A SIMPLE, DIRECT METHOD TO MEASURE DISSOLVED CO_2 USING SODA LIME

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ABSTRACT

A method for the direct assessment of the dissolved CO_2 concentration in supersaturated water is presented that is based on changes to the physical chemistry of soda lime due to uptake of CO_2. The approach is an adaptation of a standard method used for the quantification of soil respiration, and was found to agree with pCO_2 measurements made using infrared gas analysis. In this method, the soda lime is deployed in a CO_2 bucket chamber, and a water sample is allowed to outgas for 48 hours. The initial dissolved CO_2 concentration is then determined from changes in the dry mass of soda lime, which is blank-corrected and adjusted based on differences in molecular weights of soda lime before and after the chemical adsorption of CO_2. The method is applicable to highly-supersaturated surface water and emergent groundwater.

Keywords: Outgassing, soda lime, respiration, water quality, carbon cycle.

RESUMO

UM MÉTODO SIMPLES PARA A MEDIÇÃO DE CO_2 DISSOLVIDO EM ÁGUAS SUPERSATURADAS UTILIZANDO CAL SODADA. Este estudo descreve um método para avaliar a concentração de CO_2 dissolvido baseado em mudanças químicas da cal sodada relacionadas à absorção de CO_2. O método é uma adaptação de um método padrão na quantificação de respiração do solo, e apresentou resultados concordantes com as medidas de pCO_2 realizadas por analisador de gás no infravermelho (IRGA). Neste novo método, a cal sodada é colocada em uma câmera e a amostra de água é mantida liberando o CO_2 por 48 horas. A concentração de CO_2 dissolvido é calculada pela mudança na massa de cal sodada depois de corrigida pelo branco e ajustada pelas diferenças na massa molecular de cal sodada antes e depois da absorção química de CO_2. O método é aplicável em córregos e em nascentes de águas superficiais quando estão supersaturadas por CO_2.

Palavras-chave: Evasão de CO_2, cal sodada, respiração, qualidade d'água, ciclo de carbono.

INTRODUCTION

Hydrologic exports of carbon (C) from watersheds represent a key connection between terrestrial and aquatic ecosystems. Hydrologic C exports occur in a variety of forms and size fractions, including organic C in particulate (Selva *et al.* 2007) and dissolved phases (Johnson *et al.* 2006a, Waterloo *et al.* 2006), as well as inorganic C in particulate and dissolved phases (McClain & Naiman 2008, Richey *et al.* 1990). While terrestrially-derived organic C phases are crucial to downstream ecological functioning in larger streams and rivers (Gomi *et al.* 2002), inorganic C can be an even greater hydrological flux from the landscape to streams when CO_2 concentrations are also considered (Johnson *et al.* 2008).

Dissolved inorganic carbon (DIC) occurs as carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and as dissolved CO_2, with their relative contribution to total DIC dependent upon the pH of the water in question. Dissolved CO_2 has the further consideration of occurring as a gas (e.g. true dissolved CO_2, where molecules of CO_2 are surrounded by water molecules) and also as carbonic acid (H_2CO_3). However, because only about 0.15% of dissolved CO_2 occurs as H_2CO_3 (Butler 1982), it is reasonable to ignore the carbonic acid fraction when quantifying dissolved CO_2.

There is currently a great deal of interest in resolving hydrologic C exports as a means of reducing uncertainties in terrestrial carbon balances (Richey *et al.* 2002). Cole *et al.* (2007) note that there is an important gap in our knowledge about the role of small streams regarding carbon fluxes from terrestrial sources, and that streamwater C exports could help resolve carbon balances of catchments. Waterloo *et al.* (2006) estimated DOC exports by streamwater in a central Amazon watershed to account for 5-6% of the apparent C accumulation in terrestrial soils and vegetative biomass from eddy covariance measurements. As fluxes of dissolved CO_2 and bicarbonate in headwater streams result largely from terrestrial respiration (Cole *et al.* 2007), these fluxes are essential to fully quantify terrestrial respiration. For example, exports of dissolved CO_2 by headwater streams can be several times greater than DOC exports (Fiedler *et al.* 2006; Johnson *et al.* 2006b; Johnson *et al.* 2008).

Established techniques for routine measurement of dissolved CO_2 have been utilized for several decades, including the commonly used headspace equilibration technique (Kling *et al.* 1991), where the water sample is collected in a syringe and equilibrated with headspace air, with the headspace subsequently analyzed on a gas chromatograph (GC) or an infrared gas analyzer (IRGA). This represents an improvement on approaches that determine dissolved CO_2 concentrations indirectly from measurements of pH and alkalinity, as pH is difficult to measure with sufficient accuracy in natural waters (Frankignoulle & Borges 2001). Recent developments in environmental sensors have resulted in the ability to measure dissolved CO_2 directly and *in situ* using a rugged IRGA equipped with a waterproof and gas-permeable membrane (Johnson *et al.* 2007).

What remains lacking, however, is an inexpensive and direct method that would allow for routine measurements at a large number of locations without the need for subsequent analysis on a GC or IRGA. In this paper we present a method that resolves this analytical problem and can be employed in a range of settings requiring only basic laboratory equipment and soda lime. This technique was developed for measuring dissolved CO_2 concentrations in emergent groundwater draining acidic tropical soils. Herein we consider the application of the technique in the context in which it was developed: direct quantification of dissolved CO_2 concentrations in supersaturated groundwater at the terrestrial-aquatic interface.

MATERIALS AND METHODS

The methodology employed in this study is an adaptation of the soil respiration method of Edwards (1982) which uses soda lime to chemically sequester CO_2. The approach is based on the chemical reaction between CO_2 and hydroxides of calcium and sodium in the soda lime, which are converted to carbonate forms upon through chemical uptake of CO_2 as:

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \qquad (1)$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3 \qquad (2)$$

The amount of CO_2 taken up can then be determined by the weight change of the soda lime during its exposure to CO_2, after adjusting for differences in molecular weights of CO_2 and H_2O (Grogan 1998). This soil respiration method requires only that the dry mass of soda lime be determined before and after the exposure to CO_2.

We adapted this soil respiration method for use in evaluating the dissolved CO_2 concentration of aqueous samples through the use of a bucket chamber. To measure soil respiration, soda lime is placed within a static soil chamber (Edwards 1982). Here, the dissolved CO_2 concentration is determined by placing soda lime within a static bucket chamber, where the soda lime acts as a large sink for CO_2. The soda lime will absorb all CO_2 evading from the water, and will maintain near zero concentration of CO_2 in the bucket headspace. This ensures a continuous concentration gradient between the water and the headspace so that CO_2 will evade from the water sample until it is completely depleted. Specific details of the soda lime preparation and use are presented in the Procedures section. In this paper, we first describe the CO_2 bucket chamber construction and parts, followed by a description and assessment of its use.

CO_2 BUCKET COMPONENTS AND CONSTRUCTION

The bucket chamber contains a lower section where 5L of the aqueous sample is introduced, and an upper section where the soda lime is placed (Figures 1 and 2). The lower section consists of a bucket with a tightly-fitting lid, a faucet through which the water sample flows into the bucket, and a mark indicating the water depth in the CO_2 bucket chamber when it contains 5L. The faucet serves two purposes. It allows for CO_2-free air to be pumped into the bucket in order to flush ambient CO_2 from the CO_2 bucket chamber prior to soda lime and sample introduction. This CO_2-free air is generated in the field by connecting a bicycle pump to a soda lime trap, which is then connected in-line by a hose connector to the faucet (Figure 3). The faucet also allows for introduction of the water sample into the CO_2 bucket chamber. For CO_2 determination of emergent groundwater, gravity flow of groundwater through a tube connected to the point of groundwater emergence ensures that the water to be sampled enters the CO_2 bucket chamber without prior interaction with the atmosphere, thus avoiding any CO_2 evasion prior to CO_2 measurement.

Figure 1. Photograph of CO_2 bucket chamber.

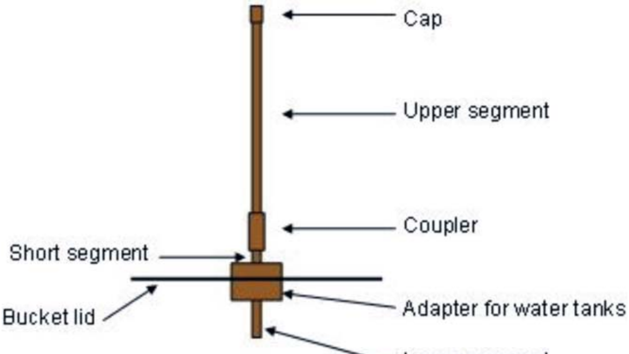

Figure 2. Diagram of PVC segments of CO_2 bucket chamber.

The top section of the CO_2 bucket chamber consists of a PVC adapter for water tanks connected to upper and lower PVC segments (20mm outside diameter; Figure 2). The small diameter PVC was chosen to provide a sufficiently long air-flow path to ensure complete interaction between CO_2 and soda lime along the air-flow path. The lower segment serves as a recipient for the pre-dried and pre-weighed soda lime for quantitative analysis. The bottom of this lower segment is fitted with fine mesh to maintain the soda lime above the water sample while allowing CO_2 to diffuse into the pre-dried soda lime. The upper portion of the PVC adapter is connected to a segment of PVC containing soda lime that has the purpose of isolating the lower segment from atmospheric CO_2. The upper segment of PVC has holes drilled in its upper 10cm to allow air flow, and the holes are covered with fine mesh to keep the soda lime from spilling out of the upper segment while preventing insects from entering. This air-flow is necessary for air displacement during the CO_2-purging prior to sample placement, as well as air displacement when filling the bucket with the water sample.

The top of the upper segment of PVC is firmly capped, while the lower portion of the upper segment is fitted with fine mesh to prevent soda lime from exiting the upper segment. This upper segment of PVC is connected to the tank adapter by means of a PVC coupler and a short segment of PVC (Figure 2). The shorter segment of PVC connected to the upper end of the tank adapter can be filed down slightly to facilitate removal of upper PVC segment. Removal of the upper section is required for placement and retrieval of soda lime in the lower PVC segment that is connected to the lower end of the tank adapter, as described in the following section.

PROCEDURES FOR USE OF THE CO_2 BUCKET CHAMBER

SODA LIME PREPARATION FOR QUANTITATIVE ANALYSIS

Soda lime for quantitative analysis is prepared in the laboratory by oven-drying granular soda lime at 105°C for 24 hours. The soda lime is then allowed to cool in a desiccator. It is then weighed into numbered soil tins which are immediately closed and sealed, and the mass of the soda lime is recorded. Weighing of soda lime and the sealing of the soil tins should proceed as rapidly as possible in order to minimize the amount of CO_2 adsorbed during handling of the soda lime. About 5g of dried soda lime is sufficient for quantifying the CO_2 of a 5L sample of CO_2-supersaturated groundwater. Since the final determination of CO_2 only depends on the mass gained by soda lime during its exposure to CO_2, it is acceptable to use an amount of soda lime that varies by ± 1g between samples.

The mass of soda lime will increase as a result of the exposure to CO_2 evading from the water sample, but soda lime mass will also increase due to CO_2 exposure during handling. Because of this, copious use of analytical blanks in parallel with CO_2 measurement is essential (Raich *et al.* 1990). Blanks should be prepared and deployed to CO_2 bucket chambers in precisely the same manner as the soda lime for CO_2 determination, with the only difference being that the CO_2 bucket chambers for the blanks are not filled with water.

CO_2 BUCKET CHAMBER PREPARATION AND USE

The CO_2 bucket is prepared prior to placement of the pre-dried and weighed soda lime. The upper PVC segment is filled with soda lime and connected to the PVC coupler. The soda lime used to fill the upper PVC segment does not need to be pre-dried nor weighed. The lid with attached PVC segments is then attached to the bucket chamber. A bicycle pump is then connected inline to a soda lime trap and the CO_2 bucket chamber (Figure 3), the faucet is opened, and CO_2-free air equivalent to twice the bucket volume is pumped through the CO_2 bucket chamber. A good seal of the lid on the bucket must be ensured and can be checked by inspecting for leaks at the bucket/lid connection using soapy water. Air should exit the CO_2 bucket chamber only through the holes on the upper PVC segment. Following the pumping of CO_2 free air through the bucket chamber, the faucet is closed, and the pump is disconnected.

With the lid still attached to the bucket, the upper PVC segment is then temporarily disconnected, and the pre-dried soda lime for quantitative analysis is placed in the lower PVC segment. A funnel facilitates the rapid transfer of the soda lime from the sealed soil tin to the CO_2 bucket chamber. The hose for delivery of the water sample to the CO_2 bucket chamber is then connected and the faucet is opened, allowing the bucket to fill up to the 5L mark. Once filled, the faucet is closed and the hose is disconnected. The pre-dried soda lime is allowed to absorb CO_2 evading from the water sample for 48 hours.

After filling the CO_2 bucket chamber with the water sample, the blank is deployed in an additional CO_2 bucket chamber. For the blank, CO_2-free air is pumped though the bucket chamber as before, and the pre-dried soda lime for the blank is placed in the lower PVC segment. Greater analytical precision can be obtained by using three CO_2 bucket chambers for soda lime samples and three CO_2 control bucket chambers for soda lime for each sampling site.

Figure 3. Photograph of flushing of CO_2 bucket chamber with CO_2-free air prior to soda lime placement.

DETERMINATION OF CO_2 CONCENTRATION BY SODA LIME

Following 48 hours of exposure to CO_2 evading from the water sample, the soda lime from the sample and blank CO_2 bucket chambers are collected. The lid is gently disengaged from the bucket, the upper PVC segment is removed, the soda lime is carefully and rapidly transferred into the corresponding soil tins using a funnel to avoid loss of the soda lime, and the soil tins are sealed for transport. The soda lime is then dried again for 24 hours at 105°C, allowed to cool in a dessicator, and weighed. Differences in the mass of soda lime are due to the adsorption of CO_2 after adjusting for differences in molecular weight of CO_2 and H_2O (Grogan 1998). If multiple CO_2 bucket chambers are used to increase analytical precision, the mean of the soda lime blanks should be subtracted from the mean of the soda lime samples.

The initial dissolved CO_2 concentration is determined by subtracting the mass gained by the soda lime used in the blank CO_2 bucket chamber from the mass gained by the soda lime used in the sample CO_2 bucket chamber. This blank-corrected value is multiplied by 1.69 to adjust for differences in mass between (a) the $CaCO_3$ in soda lime following adsorption of CO_2, and (b) the $Ca(OH)_2$ in soda lime prior to chemical adsorption of CO_2 (Grogan 1998). As an example, assume that 5.232g of oven-dried soda lime is exposed to supersaturated emergent groundwater in the CO_2 bucket chamber for 48 hours, after which its oven-dried mass is 5.504g. Also in this example, 4.681g of oven-dried soda lime used in the blank CO_2 bucket chamber has a final dry mass of 4.742g. The mass gain of the blank of 0.061g is subtracted from the mass gain of the sample of 0.272g, resulting in a blank-corrected soda lime mass gain of 0.211g. This value is multiplied by 1.69 to adjust for differences in molecular weights (Grogan 1998), resulting in a CO_2 mass accumulated by the soda lime of 0.357g CO_2. As this amount was captured from CO_2 evading from 5L of water, we divide it by 5L to solve for the dissolved CO_2 concentration: 0.071g of CO_2 L^{-1} or 71.4mg CO_2 L^{-1}, which is equivalent to 19.45 mg CO_2-C L^{-1}. If a different volume is used in the bucket, the adjusted mass accumulated by the soda lime would be divided by the volume of water that was introduced into the bucket.

There is the possibility to use the dissolved CO_2 concentration determined by soda lime to estimate the potential CO_2 evasion from water to the atmosphere. For CO_2-supersaturated groundwater with low concentrations of DOC, the potential CO_2 evasion is the equivalent to the dissolved CO_2 concentration at the time of sampling, assuming that the groundwater DOC is of low bioavailability, and that little of this groundwater DOC is respired to CO_2 by microbial activity during the 48 hour period. If sample water used with this method has an appreciable concentration of DOC that is not recalcitrant (e.g., a stream water sample), the CO_2 concentration determined will include both the CO_2 initially in solution plus the CO_2 generated by microbial activity. As the soda lime acts as a large sink for CO_2, the CO_2 bucket chamber results include both the CO_2 in excess of atmospheric equivalence as well as CO_2 equivalent to atmospheric concentration (0.15 CO_2-C L^{-1} at 25°C; Johnson *et al.* 2006b).

ASSESSMENT

We developed this method to measure dissolved CO_2 concentrations in an effort to characterize CO_2 fluxes from emergent groundwater in forested headwater catchments in the Brazilian Amazon. A description of the site can be found in Johnson *et al.* (2006b) and Johnson *et al.* (2006a).

Soda lime (6-8 mesh size) was purchased from a medical supplier in Cuiabá, a medium-sized city in interior Brazil. The drying oven used in the field laboratory was a domestic electric oven with thermostat control that was purchased locally. We placed a glass and mercury laboratory thermometer in the oven to ensure that the temperature was no less than 105°C during the drying of soda lime. Temperatures in the oven fluctuated between 105°C and 130°C, which is acceptable for the purpose of removing moisture from the soda lime without affecting its physical structure.

The length of time required for complete CO_2 evasion from emergent groundwater samples was determined experimentally, and found to take 48 hours (Figure 4). We used three CO_2 bucket chambers per time period with accompanying blanks, and found that a second-order equation fit the data quite well (R^2=0.99). The modeled peak was found to occur at 57 hours, however actual CO_2 accumulated in the first 48 hours represented 98% of the theoretical maximum. Considerations of logistical constraints suggest that 48 hours of exposure is the minimum time for soda lime in the CO_2 bucket chambers, with a maximum time of exposure of 60 hours. However, as times could vary for other sites based on temperature and CO_2 concentrations, the length of time required should be determined based on local conditions.

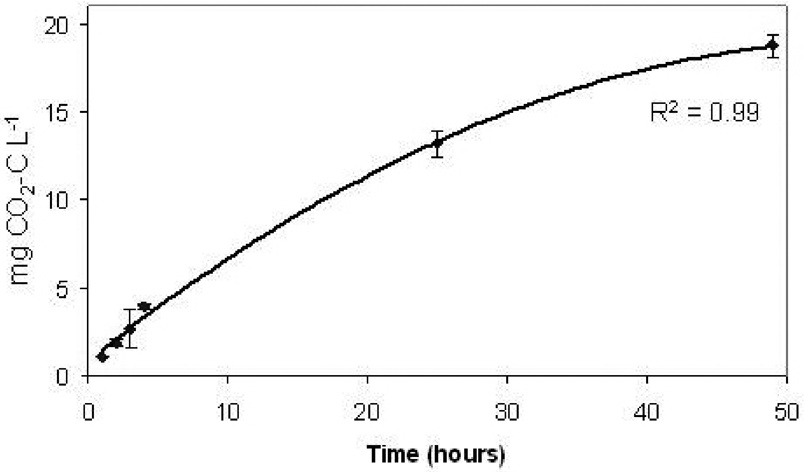

Figure 4. Determination of CO_2 captured by CO_2 bucket chamber as a function of length of exposure. The results indicate that an exposure time of 48 hours is sufficient to characterize the dissolved CO_2 concentration of emergent groundwater that is highly super-saturated with CO_2.

We also determined the CO_2 concentration *in situ* for the focused points of groundwater emergence using infrared gas analysis following Johnson *et al.* (2006b). The results of the two methods agreed quite well. The mean CO_2 concentration for emergent groundwater determined by IRGA was 19.9±1.8mg L^{-1} CO_2–C (Johnson *et al.* 2006b), whereas for the bucket chambers we found 18.7±1.4mg L^{-1} CO_2–C. It should be noted that these two methods assess the concentration of dissolved CO_2 using very different approaches. The CO_2 bucket chamber method of the present paper is based on changes to the physical chemistry of soda lime to determine the potential evasion of CO_2 from a water sample. The IRGA method determines the CO_2 concentration of water based on absorbance of infrared light by CO_2 within the gas bench of the IRGA. That the methods agree so well suggests that these two different approaches can be used in a complementary manner.

DISCUSSION AND RECOMMENDATIONS

This method was developed to assess the dissolved CO_2 concentration of surface waters and of emergent groundwaters. For both cases, we filled the CO_2 bucket chambers via gravity flow. Due to the gentle topography in the study area, this approached required a hose length of approximately 15m in order to for the hydraulic head to be sufficient to fill the CO_2 bucket chamber up to the 5L mark. In areas with steeper topography, a shorter hose length may be possible. It should also be possible to use an electric pump to fill the CO_2 bucket chamber with surface water without compromising the results. We have not attempted to pump groundwater from a well to the CO_2 bucket chamber, as it would be difficult to ensure that no CO_2 evades into the air space of the groundwater well prior to reaching the CO_2 bucket chamber.

Commercially-available granular soda lime typically contains an indicator dye that changes color when the soda lime is exhausted (e.g. saturated by CO_2). The soda lime in the upper segment should be checked periodically, and exchanged for fresh soda lime if a color change is present. Additionally, the soda lime used for samples and blanks should be from the same manufacturer's lot for all comparable samples/blanks, although the soda lime used on different sampling dates need not be from the same manufacturer's lot. An analytical balance with milligram (0.001g) precision is suitable for use in highly supersaturated water. If a balance with precision of hundredths of a gram (0.01g) is the best available, the use of replicate samples is essential to improve the precision of the CO_2 determinations. While it may not be ideal to leave CO_2 bucket chambers in the field during the 48 hour evasion period, it is unlikely that the CO_2 bucket chambers could be transported from the field during the 48 hour equilibration period without compromising the soda lime by splashing the water sample.

In summary, the methodology for assessing the potential CO_2 evasion of water using the CO_2 bucket chamber is an approach that can be deployed in a range of environments. It is particularly suitable for water that is highly super-saturated with CO_2, and has the advantages of being a direct and low cost method. The method provides a means for assessing of the CO_2 concentration of low DOC groundwater at the point of emergence at the time of sampling, as well as an approach for determining the potential CO_2 evasion of surface water containing bioavailable DOC. Caution should be taken in the interpretation of results for which there is not a large difference in mass gain between the soda lime used for the water sample CO_2 bucket chambers and the soda lime of the CO_2 bucket chambers used as blanks.

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