

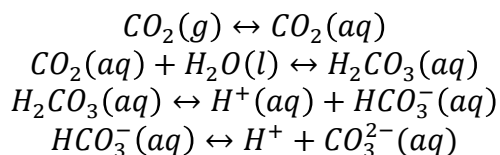
In Situ Measurement of Dissolved Carbon Dioxide in Aquatic Systems using Infrared Gas Analysis

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Introduction

It is known that the level of dissolved carbon dioxide in aquatic systems varies temporally on an annual, seasonal, and daily scale. It is important to understand the concentration dynamics of CO₂ because it has a large impact on the transport, precipitation, and speciation of various compounds. With the ongoing input of anthropogenic CO₂ into the atmosphere it is becoming increasingly important to understand the carbon cycles in their current state to understand what the changes will be in the future. While freshwater ecosystems are generally a net source of CO₂ to the atmosphere, the ocean is the largest sink of global atmospheric carbon through the dissolution into seawater. This process is represented by the chemical equations below (Dickson, Sabine, & Christian 2007).



Depending on the action of carbon sources and sinks within the observed system, these reactions can move in either direction. When more CO₂ is added to the system more carbonic acid is formed, which in turn forms more bicarbonate (releasing a Hydrogen ion), which in turn forms more carbonate ions (releasing another Hydrogen ion).

Therefore, as the partial pressure of Carbon dioxide in the atmosphere increases the dissolved CO₂ in seawater will increase and raise the concentration of H⁺ ions. The relationship of pH to H⁺ concentration is noted below (Dickson, Sabine, & Christian 2007).

$$pH = -\log [H^+]$$

This is the mechanism by which the increasing CO₂ level in the atmosphere equates to a more acidic environment in the ocean. This is an important aspect of the environment to monitor because there are many marine ecosystems that are sensitive to changes in acidity, the most well understood of which are coral reefs. The technique in this paper describes an experimental system to measure dissolved carbon dioxide in water that uses an infrared gas analyzer (IRGA) by using a non-dispersive infrared (NDIR) sensor. The CO₂ gas being measured is acquired through a gas-permeable membrane that is submerged in the environment the experimenter wants to observe. Data retrieved using this technique presents the best combination of high accuracy and high temporal frequency (Johnson *et al* 2010).

Analysis Technique: Comparison to Previous Methods

The most common indirect method of measuring CO₂ involves measurements of pH and alkalinity and requires calculation of

dissolved CO₂ based on temperature-dependent equilibrium constants. While this method does allow for continuous measurement, most pH measurements are made with a ±0.2 pH error margin, making its effectiveness quite low at determining the minute diurnal changes of aquatic ecosystems. One of the more commonly used direct methods of measurement involves the analysis of the air within the headspace of sample containers. The idea behind this is to allow the CO₂ gas to equilibrate with the empty space above the water in the container and calculate the CO₂ content in the water based on conditions such as pressure, volume, and temperature. For headspace analysis to be accurate to an acceptable degree the samples must be analyzed manually, generally done in 24 to 48 hour increments, and are usually *ex situ* (Hudson 2004). The NDIR method provides the ability to take continuous measurements *in situ* at a high degree of accuracy. The system is also considerably less complex than previous methods, leaving less room for error and having the benefit of lower cost. The importance of collecting continuous measurements with the resolution to detect small changes is high because there is a large range of dissolved CO₂ sinks and sources that can have effects at different points in time. In order to understand the concentration dynamics of any system it is necessary to record data with the appropriate temporal frequency. The use of infrared gas analyzers is not new to the study of CO₂ in water, but until recently they were only used in a laboratory setting (Johnson *et al* 2010).

Analysis Technique: Materials and Procedure

The construction of the IRGA device for this technique includes an IR light source, gas bench, and NDIR detector

housed within a cylindrical waterproof polytetrafluoroethylene (PTFE) membrane. A rugged exterior housing is required in order to protect the membrane from damage by passing debris or turbulence because the membrane itself is relatively fragile. This rugged barrier can be achieved by a metal cage or even PVC pipe that is wide enough for the device's geometry. It is also necessary to seal the infrared light source and the NDIR detector from interaction with water, as they are vulnerable to malfunction if wet. A simple method of solving this problem is to apply a coating of some waterproof substance such as PlastiDip, a rubberizing compound that provide an effective waterproof barrier covering the electronics at the interface between the measurement devices and the PTFE membrane. This rubberizing sealant also provides a way to adhere the membrane to the light source and detector. The membrane is also subject to blockage by various aspects of the environment. Biofilms can form around the device which will decrease the diffusivity by physically blocking the diffusion process between the environment and the gas chamber. High turbidity waters can also present a similar issue of membrane blockage and must be manually cleaned on a regular basis. Because the company that supplies the PTFE material does not provide the diffusivity characteristics it must be calculated in laboratory setting. The following equation can be used to derive changes in carbon dioxide concentrations (Johnson *et al* 2010).

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

The dC/L term represents the concentration gradient between the environment and that of the inside of the gas chamber (concentration of CO₂ in the chamber over the CO₂ concentration of the environment),

ΔC is the change in chamber concentration over a ten second time interval (t), V is the volume of the chamber, A is the surface area covered by the PTFE material, and D is the diffusivity coefficient with respect to CO_2 . The value for D has been experimentally determined as $0.08 \text{ cm}^2 \text{ s}^{-1}$ with an uncertainty estimated at $\pm 0.01 \text{ cm}^2 \text{ s}^{-1}$. After the diffusivity is determined for the membrane material it is possible to solve for the concentration gradient for any field data obtained. ΔC is measured from the spectral value collected by the NDIR detector and all other values are held constant. The data that is collected for the concentration gradient is subject to error from the environmental factors that must be correct for such as atmospheric pressure and temperature. Increases in water temperature cause lower output by the sensor, while an increase in pressure will increase the output by the sensor. The following equation represents the temperature corrections that must be made on the experimental data (Johnson *et al* 2010).

$$(\pm 0.003)\Delta T_s O_p = O_c$$

Where ΔT_s is equal to the degree difference from the standard (25°C), the positive or negative on the correction factor is inversely dependent upon the temperature difference (positive for temperatures below stand, negative for temperatures above standard). O_p is the pre-corrected output from the sensor and O_c is the corrected output. This equation shows that there is a 0.3% change in sensor output per degree centigrade. The following equation represents the pressure corrections that must be applied to sensor output (Johnson *et al* 2010).

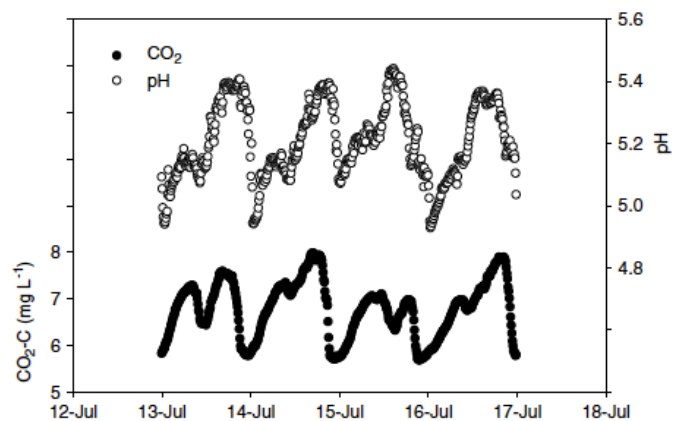
$$(\pm 0.0015)\Delta P_s O_p = O_c$$

Where ΔP_s is equal to the pressure difference from the standard (1013 hPa), the positive or negative on the correction factor is directly dependent upon the pressure difference (positive for pressures above

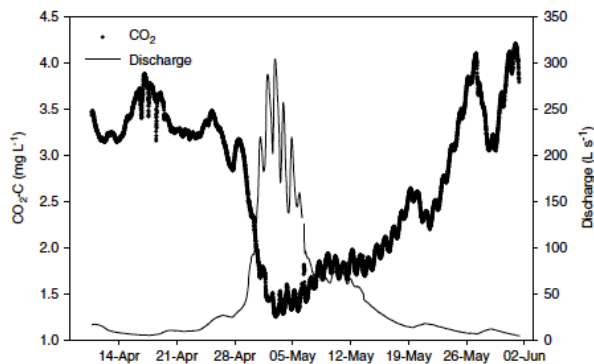
standard, negative for pressure below standard). This equation shows that there is a 0.0015% change in sensor output per hectopascal. The need to make continuous corrections for pressure differences can be eliminated by attaching the device to a float that rise and falls with the water level, keeping the pressure around the sensor constant (Johnson *et al* 2010).

Experimental Application

It is known that the dissolved CO_2 level in aquatic ecosystems fluctuates during the day due to various carbon sources and sinks. A study was done during the summer of 2007 on the edge of beaver ponds in the Mer Bleue peat lands of Canada. The sensor system described in this paper was deployed in the drainage waters of one of the ponds that generally have a high concentration of carbon dioxide. Because the *in situ* infrared gas analyzer system is able to take continuous measurements, small-scale (increments of 10 minute averages) temporal changes were detected. Detailed comparison to other parameters revealed that solar radiation and temperature play the largest role in determining the fluctuations. The figure below illustrates the diurnal variability in both CO_2 and pH (Dinsmore *et al* 2009).

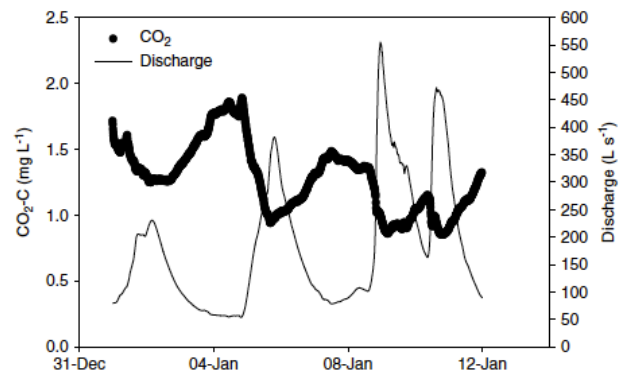


The *in situ* IRGA method has also been used to determine the relationship between spring snowmelt discharge events at high latitude locations in the Vällipuro catchment of Finland. The results from this experiment showed a clear inverse correlation between the rate of discharge and the concentration of dissolved carbon dioxide, simply caused by dilution due to the significantly increased water input. The water temperature at this site ranged from -0.3°C to 5.4°C , demonstrating that the sensor can operate under extreme cold conditions (Dawson *et al* 2004). This study also revealed another benefit to the measurement technique, in conditions where the surface water is frozen the device can be deployed at a depth that is unaffected by the freezing water. The figure below illustrates the inverse correlation between CO_2 and discharge using data obtained from the IRGA (Johnson *et al* 2010).



A similar experiment was carried out in Black Burn, Scotland to analyze the relationship with stormflow events. In this experiment an inverse relationship was observed between stream discharge and CO_2 , but the effects were less pronounced than that of the experiment in Finland. The smaller amplitude correlation could indicate that the groundwater feeding the stream is rich in carbonate minerals, thus being an input of inorganic carbon in conjunction with dilution of the stream water. The figure below shows a similar

relationship as displayed in the experiment from Finland but with smaller amplitude of variation (Johnson *et al* 2010).



All of the experiments above were carried out simultaneously with a headspace analysis technique of measuring CO_2 , which is the most common method for taking measurements in the field. The headspace method is based on the equilibration of water extracted in a syringe with the headspace of air in the syringe. Analysis of the syringe headspace was carried out in a laboratory setting using a gas chromatograph. A ratio of 20 ml of water to 20 ml of air headspace was used. There is a strong positive correlation between the data obtained for all experiments but there are statistically significant differences between headspace data and IRGA data for the Canada peat land study. The difference in values from the Canada study can be explained by the fact that the data was obtained from shallow standing water, in which a strong thermocline develops during the day. Due to the thermocline, there is a smaller concentration of carbon dioxide near the surface. The surface was disturbed when inserting the syringe to extract a sample and may have caused mixing of the shallow water column significant enough to cause a decrease in CO_2 concentration at the 10 cm measurement depth. This error reveals another advantage to the IRGA method because it does not require surface water

disturbance in order to take a measurement (Johnson *et al* 2010).

Discussion

Here the utility of the *in situ* IRGA method has been demonstrated in several environments and has been strongly correlated to the most common accepted technique. The benefits of this technique over previous methods include on-site data collection, high accuracy, simple design, low cost, high temporal frequency of measurements, and widespread application possibilities. As shown in the experimental data, another advantage to the technique is that it collects data without mixing the water column, allowing observation of the environment in its most natural state. While

the studies reported in this paper only examine freshwater systems it is also possible to use this technique to monitor fluxes in seawater and moist soils. CO₂ concentration is a very important parameter when analyzing an environmental system because it can reflect changes in ecological productivity and indicate variations in pH. With a constantly increasing concentration of carbon dioxide in the atmosphere it is becoming more important than ever to monitor the concentrations in aquatic environments, especially where ecosystems are highly vulnerable to pH swings such as coral reefs. The use of *in situ* infrared gas analyzers has been shown to be the best method when continuous measurements of dissolved carbon dioxide are required.

References

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