



Determination of free CO₂ in emergent groundwaters using a commercial beverage carbonation meter

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SUMMARY

Dissolved CO₂ in groundwater is frequently supersaturated relative to its equilibrium with atmospheric partial pressure and will degas when it is conveyed to the surface. Estimates of dissolved CO₂ concentrations can vary widely between different hydrochemical facies because they have different sources of error (e.g., rapid degassing, low alkalinity, non-carbonate alkalinity). We sampled 60 natural spring and mine waters using a beverage industry carbonation meter, which measures dissolved CO₂ based on temperature and pressure changes as the sample volume is expanded. Using a modified field protocol, the meter was found to be highly accurate in the range 0.2–35 mM CO₂. The meter provided rapid, accurate and precise measurements of dissolved CO₂ in natural waters for a range of hydrochemical facies. Dissolved CO₂ concentrations measured in the field with the carbonation meter were similar to CO₂ determined using the pH-alkalinity approach, but provided immediate results and avoided errors from alkalinity and pH determination. The portability and ease of use of the carbonation meter in the field made it well-suited to sampling in difficult terrain. The carbonation meter has proven useful in the study of aquatic systems where CO₂ degassing drives geochemical changes that result in surficial mineral precipitation and deposition, such as tufa, travertine and mine drainage deposits.

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1. Introduction

Dissolved CO₂ in groundwater is frequently supersaturated relative to its equilibrium with atmospheric partial pressure. Processes contributing to CO₂ in groundwater include terrestrial respiration, the oxidation of buried organic matter in shallow sediments (Pentecost, 2005), acid neutralization reactions with carbonate minerals (Choi et al., 1998), and migration from magma bodies (De Gregorio et al., 2011; Nordstrom et al., 2005; Ray et al., 2009). The upward migration of fossil fuel-derived CO₂ from proposed deep subsurface geologic disposal sites may also introduce exogenous CO₂ to groundwater aquifers in the future (Kharaka et al., 2010).

When groundwater with elevated CO₂ reaches the surface via springs, wells, mines, or direct pumping, CO₂ will degas towards equilibrium with the atmosphere, increasing both the pH of the water and its saturation state with respect to carbonate minerals (Mörner and Etiope, 2002). Mineral supersaturation can result in the formation of calcareous travertine and tufa deposits from

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waters containing relatively high concentrations of dissolved calcium (Herman and Lorah, 1987; Jones and Renault, 2010; Pentecost, 2005). The increase in pH can also accelerate the rates of Fe(II) oxidation and Fe(III) hydroxide formation in net alkaline mine drainage (Kirby et al., 2009). Recent studies have shown that the efflux of CO₂ from streams needs to be considered in the carbon cycle (Butman and Raymond, 2011). Geochemical studies of these waters require accurate estimates of dissolved CO₂ levels to predict and characterize precipitation and dissolution reactions.

1.1. Methods of measuring dissolved CO₂ in natural waters

1.1.1. pH-alkalinity titrations

Assuming that carbonate species are in equilibrium and that pH and alkalinity are controlled by carbonate geochemistry, any paired combination of pH, alkalinity and total dissolved inorganic carbon (DIC) can be used to indirectly calculate dissolved CO₂ (De Gregorio et al., 2011). However, small errors in pH field measurements strongly influence dissolved CO₂ estimation and depend on close attention to equipment maintenance, electrode calibration and performance, and field conditions (Macpherson, 2009). Additionally, changes in sample pH can occur shortly after sampling due to degassing or in-gassing of environmental gases (e.g. O₂, CO₂, H₂S and NH₃), mineral precipitation (e.g. calcium carbonate

or iron oxyhydroxides), microbial respiration, and other factors (American Public Health Association, 2005; Cioni et al., 2007; Neal, 2001).

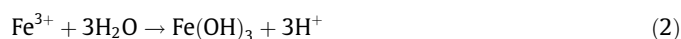
Alkalinity is commonly measured using an acidimetric titration in which an acid is added to a known volume of sample to reach an endpoint pH of 4.5, the equivalence point where the molar concentrations of bicarbonate and hydrogen are equal (Stumm and Morgan, 1996). A Gran titration is often used to linearize the titration curve using pH endpoints of 4.2 and 3.9, especially in waters of low alkalinity (American Public Health Association, 2005; Thomas and Lynch, 1960).

Acidity can be measured using an alkalimetric titration (American Public Health Association, 2005; Neal, 1988) and also used to determine CO₂. In this method, a base is added to a known volume of sample to reach a pH endpoint of 8.3, the equivalence point at which the molar concentrations of bicarbonate and hydroxide are equal (Stumm and Morgan, 1996). This method is the basis for CO₂ colorimetric test kits that use phenolphthalein as the endpoint indicator (e.g. Hach Carbon Dioxide Test Kit, Model CA-23, Hach Company, Loveland, CO).

Titration methods are based on charge balance and do not determine the specific chemical species present; the results are therefore best reported as m eq/L or eq/L, so that no assumption need be made about the contributing species. However, the estimation of CO₂ from either titration method typically assumes that total alkalinity equals the carbonate alkalinity and that the solution is in geochemical equilibrium. Therefore, the presence of non-carbonate acidity and alkalinity will result in an incorrect determination of CO₂. For example, particulate metal oxyhydroxides, common in mining waters, will dissolve at low pH.



The consumption of acidity in this reaction results in total alkalinity greater than the carbonate alkalinity and an overestimate of P_{CO₂}. Filtration of water samples may only partially eliminate this problem since iron oxyhydroxide particles can be smaller than 10 nm in size (Waychunas et al., 2005). Conversely, the formation of iron oxyhydroxides from dissolved iron will add non-carbonate acidity when the pH is titrated upward.



Aluminum also generates non-carbonate acidity by hydrolysis and precipitation of its oxyhydroxide. The presence of additional forms of acidity, such as sulfuric acid or organic acids, will also result in an overestimate of acidity. The impact of the non-carbonate acidity and alkalinity can be accounted for in the calculation for CO₂ if the full solution chemistry is known and the definition of total alkalinity includes all relevant chemical species.

1.1.2. Direct CO₂ measurements

Direct CO₂ measurements avoid uncertainties associated with pH and alkalinity determination in the field. These methods typically require the separation of dissolved gas from the water by a wide range of active or passive means (De Gregorio et al., 2011), such as water-air or host gas partitioning (Capasso and Inguaggiato, 1998; Hope et al., 1995; Watten et al., 2004), acidification (O'Sullivan and Millero, 1998), and membrane permeation (De Gregorio et al., 2011; Johnson et al., 2010). Once the CO₂ is in the gas phase, it is typically quantified using infrared detection or mass spectrometry and converted into an aqueous concentration using the Henry's Law Constant. However, in contrast to the pH-alkalinity approach, these methods are not always portable, may be subject to fouling, and are more expensive.

The carbonated beverage industry monitors high concentrations of dissolved CO₂ during the carbonation process and when

evaluating the influence of beverage additives on the mechanics of gas transfer at different CO₂ concentrations (Descoins et al., 2006). This method determines the total gas content by measuring the equilibrium pressure and temperature of a sample after its volumetric expansion in a sealed chamber (Schaden et al., 2004). In this study, we report on the use of a commercially-available beverage carbonation meter employing this approach to determine elevated dissolved CO₂ concentrations in a variety of natural waters. Dissolved CO₂ determinations were rapid, accurate, and reproducible and eliminated errors inherent in pH and alkalinity methods routinely used in the field.

2. Materials and methods

2.1. Beverage carbonation meter

The tested beverage carbonation meter (Fig. 1; CarboQC; Anton Paar GmbH, Graz, Austria) is used by the beverage industry to measure dissolved CO₂ concentrations in mineral waters, soft drinks, beers, and sparkling wines. It is relatively small (190 × 120 × 305 mm) and lightweight (3.1 kg) and is typically used to measure pressurized carbonated beverages under both laboratory and "at-line" conditions. The basic method of operation involves completely filling a measuring chamber with approximately 10 mL of sample, sealing the chamber, and expanding the volume of the chamber twice (by 10% and 30%) using a motor-driven piston with an integrated stirrer. The resulting equilibrium temperature and pressure at each volume expansion step are determined and used to calculate the net contributions of dissolved CO₂ and air based on the differences in their relative solubilities in aqueous solution during the two expansion steps. The instrument measures between 0–1000 mM CO₂ at 30 °C and 0–1667 mM CO₂ at <15 °C over 0–10 bar relative pressure (Anton Paar GmbH, 2010). The calculated results are displayed within two minutes of the start of sample measurement. An integrated rechargeable battery allows approximately 200 measurements to be performed when fully charged. The instrument can also be coupled to a pressurized filling device that pierces sealed samples (bottles or cans) and forces carbonated solutions into the meter using compressed air; this accessory was not used in the current study.

2.2. Modifications to carbonation meter standard operating procedure

In a commercial setting, carbonated beverages are typically introduced into the carbonation meter under high pressure (6 ± 0.5 bar relative) to prevent the degassing of CO₂ present in



Fig. 1. Water sample being injected into the tested carbonation meter using a 140-mL syringe and an in-line 0.45-µm filter.

high concentrations, which frequently exceed 136 mM (6 g/L). For application to natural waters and standard CO₂ solutions, minor modifications to the recommended standard operating procedures for the carbonation meter were required. Test solutions were introduced to the measuring chamber using a 140-mL syringe (w/luer-*lok*; Covidien; Mansfield, MA; Fig. 1) connected to the carbonation meter sample inlet by a short length of transparent polyurethane tubing (2.5 × 4 mm) fitted with a luer tubing connector. To protect the instrument, a 0.45- μ m syringe filter (25 mm, GD/X; Whatman, Florham Park, NJ) was connected directly to the syringe when the water was visibly cloudy. The factory-programmed setting for mineral water, which most closely approximates natural emergent waters, was used.

The beverage carbonation meter flow valve is normally adjusted to allow passage of 100–150 mL of pressurized sample through the measuring chamber within a pre-set 20 s time period to ensure full replacement of solution in the chamber and remove residual gas bubbles. To allow the passage of sufficient sample volume through the measuring chamber prior to analysis, the instrument *rinse* mode, which keeps the valves to the measuring chamber open, is activated when the sample is first introduced. After a minimum of 100 mL of sample has passed through the chamber and no gas bubbles are observed, the *start* mode is activated, which seals the chamber and initiates the measurement. None of the natural waters tested in this study degassed spontaneously to form bubbles within the syringe or measuring chamber during the sampling and measurement process, but this did occur when using commercial mineral waters carbonated under pressure and greatly supersaturated with dissolved CO₂.

2.3. Preparation and analysis of standard CO₂ solutions

One advantage of the carbonation meter is that instrument calibration with standard CO₂ solutions is theoretically unnecessary as long as the pressure and temperature sensors are accurate and calibrated (within ± 0.01 bar and ± 0.2 °C, respectively). Degassed deionized water is used to calibrate the zero reading for the instrument. However, standard CO₂ solutions, applicable to unpressurized samples, were prepared as a check on instrument accuracy and precision under laboratory and field conditions.

The general procedure for preparing CO₂ standards was adapted from that used to calibrate membrane-based CO₂ electrodes (Midgley and Torrance, 1991). In this approach, a pH buffer solution is added to a known concentration of sodium bicarbonate solution to achieve a pH below 5.0, which essentially converts all bicarbonate species to CO₂. The final CO₂ concentration in solution can be calculated from the measured CO₂ concentration by accounting for the final pH and ion interferences using geochemical speciation software.

CO₂ standards were created from stock solutions of 0.1 and 0.2 M NaHCO₃ (Fisher Scientific, Pittsburgh, PA) prepared with degassed deionized water. The stock solutions were diluted to create standard solutions ranging from 0.4 to 35 mM CO₂. This range was selected because it bracketed the CO₂ concentrations detected in field samples. An additional standard of 44 mM CO₂ was prepared but excluded from the results because it spontaneously degassed in the tubing before injection into the carbonation meter. The pH buffer solution was prepared with 294 g sodium citrate dihydrate (NaC₆H₅O₇·2H₂O; Fisher Scientific) brought to 1 L with degassed deionized water after an adjustment to approximately pH 4.3 using concentrated HCl. CO₂ standards and buffers are also available commercially from manufacturers of CO₂ electrodes (e.g. Thermo Fisher Scientific, Beverly, MA; HANNA Instruments, Inc., Woonsocket, RI). Duplicate standard CO₂ solutions were measured in parallel using three identical beverage carbonation meters to verify meter accuracy and precision and to examine the consistency of

data determined using different carbonation meters. Standard CO₂ solutions were measured by adding 100 mL to a 140-mL syringe with the plunger removed. Ten mL of pH buffer were added by pipette to the syringe and the plunger was immediately replaced. Air in the syringe was displaced and most of the remaining solution was injected into the carbonation meter. Small aliquots (approximately 5 mL) of sample were retained for the determination of final pH.

In this paper, CO₂ is reported as the dissolved concentration in mmol/L (mM). This eliminates confusion regarding the chemical species being measured (i.e. mM CO₂ = mM inorganic C), and represents the measured concentration in water, not a hypothetical gas phase. Additionally, the range of CO₂ concentrations in most natural waters falls between 0.1 and 100 mM, providing a convenient scale of reference for the reader. This also avoids the use of the terms “enhanced” or “excess” P_{CO_2} (the ratio of the P_{CO_2} in the sample with atmospheric equilibrium), which requires an assumption for the value of the current atmospheric P_{CO_2} . H₂CO₃^{*}, or apparent carbonic acid, is the sum of H₂CO₃ and the dissolved CO₂; however, H₂CO₃^{*} effectively equals the dissolved CO₂ concentration because the dissolved CO₂ concentration greatly exceeds the H₂CO₃ concentration (Stumm and Morgan, 1996).

2.4. Sample collection and field operation of the beverage carbonation meter

Under field conditions, water samples for CO₂ measurement were collected by submerging a 140-mL syringe under water with the piston removed, reassembling it completely filled, and injecting the sample into the carbonation meter, typically within 10 s of sampling. Under conditions where complete syringe submersion under water was impossible, samples could be drawn into the syringe by retracting the piston very slowly to avoid sample degassing. Replicate measurements were routinely made to determine sample precision. Degassed deionized water was measured before and after each set of field analyses to confirm a zero reading of <0.23 mM CO₂ (10 mg/L) on the instrument and to rinse the sample chamber. The instrument was used in the field regularly, including under inclement weather conditions, using appropriate instrument cover and protection.

2.5. Field and laboratory analysis

Sample pH and temperature were measured using an Orion 4-Star bench top pH/ISE meter (Thermo Fisher Scientific, Beverly, MA) with combination pH electrode in the laboratory and an YSI 556 MPS multi-parameter instrument (YSI, Inc., Yellow Springs, OH) with either a pH electrode or pH/ORP combination electrode in the field. Two-point calibration of electrodes using certified buffers (Fisher Scientific) was performed prior to data collection. Temperature and pH were measured in-situ at the same location where the CO₂ water samples were collected. Alkalinity was measured using a two-endpoint method (pH 4.2 and 3.9) and calculated using a Gran function (Thomas and Lynch, 1960). A digital titrator (Hach Company, Loveland, CO) was used to titrate samples using 1.6 N sulfuric acid. The alkalinity of field samples was measured immediately after sampling or within 24 h for samples preserved on ice.

All samples for chemical analysis were filtered through 0.45- μ m filters (Whatman GD/X). Samples for elemental analysis were preserved with trace-metal-grade nitric acid and analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 3000 Radial View spectrometer using US EPA method 200.7. Samples for anion analysis were kept cold prior to analysis on a Dionex ion chromatography system (Sunnyvale, CA). The percent recovery of calibration check

standards typically had a standard deviation of 2% or less per element. The US EPA quality control guideline of one duplicate, one standard recovery, and one spike recovery for every 10 analyses was employed (US EPA, 1983).

2.6. CO_2 calculations using the pH/alkalinity/geochemical model approach

The MINTEQA2 equilibrium speciation model (Allison et al., 1991) was used to calculate dissolved CO_2 in standard solutions and field samples based on sample pH and alkalinity while incorporating adjustments for temperature, ionic strength, and solution composition. When the chemical composition of a solution was known, the speciation was calculated by adding the total carbonate concentration as the CO_3^{2-} component or using data from the alkalinity titration. The resulting molar concentration of H_2CO_3^* was equated to the dissolved CO_2 for comparison with the carbonation meter measurements. These assumptions were also tested using the low-temperature aqueous geochemical program PHREEQC (Parkhurst and Appelo, 1999), with identical results.

3. Results

3.1. CO_2 determination in standard solutions using the beverage carbonation meter

There was good agreement between known concentrations of dissolved CO_2 in standard solutions and the values determined independently using three identical carbonation meters (Fig. 2). The dissolved CO_2 in standard solutions ($\text{CO}_2\text{-Calc.}$) prepared using sodium bicarbonate was calculated using MINTEQA2 (Allison et al., 1991) to account for changes in the pH and solution composition after the citrate buffer was added. Slight variations observed for $\text{CO}_2\text{-Calc.}$ values among replicate standards were due to minor differences in the final pHs of the buffered solutions. The use of $\text{CO}_2\text{-Calc.}$ for comparison confirmed that the carbonation meter was measuring only the dissolved form of CO_2 .

The average relative standard error (RSE) between $\text{CO}_2\text{-Calc.}$ and the measured CO_2 ($\text{CO}_2\text{-Meas.}$) ranged from -1.9% to 6.8% (Table 1). The two highest RSE values obtained (17.2% and 18.2%) were for the lowest concentration standard; their average error was 0.08 mM, which is less than the manufacturer's reported resolution of 0.23 mM (0.01 g/L). The greatest error (1.6 mM) was for the highest concentration standard and had a corresponding RSE less than 5%. The measured values were biased slightly low in the

middle range of concentrations and slightly high at the extremes although the overall RSE was small. Regression analysis determined slopes of 1.00, 1.03, and 1.03 for the three datasets with R^2 values of either 0.998 or 0.999 (Table 1).

A method detection limit for CO_2 was calculated using a single-concentration method (US Environmental Protection Agency, 1986). Based on the analysis of eight standards of 0.94 mM CO_2 , the detection limit was 0.14 mM. Deionized water blanks ($n = 6$) all measured less than 0.1 mM. These samples were not degassed prior to analysis but were analyzed to verify that the water did not contain CO_2 greater than the minimum detection limit.

3.2. CO_2 determination in natural waters using the beverage carbonation meter versus the pH-alkalinity method

To test the carbonation meter under field conditions, 60 different emergent waters were sampled; CO_2 concentrations in 40 of these samples were measured using the carbonation meter ($\text{CO}_2\text{-Meas.}$) and estimated based on pH, alkalinity titration, and water compositional data ($\text{CO}_2\text{-T.}$) The sampling sites included low-temperature carbonate and sandstone springs, tufa-depositing springs, thermal and mineral springs, and coal mine-impacted waters. For the purpose of this study, thermal-mineral and carbonate waters were arbitrarily differentiated by temperature, being either above or below 20°C , respectively. As a group, carbonate waters had a mean temperature and electrical conductivity of 12.9°C and $566\ \mu\text{S}/\text{cm}$ ($n = 18$), while thermal-mineral spring waters had corresponding mean values of 28.0°C and $912\ \mu\text{S}/\text{cm}$ ($n = 11$). The representative major ion chemistry of the sampled waters is summarized on a Piper diagram (Fig. 3).

Carbonate and thermal-mineral waters generally had best agreement between the directly measured and estimated CO_2 concentrations (Fig. 4). The single sandstone spring had a high RSE because although it contained measurable CO_2 , it contained no detectable alkalinity. The coal mine waters had the greatest range of RSE with $\text{CO}_2\text{-Meas.}$ nearly always being lower than $\text{CO}_2\text{-T.}$ Possible explanations for the discrepancy include that (1) the waters are geochemically unstable and undergo rapid pH change and mineral precipitation as they emerge from the mine, (2) they may contain non-carbonate alkalinity in the form of small particulate metal hydroxides, and (3) they contain very little alkalinity, resulting in greater error in the titration data.

The estimated and measured values were positively correlated in a linear fashion (Fig. 4) but with regression coefficients lower than those obtained for CO_2 standard samples (Table 1). Regression

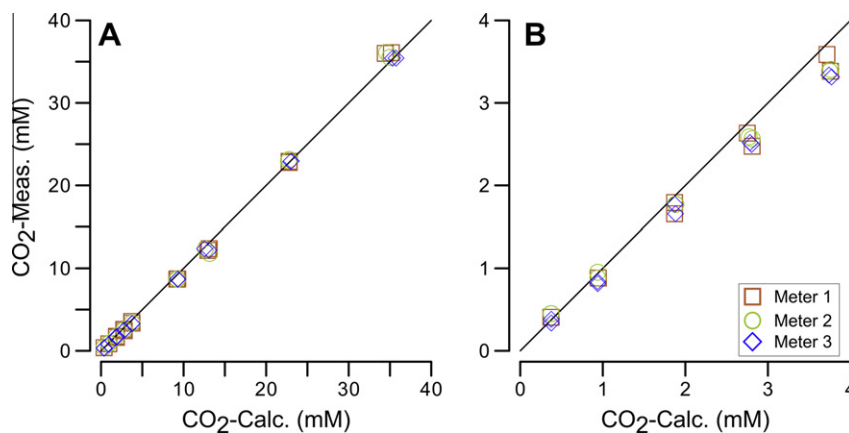


Fig. 2. CO_2 Concentrations in standards as measured by three carbonation meters ($\text{CO}_2\text{-Meas.}$) for the full data set [A] and enlarged for the low-concentration data [B]. The $\text{CO}_2\text{-Calc.}$ is the standard concentration based on known solution chemistry and adjusted for the final pH after buffering. The solid line has a slope of 1. Associated statistics are shown in Table 1.

Table 1

Summary of regression analysis and error for comparison between known and measured concentrations of CO₂ using three individual carbonation meters.

Parameter		Meter 1	Meter 2	Meter 3
Number	<i>n</i>	18	18	18
Error (mM)	\bar{x}	-0.054	-0.056	-0.243
	Min; Max	0.028; 1.61	0.018; 1.54	-0.034; -0.856
Relative standard error (%)	\bar{x}	-3.33	-1.91	-6.81
	Min; Max	0.124; -13.4	1.35; 18.2	-0.20; -14.6
Linear regression	Intercept	-0.37	-0.34	-0.28
	Slope	1.03	1.03	1.00
	<i>R</i> ²	0.998	0.998	0.999
Spearman ρ correlation for non-parametric data		0.993	0.989	0.989

Nine concentrations of CO₂ (from 0.4 to 35 mM) were measured in duplicate on each meter. Each solution was made independently from the stock solution. Error was calculated as the difference between the measured (CO₂-Meas.) and the known (CO₂-Calc.) concentrations; relative standard error is the error divided by the known concentration. The residuals for the regression fits were not significantly different from normal.

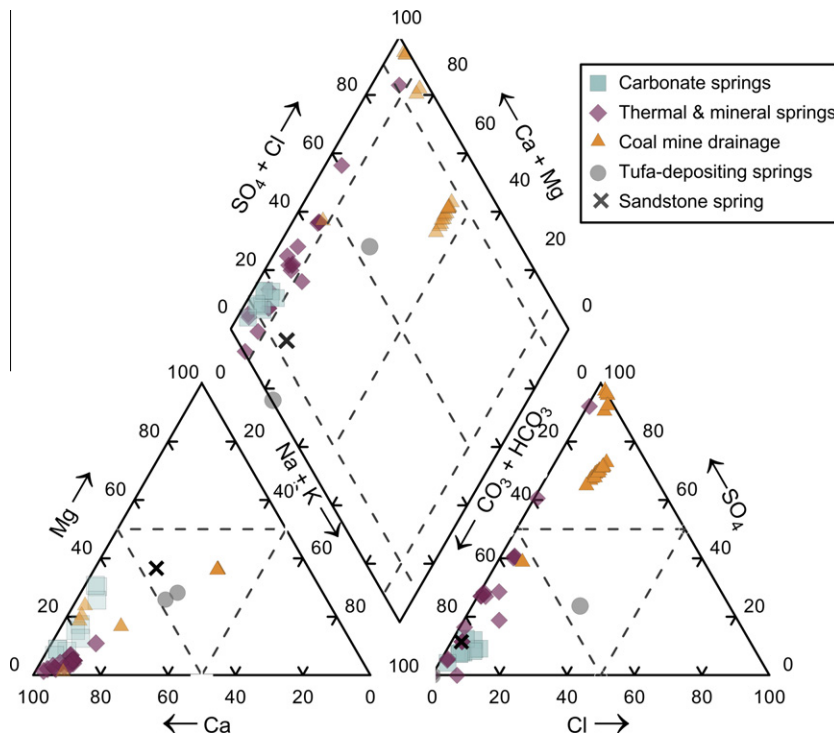


Fig. 3. Piper diagram of water sample compositions used in this study, with percent concentrations calculated from meq/L concentrations. Carbonate springs and coal mine drainage waters generally define the respective calcium-carbonate and calcium-sulfate end members. The thermal-mineral spring waters extend throughout that range due to variation in sulfate concentrations.

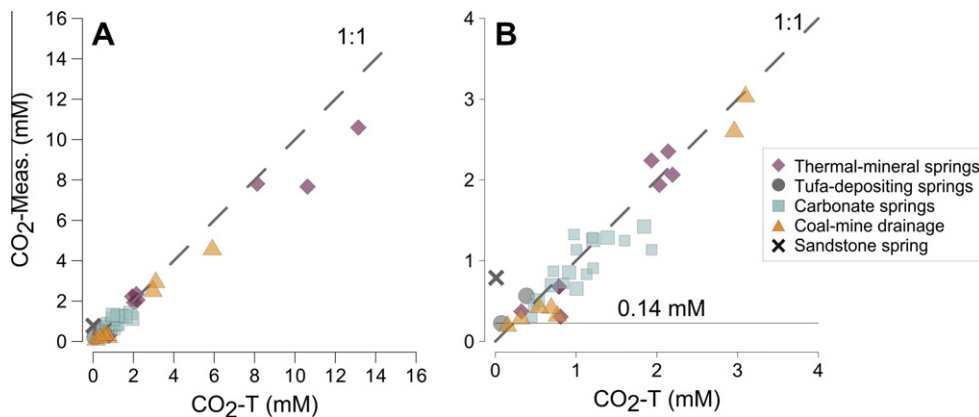


Fig. 4. Comparison of dissolved CO₂ concentrations in 40 different spring and mine waters measured directly using the carbonation meter (CO₂-Meas.) and calculated based on alkalinity titration and water composition (CO₂-T). The horizontal line indicates the minimum detection limit; the dashed line represents a 1:1 slope.

Table 2

Summary of regression analysis and error for comparison between CO₂ concentrations determined on the carbonation meter (CO₂-Meas.) and calculated from alkalinity titration (CO₂-T).

Parameter		Carbonate springs	Thermal-mineral springs	Coal mine drainage
Samples	n	18	11	8
CO ₂ -Meas. (mM)	Min; Max	0.30; 1.4	0.31; 10.6	0.23; 4.70
Error (mM)	\bar{x}	-0.12	-0.52	-0.28
Relative standard error (%)	Min; Max	-0.02; -0.80	0.05; -2.95	0.001; -1.21
	\bar{x}	-15.2	-21.1	-24.4
Linear regression	Min; Max	-0.27; -53.3	-3.9; -38.4	0.40; -118
	Intercept	0.280	0.321	0.016
	Slope	0.620	0.783	0.836
	R ²	0.625	0.970	0.976
Spearman ρ correlation for non-parametric data		0.766	0.905	0.934

Error calculated as the difference between the (CO₂-Meas.) and (CO₂-T.) concentrations, relative error as the error divided by the CO₂-Meas. Sandstone (n = 1) and tufa-depositing (n = 2) not included.

analysis of the complete dataset provided a slope of 0.80 and a coefficient of variation (R²) of 0.976, comparable to values obtained using only the thermal-mineral spring waters or the mine drainage (Table 2). Although the set of carbonate spring waters had the lowest R² (0.625), this is due to the smaller range of measured concentrations (0.78 mM vs. 3.0 for thermal-mineral waters and 1.21 mM for coal mine drainage).

4. Discussion

4.1. Range of dissolved CO₂ concentrations found in natural waters

The concentrations of CO₂ measured in natural waters in this study fell between the calculated MDL (0.14 mM) for the carbonation meter and the upper concentration tested for instrument verification (35 mM). They also fell within a range of CO₂ data in the literature for a wide range of water types (Fig. 5). Higher concentrations of CO₂ have been reported for groundwater overlying CO₂-sequestration test sites (Kharaka et al., 2010), travertine-depositing springs (Pentecost, 2005), coal mine drainage (Jarvis, 2006; Mayo et al., 2000), mineral springs (Cartwright et al., 2002; Siegel et al., 2004), and faulted rock- (Keating et al., 2009) and volcano-associated springs (Chiodini and Frondini, 2001) (Fig. 5E through K). This selection of sites is not intended to be exhaustive,

but to provide a range of values for different types of water sources for which researchers have reported dissolved CO₂.

4.2. Use of carbonation meter for environmental analyses

4.2.1. Field use

The short time for analysis allowed for the collection of up to 17 replicates at some sites. The highest RSD for a set of replicates was 3.3%, indicating good precision when CO₂ concentrations are above the MDL. Although the meter is not specifically intended for outdoor work, it is designed for use under wet industrial conditions, and we have found it to be sufficiently water-resistant for field sampling as well, as long as reasonable precautions for its protection from water and direct sunlight are taken. Improvisation is sometimes required to collect an undisturbed water sample using a 140-mL syringe, but this is generally a satisfactory sampling method. Water samples can also be pumped continuously through the carbonation meter, which can aid in the analysis of water from locations too remote to be sampled by hand.

Potential errors in carbonation meter use include mechanical errors, such as out-of-calibration temperature and pressure sensors, but center mainly around proper collection and processing of field samples. Ideal circumstances allow the complete submersion and reassembly of syringe components and immediate intro-

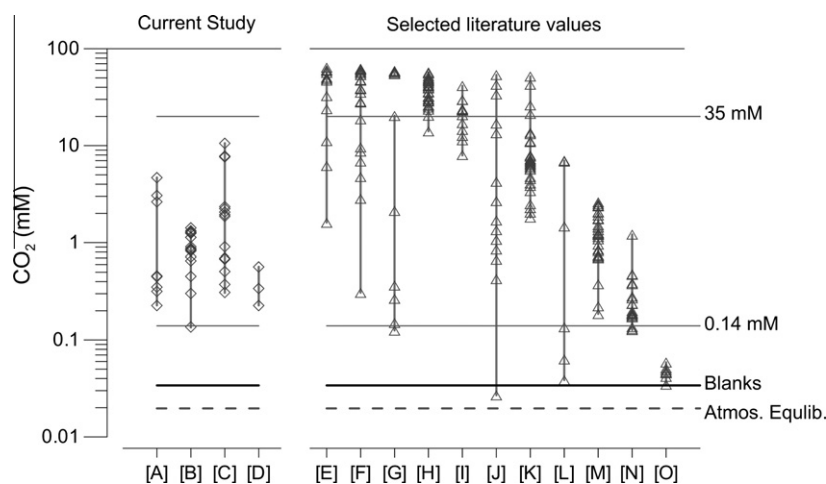


Fig. 5. Comparison of the CO₂ concentrations measured in this study with reported literature values. This study includes: [A] coal mine discharge PA, [B] carbonate waters WV, [C] thermal-mineral waters PA, WV and VA, and [D] tufa-depositing waters PA. Literature CO₂ data include: [E] a CO₂-sequestration site (ZERT) MT (Kharaka et al., 2010), [F] travertine-depositing sites worldwide (Pentecost, 2005), [G] coal mine drainage UT (Mayo et al., 2000) and the United Kingdom (Jarvis, 2006), [H] mineral springs, Australia (Cartwright et al., 2002), [I] mineral springs Saratoga Springs NY (Siegel et al., 2004), [J] groundwater from faulted rocks Chimayo NM (Keating et al., 2009), [K] volcano-associated springs Italy (Chiodini and Frondini, 2001), [L] thermal-springs Yellowstone National Park WY (Nordstrom et al., 2005), [M] carbonate springs WV (Vesper et al., 2009), [N] carbonate streams WV (Vesper et al., 2009), [O] acidic freshwater streams Wales (Neal and Hill, 1994). Literature concentrations were either unit-converted from the reported values or calculated using the data provided. Data for Saratoga Springs were calculated from supplemental data from Siegel et al. (2004) using an average temperature of 15 °C. Horizontal lines indicate the highest calibration standard for the carbonation meter (35 mM), the method detection limit (0.14 mM), the average reading for deionized water blanks (1.5 ± 2.7 mM, n = 125), and dissolved CO₂ in equilibrium with atmospheric P_{CO₂} (for 10^{-3.5} atm).

duction of the sample to the carbonation meter. Loose connections between the syringe, syringe filter, tubing or its fittings can result in the introduction of air into the sample or loss of CO₂. Use of an in-line syringe filter increases the force required to manually process each sample and the time to pass a minimum volume (100 mL) of water through the sample chamber. In practice, we used the syringe filter only when sampling extremely turbid waters capable of fouling the sample chamber.

The propagation of pH error to the alkalinity-estimated CO₂ depends on the solution chemistry. For example, in a water sample with 2.5 mM Ca²⁺, 2.5 mM dissolved inorganic carbon (DIC), and a pH of 7, pH errors of 0.05 and 0.1 result in CO₂ estimation errors ranging from 11% to 27%, respectively. If the pH measurement is biased low, the CO₂ concentration will be overestimated, and *vice versa*. For water with the same example chemistry, a 0.1 meq/L error in alkalinity determined via titration results in an independent CO₂ error of approximately 4%.

4.2.1.1. Lack of interference from non-carbonate alkalinity. The presence of non-carbonate alkalinity does not affect the CO₂ determined using the carbonation meter. If non-carbonate alkalinity is present, and the total alkalinity is used for the calculations, the CO₂ will be overestimated. Hunt et al. (2011) found this to be true for 15 river systems where natural organic matter contributed significantly to the total alkalinity. If the type and concentration of the non-carbonate alkalinity is known, it can be accounted for in the calculation of CO₂ by determining the carbonate contribution as the difference between the total and the non-carbonate alkalinity. The success of this strategy depends on whether the non-carbonate contribution can be quantified and if suitable thermodynamic constants are available for incorporation into the geochemical model. Hunt et al. (2011) recommend that CO₂ be determined from the DIC, rather than the alkalinity, to resolve this problem. However, if any sample degassing occurs, DIC is lost and CO₂ is underestimated. A direct means of determining CO₂, such as use of the carbonation meter, circumvents both of these sources of error.

4.2.1.2. Ability to measure chemically-unstable waters. Direct measurement decreases error in chemically-unstable waters. Mine drainage waters can have elevated CO₂ (Kirby et al., 1999) and high concentrations of hydrolysable metals (e.g., Al and Fe) that can precipitate due to oxidation or the rise in pH from CO₂-degassing. The carbonate meter eliminates the need to process these samples in an inert atmosphere because the water sample can be collected, filtered, and injected without it having to contact the atmosphere.

4.2.2. Potential limitations

4.2.2.1. Minimum detection limit of carbonation meter. Studies concerned with the biogeochemistry, hydrology and ecology of streams, rivers, wetlands and lakes are often interested in determining very low concentrations of CO₂ (approximately 50 μM) as they relate to the interaction of groundwater with surface waters and the influence of evasion rates and photosynthesis on CO₂. Many systems of interest thus have CO₂ concentrations of interest well below the 0.14 mM MDL of the carbonation meter.

4.2.2.2. High temperature. The tested carbonation meter has a stated temperature range of operation between 0 and 30 °C, consistent with its intended use for the measurement of carbonated beverages. However, this potentially limits its use in the sampling of geothermal waters, which commonly fall above this temperature range (Nordstrom et al., 2005; Ray et al., 2009). Preliminary tests done on CO₂ standards (0, 2.27 and 4.54 mM CO₂) at temperatures between 20 and 50 °C gave identical results on the carbonation meter (data not shown), but the efficiency of the meter outside that range was not tested. Geothermal water could be passed through an ice-cooled

loop of tubing (Stefánsson et al., 2007) prior to injection into the carbonation meter to bring the water sample into a desirable temperature range.

4.2.2.3. Gases other than CO₂. Although the gas content of emergent groundwater is dominated by CO₂ and N₂, other gases, such as H₂S, He, H₂, Ar, O₂ and CH₄, are found as well, especially in geothermal waters (Nordstrom et al., 2005; Ray et al., 2009). Hydrogen sulfide, in particular, is highly soluble in water and would be indistinguishable from CO₂ by volume expansion analysis in the carbonation meter. However, H₂S usually occurs in much smaller concentrations than CO₂ in natural waters. For example, at Yellowstone National Park (USA), Angel Terrace Spring (71.4 °C, pH 6.43) contained 7.0 mM CO₂ compared to 0.088 mM H₂S, which was the highest concentration of H₂S reported in that study (Nordstrom et al., 2005). The American Public Health Association (2005) reports an odor threshold range for H₂S of approximately 0.74–7.35 nM. The highest value in this range is over 10,000 times lower than the carbonation meter detection limit for CO₂ (0.14 mM). It can therefore be concluded that samples having no detectable H₂S odor are unlikely to contain sufficient amounts of the gas to cause instrument interference. If it is of concern, H₂S can be chemically determined independently. In our study, one site (Jefferson Warm Springs, VA) had a strong odor of H₂S. The measured concentration of H₂S in water (0.005 mM) was still 74 times lower than the measured CO₂ concentration of 0.37 mM and would be insignificant. Some groundwaters associated with oil deposits, magmatic activity, and deep reducing aquifers have been reported to attain concentrations of H₂S in excess of 2.9 mM (Kresic, 2006), which would interfere with direct CO₂ analysis using the carbonation meter. Geologic carbon sequestration activities may also introduce higher concentrations of H₂S to groundwater in particular environments due to the co-injection of other gases captured from power plant emissions in addition to CO₂ (e.g. NO_x, SO_x, H₂S, O₂ and N₂; Wei and Li, 2011).

4.2.2.4. Potential analysis of deep subsurface waters. Field analysis of CO₂ in groundwaters from deep wells may be needed to identify leakage from geologic faults and natural CO₂ reservoirs in sedimentary basins, enhanced oil recovery fields, and geologic carbon sequestration sites into overlying groundwaters (Zimmer et al., 2011). Solutions collected under pressure from deep underground could potentially be measured directly at the surface with the carbonation meter. Various devices sample water with dissolved gases from deep boreholes while keeping sample at formation pressure during ascent to the surface (Nurmi and Kukkonen, 1986; Simpkins and Parkin, 1993; Yager and Fountain, 2001).

5. Conclusions

A new method for field measurement of dissolved CO₂ in natural waters based on temperature and pressure changes determined during sample volume expansion was tested using a beverage carbonation meter. Laboratory studies showed that measurement of CO₂ in prepared standards was highly accurate and precise. The carbonation meter functioned well under field conditions and provided accurate and reproducible results for a range of hydrochemical facies including low ionic strength, carbonate, thermal-mineral and coal mine waters. Forty different emergent waters were compared using the carbonation meter and the conventional pH/alkalinity approach to determine *in situ* CO₂ concentrations. The method eliminates potential errors in CO₂ estimation inherent in the pH/alkalinity approach, such as difficulties obtaining stable pH readings due to CO₂ degassing and mineral precipitation, the presence of non-carbonate alkalinity sources, and human titration

error. We believe that the method represents a viable alternative and improvement over the conventional pH/alkalinity approach to the measurement of CO₂-enriched waters.

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