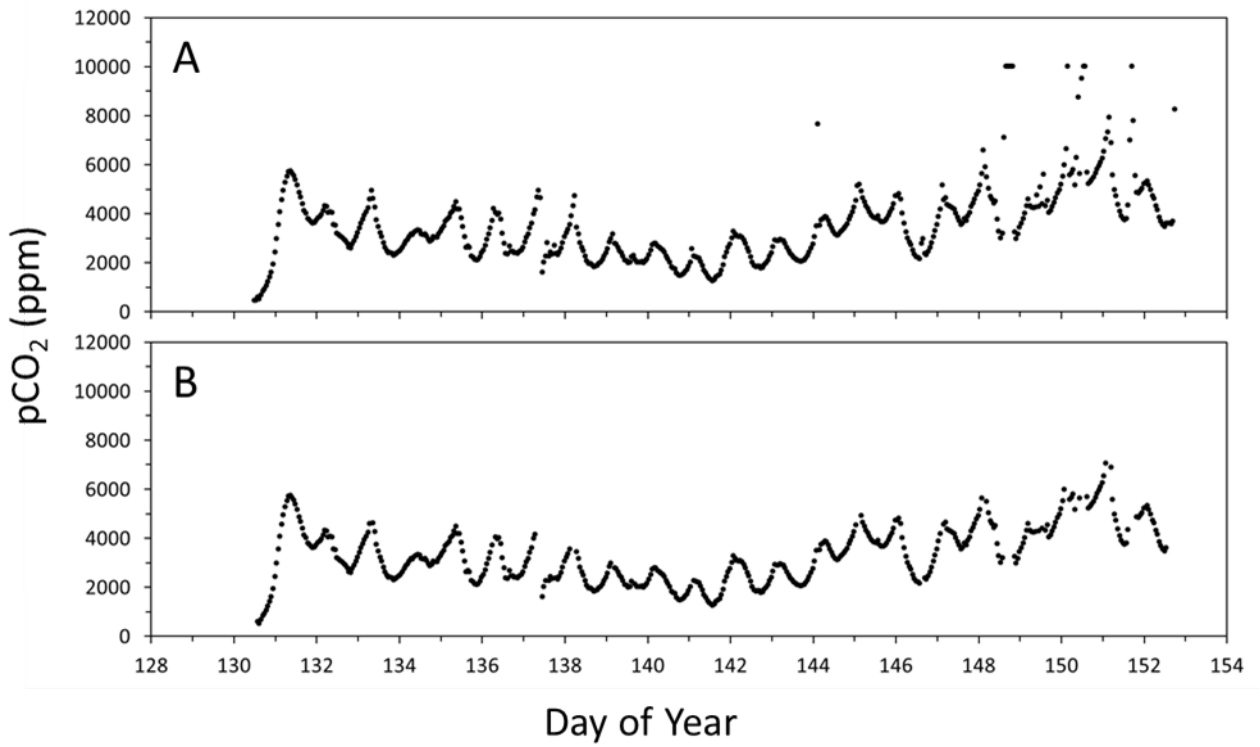

Figure 8. Example of long-term monitoring of pCO_{2aq} at 1h intervals in a small shallow boreal wetland pond (mean depth 1 m). Panel **A** shows raw data indicating spikes in the data most likely due to condensation events (or possibly related with animals temporary visiting the chambers; insects, frogs, 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.

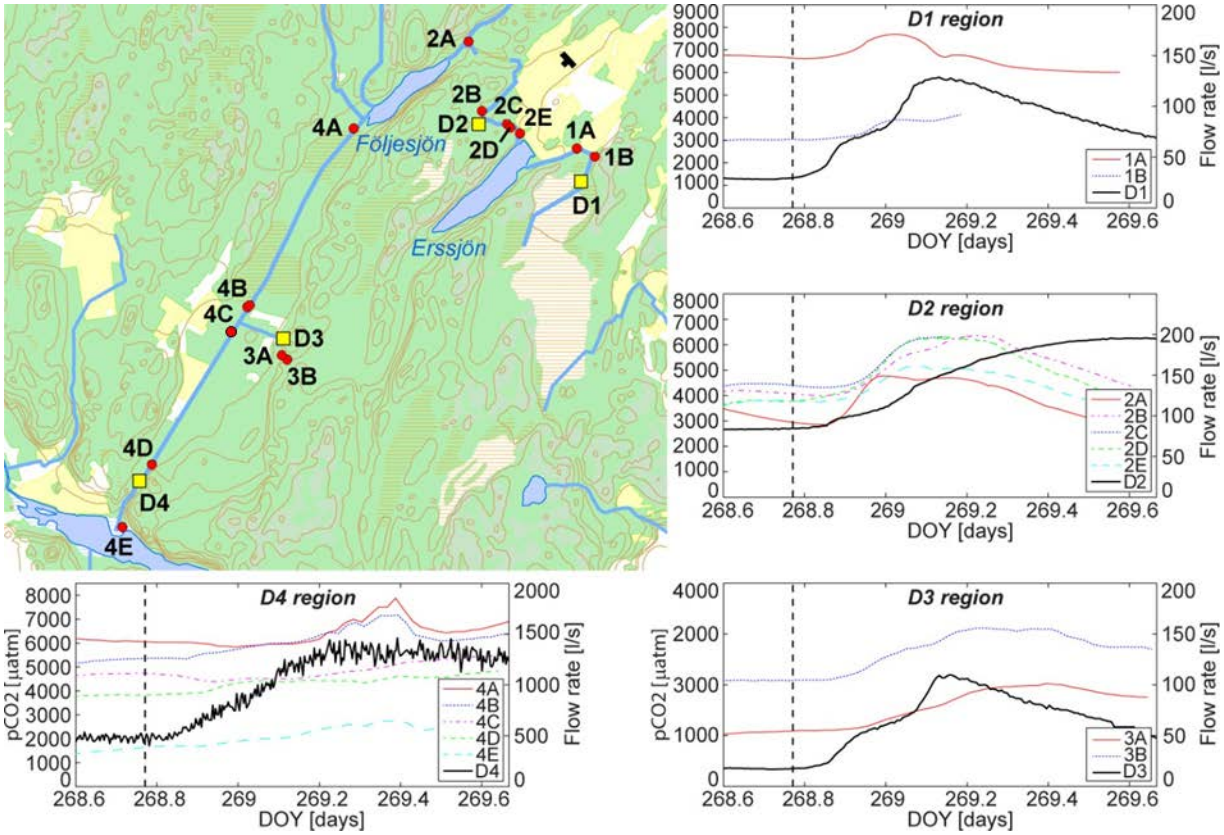

Figure 9. Example of 24 h of data from 14 CO_2 logger-chamber units placed on the main streams in a catchment stream network to log stream pCO_{2aq}. Yellow squares (D1 – D4) denote water discharge stations representing stream regions and the water flows from D1 to D4 with the D3 stream being a tributary entering the main stream upstream of D4. The red dots represent the CO_2 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 pCO_{2aq} 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.