ECOHYDROLOGY
Ecohydrol. **3**, 68–78 (2010)
Published online 23 October 2009 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/eco.95

Direct and continuous measurement of dissolved carbon dioxide in freshwater aquatic systems—method and applications

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ABSTRACT

Understanding of the processes that control CO_2 concentrations in the aquatic environment has been hampered by the absence of a direct method to make continuous measurements over both short- and long-term time intervals. We describe an *in situ* method in which a non-dispersive infrared (NDIR) sensor is enclosed in a water impermeable, gas permeable polytetrafluoroethylene (PTFE) membrane and deployed in a freshwater environment. This allows measurements of CO_2 concentration to be made directly at a specific depth in the water column without the need for pumps or reagents. We demonstrate the potential of the method using examples from different aquatic environments characterized by a range of CO_2 concentrations (0·5–8·0 mg CO_2-C l^{-1}, equivalent to *ca* 40–650 μmol CO_2 l^{-1}). These comprise streams and ponds from tropical, temperate and boreal regions. Data derived from the sensor was compared with direct measurements of CO_2 concentrations using headspace analysis. Sensor performance following long-term (>6 months) field deployment conformed to manufacturers' specifications, with no drift detected. We conclude that the sensor-based method is a robust, accurate and responsive method, with a wide range of potential applications, particularly when combined with other *in situ* sensor-based measurements of related variables. Copyright © 2009 John Wiley & Sons, Ltd.

KEY WORDS dissolved CO_2; terrestrial respiration; *in situ* monitoring; infrared gas analysis

Received 10 March 2009; Accepted 26 August 2009

INTRODUCTION

Supersaturation of CO_2 in surface water results from benthic respiration and pelagic mineralization (Jonsson *et al*., 2003), as well as from terrestrial respiration and weathering products delivered by sub-surface or groundwater inflow (Holmes, 2000). CO_2 supersaturation is typical of most surface water systems in boreal, temperate and tropical systems (Cole *et al*., 1994, 2007; Kling *et al*., 1991; Richey *et al*., 2002). This is particularly true of peatland drainage systems where connectivity between streams and the peatland CO_2 repository leads to lateral outflow and significant evasion of CO_2 (Hope *et al*., 2001, 2004; Dawson *et al*., 2004; Billett and Moore, 2008). Recent isotopic evidence suggests that geogenic sources (carbonate weathering) also contribute to CO_2 supersaturation in aquatic systems (Mayorga *et al*., 2005; Billett *et al*., 2007; Waldron *et al*., 2007). Under favorable conditions with the right levels of light and nutrients, photosynthetic uptake of CO_2 in the water column can lead to under-saturated conditions. As the sources and sinks of dissolved CO_2 are varied and dynamic in space and time, the measurement of dissolved CO_2 concentrations in surface water systems is of interest to researchers from a range of disciplines concerned with the biogeochemistry, ecology and hydrology of streams, rivers, wetlands and lakes. It is also a parameter of interest for questions related to terrestrial–aquatic connectivity of groundwater and surface water (Holmes, 2000), and the carbon cycle in general (Cole *et al*., 2007). This also applies to sub-surface saturated and unsaturated zones in the terrestrial environment.

Until now, researchers in fresh water systems have been largely constrained to either making spot measurements of dissolved (or 'free') CO_2 from grab samples through analysis of a headspace equilibrated with sampled water (Kling *et al*., 1991; Hope *et al*., 1995) or indirect estimation of dissolved CO_2 concentration from measurements including pH and alkalinity (Neal *et al*., 1998). One of the most consistently used indirect approaches involves the calculation of dissolved CO_2 from pH and alkalinity based on temperature-dependent equilibrium constants (Stumm and Morgan, 1995). While continuous measurement of pH and temperature have become common through the use of multi-parameter sensors and other

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devices, the accuracy of pH measurements of commonly utilized sondes [±0·2 pH units for sondes by Hydrolab (Hach Environmental, 2008) and YSI (YSI Environmental, 2008)] suggests that small-scale temporal changes in dissolved CO_2 concentrations might be lost in the uncertainty terms of CO_2 calculations derived from pH measurements.

Direct determination of dissolved CO_2 concentrations by the commonly used headspace method of Kling *et al.* (1991) using automated water sampling to permit increased sampling frequency is problematic because concentrations of dissolved CO_2 are affected by degassing in the sample bottle. Instead, researchers have relied upon 24–48 h round-the-clock manual (spot) sampling for direct measurement of diurnal dynamics in pCO_2 (e.g. Guasch *et al.*, 1998; Dawson *et al.*, 2001; Dinsmore *et al.*, 2009).

Direct *ex situ* measurements of CO_2 using in-line instruments rather than sample collection for subsequent laboratory-based analysis have generally used one of two approaches: (1) headspace equilibration within a large chamber (3 l (Abril *et al.*, 2006) to 8 l (Frankignoulle *et al.*, 2001)) followed by gas analysis of the headspace air, or (2) diffusion from solution into a gas-permeable tubing that is circulated within a closed loop and across the gas bench of an external infrared gas analyser (IRGA) (e.g. Sellers *et al.* (1995); Hari *et al.* (2008)). While these instruments have allowed analysis in the systems for which they were designed, they are considerably more complex than the approach described in this paper. In an additional approach, Baehr and DeGrandpre (2004) present a reagent-based spectrophotometric method for continuous *in situ* monitoring of pCO_2; however, this method is limited to dissolved CO_2 concentrations less than 2000 µatm, which is frequently exceeded in productive freshwater aquatic systems and super-saturated peatland streams.

Due to the range of dissolved CO_2 sources (e.g. dissolved organic carbon (DOC) mineralization, groundwater and stormwater delivery, invasion from the atmosphere) and sinks (e.g. CO_2 consumption via aquatic photosynthesis, CO_2 evasion from water surfaces) that occur on diurnal (Guasch *et al.*, 1998) and shorter time scales (Johnson *et al.*, 2007), continuous measurement of dissolved CO_2 is required to correctly represent concentration dynamics. Clearly, our understanding of the processes that control CO_2 dynamics in aquatic systems would be enhanced by the ability to make direct *in situ* and continuous measurements of CO_2 over a wide range of concentrations and with high temporal frequency. Several recent papers use such a method (Dinsmore and Billett, 2008; Dinsmore *et al.*, 2009; Johnson *et al.*, 2007, 2008). Here we aim to describe for the first time the method in detail and demonstrate its potential range of applications.

In this paper, we present a simple method for the direct *in situ* and continuous measurement of dissolved CO_2 using infra-red gas analysis. We demonstrate the method and its potential applications in a range of aquatic environments ranging from the tropics to temperate and boreal regions. We also compare CO_2 concentrations measured by the sensor with those determined by previously established methods such as headspace analysis. Our aim is not to provide a complete interpretation of the various datasets, but to demonstrate the potential of the method to enhance understanding of CO_2 dynamics in a range of aquatic environments.

MATERIALS AND PROCEDURES

Direct and continuous *in situ* monitoring of dissolved CO_2 in the present method is achieved by deploying the sensor head of an IRGA directly into the aqueous environment. In our approach, the light source, detector and gas bench of an IRGA are enclosed within a waterproof and gas-permeable membrane and deployed *in situ* at the point of measurement in the water column of a stream, river, lake or wetland (Figure 1). A cable connects the IRGA sensor to the instrument controls located on a ground-mounted or floating platform, while an external power source and data acquisition system allow continuous and long-term monitoring. No pumps or other ancillary equipment are required for operation.

The method requires a suitably rugged IRGA with a physical separation between (1) the IR source, detector and gas bench, and (2) the transmitter electronics, power

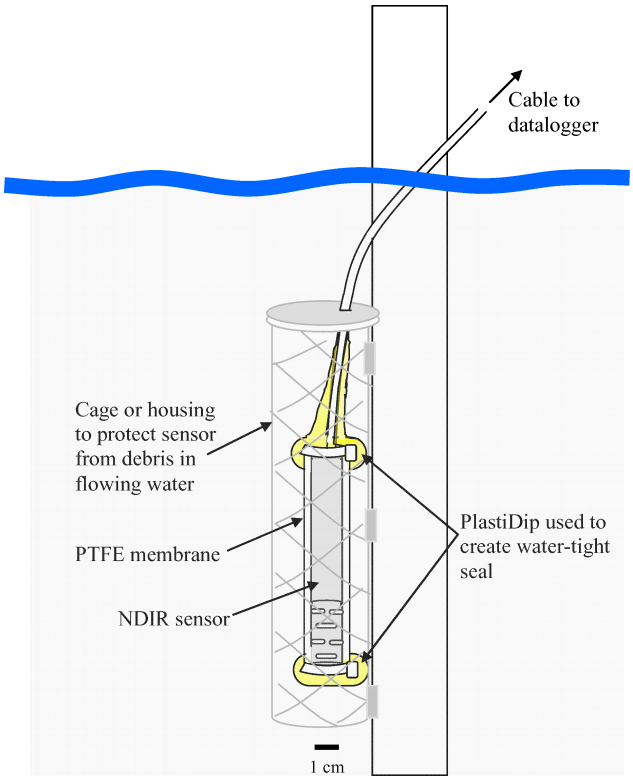

Figure 1. Diagram of IRGA sensor sheathed in PTFE tubing and deployed *in situ*. The sensor dimensions are 2 cm by 15 cm (diameter and length, respectively). The cable leads from the sensor to the transmitter electronics, power supply and data acquisition system located inside waterproof housing on the streambank.

DOI: 10.1002/eco

supply and data acquisition system. Of the commercial IRGAs available at present, we are aware of only carbon dioxide transmitters manufactured by Vaisala (Helsinki, Finland, GMT220 and GMM 220 series) that meet these requirements. These IRGAs were designed to measure CO_2 concentrations in humid environments using a single-beam dual-wavelength non-dispersive infrared (NDIR) light source and a silicon-based sensor, and were originally adapted for environmental research for use in soils by Tang *et al.* (2003) and Jassal *et al.* (2004). The sensors are compact, measuring approximately 2 cm in diameter by 15 cm long. The cable connecting the sensor and transmitter is available in lengths up to 10 m.

The key to aqueous deployment of the IRGA sensor is the use of a protective expanded polytetrafluoroethylene (PTFE) tube or sleeve that is highly permeable to CO_2 but impermeable to water. The material is available for purchase as a flexible tube that fits over the IRGA sensor (Product number 200-07; International Polymer Engineering, Tempe, Arizona, USA). As the manufacturer was unable to provide diffusivity characteristics of the expanded PTFE, we determined them in the laboratory.

The diffusivity measurements were made under quasi steady-state conditions. CO_2 was introduced into a large volume (V) aluminum chamber at high concentration ($C = \sim 16\,000$ ppm) and allowed to diffuse out of the chamber against ambient CO_2 concentration ($C_0 = 420 \pm 35$ ppm) through a small opening of known area (A) covered with a single layer of the expanded PTFE by slicing the tubing and laying it flat. The change in chamber CO_2 concentration was repeatedly measured by continuously circulating the chamber gas through a LI-820 IRGA at 600 cm^3 min^{-1}. Values for k_a and D were then calculated assuming quasi steady-state conditions (e.g. very small diffusion time) using

$$\frac{V\Delta C}{At} = k_a C \tag{1}$$

and

$$\frac{V\Delta C}{At} = D\frac{dC}{L} \tag{2}$$

where ΔC is the change in chamber concentration over time t (10 s time steps), L is the thickness of the fabric (1 mm) and dC/L is the concentration gradient across the fabric, i.e. concentration difference between mean C in the chamber over 10 s and that outside the chamber.

The transfer coefficient k_a and diffusivity D of the expanded PTFE fabric for CO_2 were found to be $0{\cdot}8 \pm 0{\cdot}1$ cm s^{-1} and $0{\cdot}08 \pm 0{\cdot}01$ cm^2 s^{-1}, respectively (means ± 1 SD, $n = 9$ determinations for each of k_a and D). Since diffusion of CO_2 in water ($1{\cdot}77 \times 10^{-5}$ cm^2 s^{-1} at 20 °C) is about 10 000 times slower than in air ($1{\cdot}59 \times 10^{-1}$ cm^2 s^{-1} at 20 °C) (Scott, 2000), the material diffusivity of the PTFE tubing and its transfer coefficient indicate that it presents a negligible barrier to CO_2 diffusion and temporal response of the sensor. The sensor response time in air is given as 30 s (Vaisala Oyj, 2008), which will vary for aquatic deployments based on water temperature and flow conditions. In practice, we have found the sensor response time to be consistent with that of other water quality sensors (e.g. electrical conductivity and dissolved oxygen sensors).

Sensor preparation

The PTFE tubing must be sealed and made impermeable to water at both the cable end and non-cable end of the sensor (Figure 1). This is a key part of the set-up. A method that has proven effective for the water-tight, long-term (>1 year) deployment in streams involves the application of a rubberizing compound that forms an impermeable surface, sealing the PTFE tubing to the sensor. We have used Plasti Dip (Plasti Dip International, Blaine, MN, USA) for this purpose.

A self-adhesive felt tab or similar item (e.g. plastic/polypropylene disk) is fixed onto the end of the sensor casing/housing. Since the purpose of the disc/tab is to stop the rubberizing compound from entering beneath the PTFE tubing when sealing the sensor, the disc/tab needs to be of a similar diameter to the PTFE tubing (20 mm). The PTFE tubing is placed over the sensor and fastened to the disc/tab and to the sensor cable using small plastic cable ties. The rubberizing compound is first applied to the disc/tab by dipping the PTFE-sheathed sensor into the product until the cable tie and disk/tab are no longer visible. As the rubberizing compound contains volatile organic compounds, the sealing of the IRGA sensor must be done in a well-ventilated area.

The rubberizing compound is then applied to the cable end of the sensor either by dipping or using a small brush or similar item, with the goal of coating the union of the sensor cable and the PTFE tubing, including the cable tie. Since tiny holes may form in the applied rubberizing compound due to volatilization during drying, it is recommended to apply two additional coats (three in total). The rubberizing compound should be permitted to dry thoroughly between coats, and one should pay particular attention to seal any small holes that may be visible in the previously applied layer. Two to four hours of drying between coats of rubberizing compound is required prior to the next application. Following the third application, any visible holes were inspected, which were touched up with spot applications of the rubberizing compound using a small brush, allowing for thorough drying time between touch-up applications as needed. Overall it is important to apply sufficient rubberizing compound to seal the system, while avoiding covering the PTFE tubing area directly above the air-entry slots on the enclosed NDIR sensor.

Further protection of the water-proofed IRGA will vary depending on deployment scenarios. We have secured the sensor within a perforated PVC tube using cable ties for use in both flowing and still water. This allows flowing water to interact with the IRGA without the PTFE tubing suffering damage from floating or submerged debris. In the case of still water, the PVC protection prevents damage to the PTFE tubing by aquatic biota. We have also used a small wire mesh cage (mesh size 6 mm)

DOI: 10.1002/eco

to enclose the sensor, the aim being to protect the PTFE tubing from large particle damage (including ice) during high flow events, while minimizing the effect on flow around the sensor. The IRGA sensor should be removed for inspection and cleaning of the PTFE tubing periodically depending upon the amount of in-stream biological activity or geomorphic changes to the stream channel. Biofilms can be gently rinsed off the PTFE tubing using clean water and a non-abrasive towel. Small stones and detrital materials can be removed from the PVC tube without removing the IRGA sensor, although any major accumulation of materials will likely require removal of the sensor to dislodge foreign materials from the PVC tube. In all cases, care must be taken to avoid damaging the PTFE tubing, particularly during installation. Since direct contact with water will damage the enclosed sensor, minor abrasions in the PTFE tubing must be repaired before submergence by applying a small amount of rubberizing compound to the damaged area.

Sensor deployment and data processing

For continuous monitoring, the IRGA must be supplied with power (DC power in the case of remote deployments), and output recorded with a data acquisition system. A digital timer can be used to cycle the IRGA on and off for measurements at reduced frequency to conserve power. Although this is particularly useful in the case of remote deployments where routine site visits are relatively infrequent, it takes at least 2–3 min for the sensor to stabilize as long as it has remained *in situ* during the power down period. The sensor can be mounted vertically or horizontally within the water column.

In flashy systems where temporal dynamics are of interest, continuous power and data logging is necessary. The Vaisala GMT series IRGAs require 24 V power if used with DC power. In practice, this can be accomplished through the use of two 12-V deep-cycle batteries deployed in series, which can be supplemented through a photovoltaic power source. There is an alternative GMM series IRGA that can be built for 12 VDC or 24 VDC; however, the manufacturer reports that GMM instrumentation housing is less rugged and thus requires additional protection. In our experience and in poor field conditions (frequent snow showers/night-time sub-zero temperatures), a 24-V sensor (and visual display unit) will run continuously for ~10 days while draining 2×85 Ah 12 V batteries to half capacity (draining batteries beyond half capacity significantly reduces battery life). A 12 VDC GMM series sensor with 2×85 Ah 12 V batteries connected in parallel would also provide power for ~10 days. While the visual display unit of the GMT series sensor is useful, its omission and reliance on the logger display can reduce power consumption.

As infrared gas analysis is subject to the universal gas law, sensor output as a partial pressure of CO_2 (e.g. pCO_2) must be corrected for changes in both temperature and barometric pressure. Increases in water temperature cause a decrease in sensor output, while increases in atmospheric pressure cause an increase in sensor output. The post-measurement correction of sensor output as pCO_2 related to changes in temperature and pressure were determined empirically for the Vaisala GMT IRGAs (Vaisala Oyj, 2008). Pre-corrected sensor output needs to be reduced by 0·15% of the measured reading per hPa increase in pressure relative to calibration pressure (typically 1013 hPa). Pressure readings below the calibration pressure require increasing the sensor output by 0·15% of the measured reading per hPa. Pre-corrected sensor output also needs to be increased by 0·3% of the measured reading per °C of increased temperature relative to calibration temperature (typically 25 °C). Water temperature above the calibration temperature requires decreasing the sensor output by 0·3% of the measured reading per °C.

An additional correction is required when sensors are deployed in an aquatic environment. Water depth affects the pressure exerted on the sensor, and this water depth correction is added to the atmospheric pressure correction. For example, 10 cm water depth above the sensor location corresponds to an increase in pressure of 9·81 hPa. If sensor output is 1000 ppm pCO_2, the output needs to be reduced by 14·72 ppm because of the additional pressure exerted by the increased water level. If the water depth varies relative to the sensor location, a depth correction must be determined for each measurement time interval (e.g. by recording water depth using a pressure transducer or other water level sensor). This can be avoided if the sensor is attached to a float such that it remains at a constant depth below the water surface. In vertically oriented sensor deployments, the depth of reference corresponds to the mid-point of the sensor's gas bench (the slotted portion of sensor indicated in Figure 1). There is no need to correct for humidity within the gas bench as the sensor is stable at up to 100% relative humidity.

In situ measurements of temperature, atmospheric pressure and water level should be made at the same time interval to permit both post-measurement correction of pCO_2 and the determination of dissolved inorganic carbon as dissolved CO_2. The mass equivalence of dissolved inorganic carbon in the dissolved CO_2 form is typically reported as mg l^{-1} of CO_2-C, and is calculated via Henry's Law (Plummer and Busenberg, 1982) based on the temperature of the water where the sensor is located and the partial pressure of CO_2 in solution. For example, 1000 ppm is equivalent to 2·84 mg CO_2-C l^{-1} at 5 °C; 2·01 mg CO_2-C l^{-1} at 15 °C; and 1·50 mg CO_2-C l^{-1} at 25 °C.

The Vaisala sensors are shipped with certificates of calibration. For assessing the accuracy of a sensor following field deployment, there are a number of options available. For instance, a sensor can be evaluated following deployment against a separate sensor with valid calibration or a CO_2 analysis system of known performance. This approach avoids the need to remove the PTFE membrane from the sensor, and can be utilized with a second Vaisala sensor or any CO_2 analysis system

DOI: 10.1002/eco

that would permit a robust evaluation over the calibration range of the Vaisala sensor (e.g. Licor IRGA or other comparable system). Alternatively, Vaisala manufactures a 'field check adapter' (e.g. chamber for pump-aspirated sampling systems, model 26150GM) which can be used with calibration gases. However, the snug fit of the field check adapter requires removal of the PTFE membrane to achieve a proper seal. Our experience is that the sensors showed a strong linear response over the full measurement range. Although comparison among individual sensors and standard gases showed consistent differences, these can be corrected by applying a sensor-specific linear correction factor. We therefore recommend that before and after use the sensor CO_2 concentration readings are compared to gas standards across the full range and the absolute values corrected accordingly.

ASSESSMENT

We have used *in situ* sensors for continuous measurement of CO_2 concentrations in a range of environments. These include aquatic systems dominated by high biological activity and those dominated by physical/hydrological processes (storms/snowmelt). Each example highlights the importance of different processes affecting CO_2 concentration and include the following:

1. Short-term dynamics of CO_2 relative to dissolved oxygen, pH and electrical conductivity, demonstrating CO_2 dynamics relative to other water quality parameters during stormflow in a tropical headwater stream;
2. Diurnal cycling of CO_2 in beaver ponds in a temperate wetland, providing an example of the effect of light and temperature on CO_2 concentration;
3. Long-term seasonal changes in CO_2 concentrations during the ice-free period in a boreal forested headwater catchment;
4. Changes in CO_2 concentrations during the spring snowmelt event in a boreal forested peatland; and
5. Effect of stormflow on CO_2 concentrations in streams draining a temperate peatland.

Stormwater CO_2 dynamics in a tropical forested headwater stream

An IRGA CO_2 sensor was deployed in a forested headwater stream draining a 2-ha catchment near Juruena, Brazil (10·42 °S, 58·77 °W). Dissolved oxygen (DO) in streamwater was determined using a Hydrolab DataSonde 4 sensor (Hach Environmental, Loveland, Colorado, USA). Data for hydrological fluxes and water quality parameters were recorded at 5-min intervals (Figure 2). In this deployment, the IRGA sensor was attached to a float such that the sensor location remained 10 cm below the water surface at all times. The sensor and float were free to rise and fall within a perforated PVC pipe (100 mm diameter) fixed within the stream at a location adjacent to the point of discharge measurement.

Dissolved CO_2 was inversely correlated with DO, indicating contributions from more aerated hydrological flow paths early in the event. These flow paths include direct precipitation and through-fall as well as overland flow. The pulse of CO_2 arriving on the falling limb

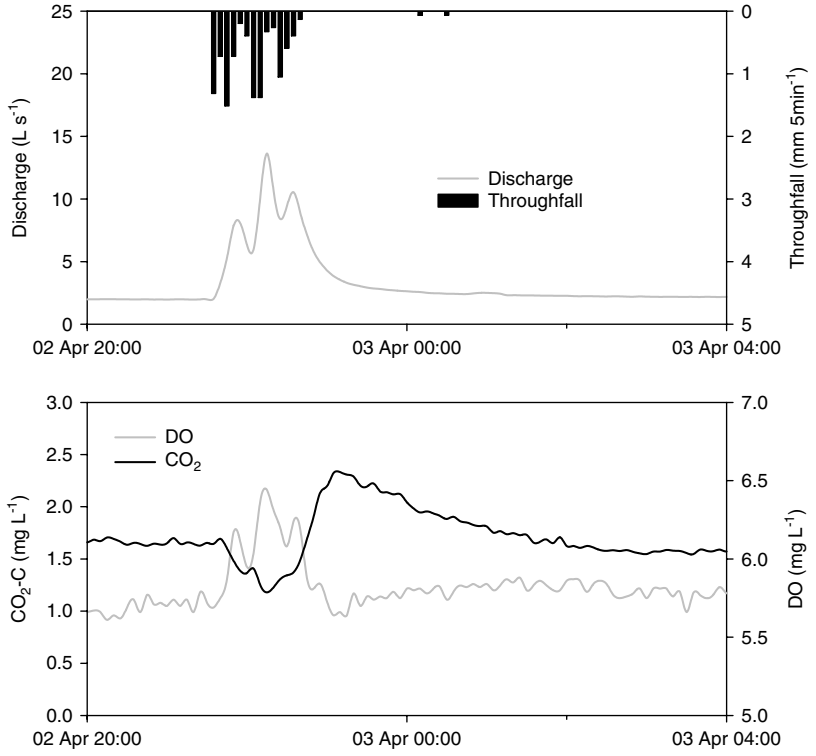

Figure 2. Short-term dynamics of dissolved CO_2 in a tropical headwater stream near Juruena (Brazil) relative to throughfall and stream discharge (top panel) and dissolved oxygen (DO, lower panel).

DOI: 10.1002/eco

of the storm hydrograph indicates contributions of soil CO_2 delivered by flow paths with a longer response time (Johnson *et al.*, 2007).

Diurnal cycling

During summer 2007, sensors were used in a study of soil–stream connectivity at the margins of a beaver pond in Mer Bleue peatland (45·40 °N, 75·50 °W) Canada (Dinsmore *et al.*, 2009). Drainage waters at Mer Bleue were characterized by a high degree of CO_2 (and CH_4) super-saturation (Billett and Moore, 2008). The sensor detected small-scale temporal changes in CO_2 concentrations; measurements were made each minute with 10-min averages recorded. The data presented in Figure 3 for a sensor located at 10 cm depth show strong diurnal cycles in both CO_2 concentration and pH (CSIM11 pH sensor deployed at the same depth). A detailed statistical analysis of the CO_2 data suggests that both solar radiation and temperature are key drivers of CO_2 production/consumption during the summer months (Dinsmore *et al.*, 2009).

Long-term seasonal changes

To investigate and connect changes in supersaturation of CO_2 in stream water with hydrology, it is necessary to have high-resolution data since hydrological events such as snowmelt and storms often take place within a few days or even hours. During the ice-free period of 2007, a high-resolution continuous record of CO_2 concentrations from the 50-ha Nyänget catchment (64·14 °N, 19·46 °E) situated in northern Sweden was made (Figure 4). This is a sub-catchment of the Krycklan Catchment Study Area and comprises 15% peatland and 85% forest. Its hydrochemistry has been monitored regularly over the last 25 years (e.g. Bishop *et al.*, 1990; Köhler *et al.*, 2008). Hourly data were collected from spring thaw to the autumn freeze and show low summertime CO_2 concentrations and a weak ($R^2 = 0{\cdot}28$) positive linear relationship between CO_2 concentration and discharge. This relationship was not observed from manual spot-sampling in nearby streams where CO_2 concentrations decreased during high flows (data not shown). One explanation could be that the monitored site is influenced by a peatland situated 800 m upstream where CO_2

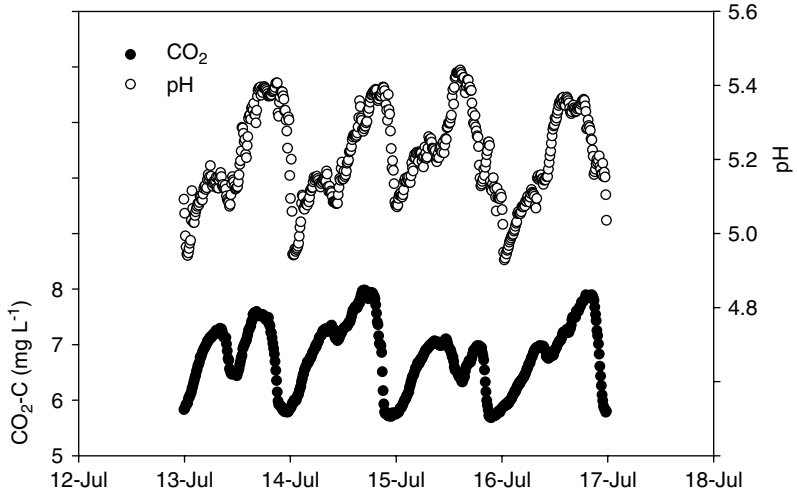

Figure 3. Small-scale temporal changes in CO_2 concentrations and pH in a beaver pond at Mer Bleue peatland (Canada) during 2007.

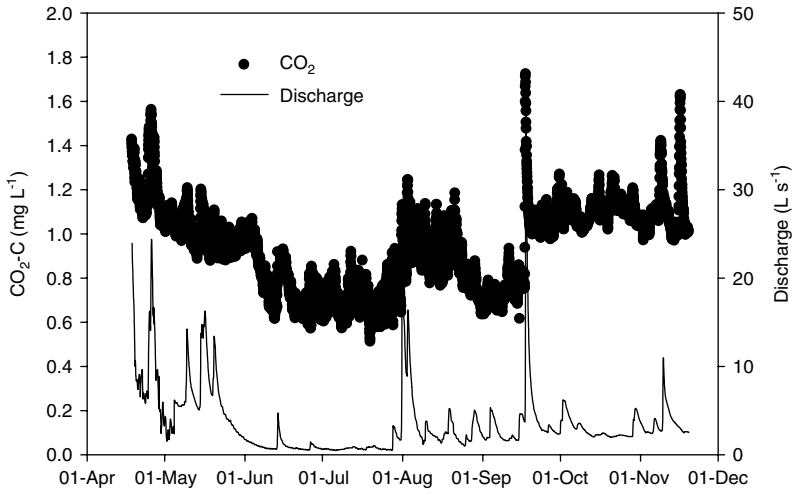

Figure 4. Seasonal variability during 2007 in CO_2 concentration and discharge at the outlet of the Nyänget catchment (N. Sweden).

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concentrations up to 15 times higher were observed compared to the monitoring location. A short retention time of stream water between the peatland and the monitored site, leading to decreased time for degassing of CO_2 to the atmosphere, might explain the higher CO_2 concentration at higher flows. However, there are seasonal differences in the relationship, showing that parameters other than hydrology affect in-stream CO_2 concentrations.

Spring snowmelt event

The CO_2 sensors have also been used in cold water conditions to measure the spring snowmelt release of CO_2 at the end of the winter in streams draining boreal forested peatlands in Finland. In this example (Figure 5), the sensors were deployed for 2 months and measurements made every minute with data recorded as a 10-min average. Air and water temperature varied from −11 to −24 °C and from −0·3 to +5·4 °C, respectively. At times, the water surface was frozen while the sensor was deployed below the frozen surface. Here data are shown from the Välipuro catchment (63·52 °N, 28·40 °E) in E. Finland: a 86-ha catchment containing 56% peatland. Changes in CO_2 concentration show the importance of hydrology and temperature. Significant dilution of CO_2 concentration occurred during the melting of the snow pack followed by recovery with an increase in concentration as water levels fell. Superimposed on this seasonal cycle was a secondary diurnal change in CO_2 concentration apparently related to differences between day and night temperatures.

Stormflow response

In temperate, wet climates, a significant amount of hydrochemical research on solutes focuses on the use of concentration–discharge relationships to identify hydrological drivers and source areas within catchments (e.g. Edwards, 1973). Direct measurements of changes in CO_2 concentration during storm events have been studied using protected CO_2 sensors in a peatland catchment in Central Scotland (Dinsmore and Billett, 2008). Auchencorth Moss (55°47′34N; 3°14′35 W) is a 335-ha catchment containing 85% peat, which drains into the Black Burn, a DOC-rich stream with a 'flashy' hydrological

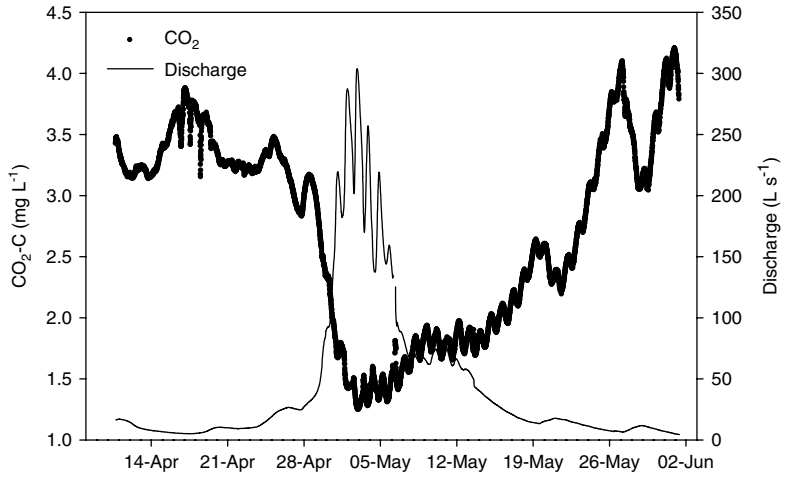

Figure 5. Temporal changes in streamwater CO_2 concentration and discharge during the 2008 spring snowmelt period in the Välipuro catchment (E. Finland).

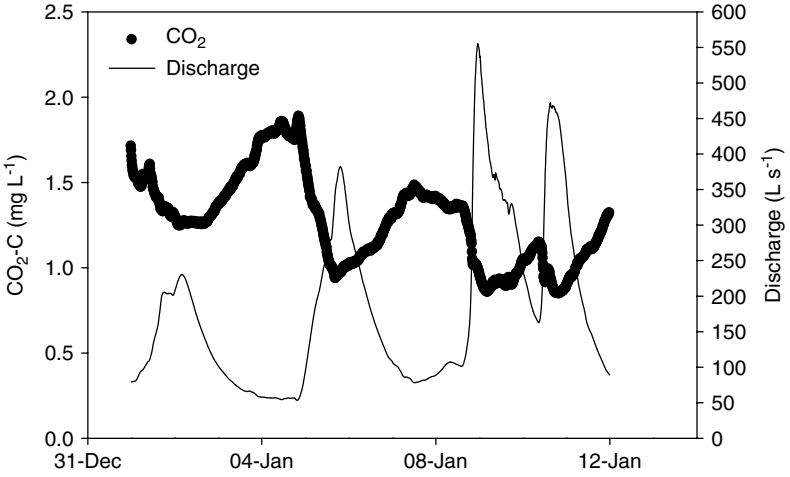

Figure 6. Changes in dissolved CO_2 concentration in response to four stormflow events in January 2008 in Black Burn. Data points are 10-min averages of measurements made at 1-min intervals. Discharge is represented by the thin line.

DOI: 10.1002/eco

response (Billett *et al*., 2004). In contrast to the Nyänget catchment (Figure 4), CO_2 concentrations show a negative relationship with discharge (Figure 6), suggesting that CO_2-enriched groundwater derived from deep peat or the underlying parent material is a major source of streamwater CO_2 (Billett *et al*., 2007).

Comparison of sensor versus headspace CO_2 concentrations

We compared CO_2 concentrations produced using the *in situ* sensor method described above with a commonly used headspace method (Kling *et al*., 1992; Hope *et al*., 1995; Dawson *et al*., 2004). The headspace method is widely regarded as the best direct, field-based method for measuring CO_2 concentrations in surface waters. It is based on the equilibration of a specific water : headspace ratio in a sealed syringe, analysis of the headspace in the laboratory using a gas chromatograph (GC) and calculation of dissolved CO_2 concentration using Henry's Law (Kling *et al*., 1991; Billett and Moore, 2008). At two of the sites (Auchencorth Moss and Välipuro) 40 ml of streamwater was equilibrated with 20 ml of ambient air, shaken underwater for 1 min and subsampled in an airtight nylon syringe prior to subsequent analysis. Due to high streamwater CO_2 concentrations, a ratio of 20 ml water : 20 ml headspace was used at Mer Bleue.

At Black Burn (Auchencorth, Scotland), the mean CO_2 concentrations ($n = 11$) measured by the headspace and sensor were 2·88 and 2·52 mg l^{-1}, respectively. The difference between the two methods was significantly different ($t = 3{\cdot}33$, $p = 0{\cdot}004$, $n = 11$). Concentrations plot close to the 1 : 1 line (Figure 7a) and were strongly correlated ($r = 0{\cdot}93$, $p \leq 0{\cdot}001$). A second comparison carried out at Välipuro (Finland) showed that the two methods were not significantly different ($t = 0{\cdot}81$, $p = 0{\cdot}21$, $n = 35$). Mean CO_2 concentrations measured by the headspace and sensor methods were 2·81 and 2·74 mg C l^{-1}, respectively (Figure 7b), with a strong correlation between the headspace and sensor data ($r = 0{\cdot}77$, $p \leq 0{\cdot}001$). A comparison between the two methods made in the Mer Bleue beaver pond (10 cm depth) found that headspace concentrations (mean = 6·88 mg C l^{-1}) were significantly different ($t = 3{\cdot}66$, $p = 0{\cdot}003$, $n = 10$) than sensor concentrations (mean = 8·61 mg C l^{-1}), though headspace and sensor concentrations were also significantly correlated (Figure 7c, $r = 0{\cdot}74$, $p \leq 0{\cdot}05$). A fourth comparison of the measurement of CO_2 using the Vaisala sensor was made using a different indirect 'headspace' method based on a set of samples collected from the Nyänget catchment in northern Sweden (Figure 7d). The samples were characterized by much lower overall CO_2 concentrations than

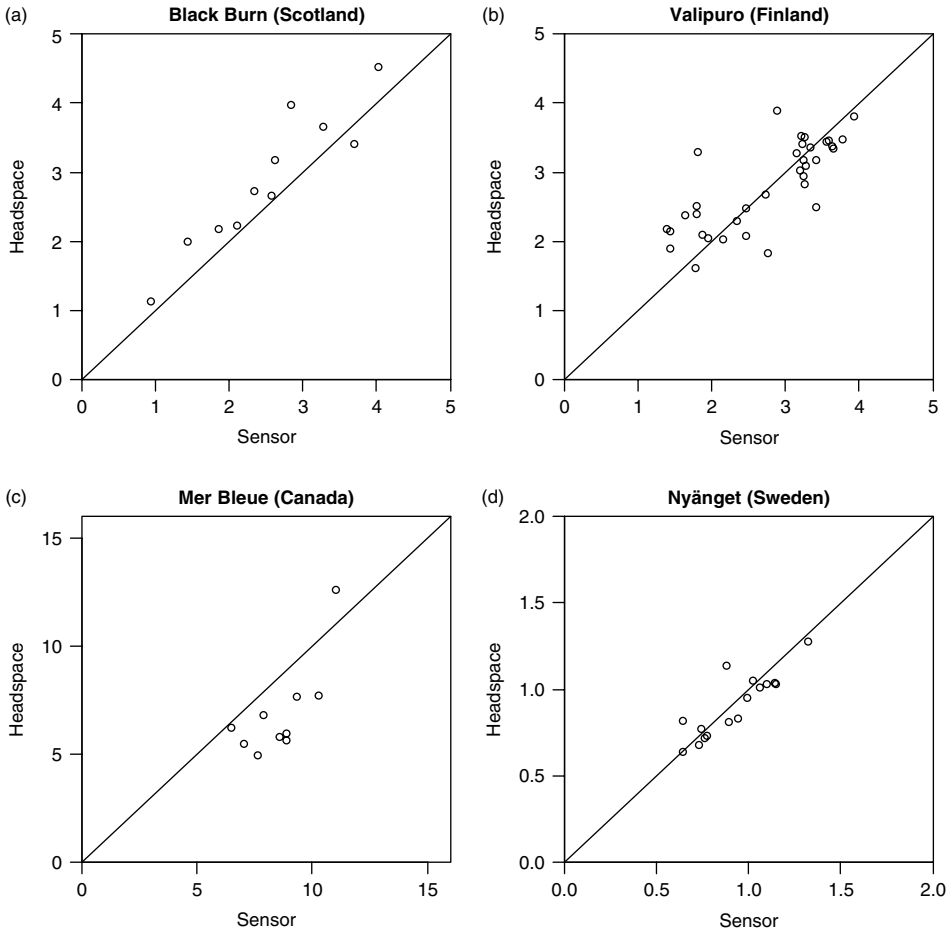

Figure 7. A comparison of CO_2 concentrations (mg C l^{-1}) measured using *in situ* sensors with the headspace method (a–c) and an indirect DIC headspace method (d). The solid line in each panel plots the 1 : 1 line.

DOI: 10.1002/eco

the other sites, with mean CO_2 concentrations of 0·91 (headspace) and 0·92 mg C l^{-1} (sensor). The indirect method involved injecting 5 ml of streamwater into a sealed glass vial using a sterile syringe. Prior to injection, the vial was filled with 0·5 ml of 0·6% HCl and N_2 at atmospheric pressure. Acidification of the sample converts all dissolved inorganic carbon to CO_2, which is then determined by the GC; dissolved CO_2 is then calculated from temperature and pH-dependent equilibria. In the Nyänget intercomparison, CO_2 concentrations plotted close to the 1 : 1 line (Figure 7d), were not significantly different ($t = 0{\cdot}57$, $p = 0{\cdot}29$, $n = 16$) and were strongly correlated ($r = 0{\cdot}86$; $p \leq 0{\cdot}001$).

The most significant methodological difference in absolute CO_2 concentrations occurred in the comparison carried out in standing water (Mer Bleue) at 10 cm depth in a CO_2-rich, high-light, high-temperature environment. In the summer, the beaver pond develops a strong thermocline during the day, associated with a significant increase in CO_2 concentration with depth (Dinsmore *et al.*, 2009). Physical disruption of the water surface during collection of a syringe sample for headspace analysis at 10 cm depth will lead to mixing of shallow and deeper waters and hence a lowering of the CO_2 concentration at the sample point. This will lead to a lower headspace CO_2 concentration compared to the sensor. It should also be noted that while the headspace CO_2 concentration is an instantaneous measurement, the sensor values at Mer Bleue were integrated by the data logging program over a 10-min period which removes some of the short-term fluctuations in CO_2 concentration. This also highlights the advantage of having a static measurement point (the sensor) in a water column which is characterized by a strong vertical CO_2 concentration gradient.

In shallow, well-mixed turbulent streams, strong vertical stratification of CO_2 concentrations is less likely to occur. In the Välipuro comparison, the four samples that plot furthest from the 1 : 1 line were collected during peak flows in the spring snowmelt period. At this time, the water column was up to 140 cm deep, with the greatest distance between the fixed sensor and the headspace sampling depth of 10 cm. The differences in CO_2 concentrations observed at this specific time could imply that the two methods were sampling chemically different (unmixed) parts of the water column.

Any intercomparison of an in-stream measurement with a syringe-based sample for headspace analysis which is analysed remotely in the laboratory also needs to take into consideration the possibility of consistent errors leading to, in this case, a reduction in headspace CO_2 concentrations. These can include 'leaky' syringes (more likely in cold conditions) and the potential for atmospheric contamination when (1) the equilibrated headspace is transferred from the sample syringe to the gas-tight nylon syringe and (2) when the sample is injected into the GC. It should be noted that there are a wide range of approaches that are often termed 'headspace analysis'. Recent advances in headspace analysis include automated GC systems in which losses during analysis are minimized (cf., Waldron *et al.*, 2007).

In terms of studies of temporal variability, when trends rather than absolute concentrations are important, the sensor-based and headspace methods compare reasonably well, although the headspace method produces a rather 'coarse' measurement of change compared to the continuous measurements produced by an in-stream sensor. For this reason, the headspace method is less likely to capture lower amplitude (e.g. diurnal) changes in CO_2 concentrations.

DISCUSSION

The combination of a Vaisala sensor with a gas permeable, water impermeable membrane allows, for the first time, *in situ* measurements of CO_2 concentrations to be made continuously in a range of aquatic systems using an in-stream sensor. This methodological step has the potential to improve our understanding of the processes that affect CO_2 concentrations in a whole range of aquatic systems and to link these to other parts of the terrestrial system, particularly when run in parallel with other *in situ* sensors.

Here we have demonstrated the utility of this method by its use in warm tropical water, groundwater, cold northern temperate surface waters and wetland beaver ponds. We have evaluated the sensor's performance in surface water systems ranging in temperature from 0·3 °C to +26 °C, and in CO_2 saturation from *e*pCO_2 4 to 70 (*e*p refers to excess partial pressure; streamwater with an *e*pCO_2 value of 10 has a pCO_2 concentration 10 times greater than atmospheric CO_2). The Vaisala IRGA has an operating temperature range of −20 °C to +60 °C, and can be factory-calibrated for concentration ranges of 0–2000 ppm pCO_2 up to 0–20% pCO_2 (e.g. 200 000 ppm). The stated accuracy of the sensors is ±1·5% of calibration range +2% of reading (Vaisala Oyj, 2008). For comparison with dissolved gas analysis in water samples using a GC headspace equilibration, the standard operating procedure used by US EPA Region 1 indicates that analysed values should be within 15% of the expected value for QA/QC (Hudson, 2004).

Overall, we have found the sensor output to be stable (e.g. no 'spiking') and reliable, with no need for gap-filling or data-cleaning. The sensors have proven robust, very transportable, flexible and easy to maintain. Long-term drift should be evaluated by checking sensor response prior to and after installation, which is standard practice for any sensor deployment. However, the major advantage of the sensors is their responsiveness and their ability to measure short-term temporal changes in CO_2 concentrations.

Jassal *et al.* (2004) evaluated the Vaisala sensor following 2 months of continuous use while embedded at 20 cm depth in a forest soil, and found no change to the slope or offset of the sensor for post-deployment compared with pre-deployment. We evaluated a sensor

DOI: 10.1002/eco

following more than 6 months deployed in a stream in British Columbia, where dissolved CO_2 concentrations varied eight-fold (0·5–4 mg CO_2-C l^{-1}), and water temperatures ranged from 0·5 to 16 °C. The field-deployed sensor was compared post deployment in parallel with a new, factory-calibrated sensor by placing both new and used sensors within a testing chamber similar to that used to evaluate the PTFE diffusivity. The CO_2 concentration in the chamber was quickly brought to 8000 ppm and allowed to return to ambient concentration over a 1-h period. The sensor that had been in the field performed well within the manufacturer's stated accuracy relative to the factory-calibrated sensor throughout the full range of measurements. Our experience and that of our colleagues (M. Dornblaser, pers. comm.) have found that performance is best assessed by determining sensor-specific output against a range of calibration gases before and after deployment. We recommend that this approach be undertaken to improve accuracy and to evaluate any potential sensor drift during deployment.

The advantages of *in situ* (direct) compared to *ex situ* (often indirect) methods are numerous. This new method has also been shown to be effective in both well-mixed surface waters as well as poorly mixed water columns, where headspace syringe sampling can disturb natural concentration profiles. In addition, while the method detailed here uses the same kind of sensor as that recently described by Hari *et al*. (2008) and aims to achieve the same result, a significant advance is in the ability to deploy a water-tight sensor at the point of measurement. This not only improves precision and response time, but also avoids the need to artificially pump/circulate air to an *ex situ* sensor located above the water surface.

Although the examples described here are for aquatic systems, the sensor has the potential to be deployed in wet subsurface environments, such as saturated peatlands and wetlands and various unsaturated (but frequently wet) soils. Up to now, many soil-based studies of CO_2 cycling have been restricted to near-surface (aerated) horizons (Tang *et al*., 2003; Jassal *et al*., 2004). The potential to make subsurface multi-depth measurements using an array of sensors in both the saturated and unsaturated zones would significantly enhance process-level understanding of C cycling in soils. In addition, our understanding of connectivity between soils and waters will be enhanced by direct *in situ* CO_2 measurements, for example in the study of the link between CO_2 cycles in the soil/riparian/hyperheic zone and the water column (e.g. Dinsmore *et al*. (2009)).

ACKNOWLEDGEMENTS

Development of this method was supported through grants from the Cornell Program in Biogeochemistry and Natural Sciences and Engineering Research Council of Canada to MSJ. MFB, KJD and KD acknowledge the support of the UK Natural Environment Research Council. MW acknowledges funding by the Swedish Research Council; Kevin Bishop and the *Krycklan* crew (especially Peder Blomkvist) are thanked for technical and field assistance.

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