A Field-Based Method for Determination of Dissolved Inorganic Carbon in Water Based on CO_2 and Carbonate Equilibria

Dorothy J. Vesper · Harry M. Edenborn · Anthony A. Billings · Johnathan E. Moore

Abstract The processing, storage, and flux of inorganic carbon in rivers and streams play an influential role in the lateral transfer of atmospheric and terrestrial carbon to the marine environment. Quantifying and understanding this transfer requires a rapid and accurate means of measuring representative concentrations of dissolved inorganic carbon (DIC) and CO_2 in field settings. This paper describes a field method for the determination of DIC based on the direct measurement of dissolved CO_2 using a commercial carbonation meter. A 100-mL water sample is combined with 10 mL of a high ionic strength, low-pH, citrate buffer, mixed well, and the dissolved CO_2 concentration is measured directly. The DIC is then calculated based on the dissolved CO_2 concentration, buffer-controlled ionic strength, pH, and temperature of the mixture. The method was accurate, precise, and comparable to standard laboratory analytical methods when tested using prepared sodium bicarbonate solutions up to 40 mM DIC, North Atlantic seawater, commercial bottled waters, and carbonate spring waters. Coal mine drainage waters were also tested and often contained higher DIC concentrations in the field than in subsequent laboratory measurements; the greatest discrepancy was for the high-CO_2 samples, suggesting that degassing occurred after sample collection. For chemically unstable waters and low-pH waters, such as those from high-CO_2 mine waters, the proposed field DIC method may enable the collection of DIC data that are more representative of natural settings.

Keywords Dissolved inorganic carbon (DIC) · Dissolved carbon dioxide (CO_2) · Carbonate geochemistry

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1 Introduction

The storage, processing, and flux of carbon associated with terrestrial waters are important yet still poorly quantified components of the global carbon cycle. The estimated carbon storage capacity for terrestrial waters is small relative to terrestrial soils (Regnier et al. 2013), but the biogeochemical processing of dissolved inorganic carbon (DIC) is critical to aquatic ecosystem function, and rivers provide the means of transferring DIC from terrestrial settings to the atmosphere or oceans. Recent studies have estimated the storage and flux of DIC associated with inland waters; however, these estimates are rarely based on direct DIC or CO_2 measurement

(Butman and Raymond 2011; Stets and Striegl 2012; Lauerwald et al. 2013; McDonald et al. 2013). Instead, the DIC concentrations used are typically calculated from commonly available, yet inherently less accurate, pH and alkalinity data. In a recent review of carbon transport via terrestrial waters, Regnier et al. (2013) concluded that the limited amount of directly measured CO_2 and carbon-related data was a significant limitation in evaluating the importance of this reservoir within the overall global carbon cycle.

The three major avenues for the loss of DIC from terrestrial waters are conversion of DIC to organic carbon, CO_2 degassing to the atmosphere (evasion), and DIC export to the ocean reservoir. The magnitude of the inorganic processes depends upon the total concentration and speciation of DIC in water; the latter can be calculated if any two of the following three variables are known: pH, DIC, and the concentration of a single carbonate species (Deffeyes 1965; Butler 1982). Typically, the third variable—a single carbonate species—is determined by equating the alkalinity to the bicarbonate concentration and back-calculating the CO_2 partial pressure (P_{CO2}) based on carbonate equilibrium reactions (White 1988; Stumm and Morgan 1996). This yields the hypothetical P_{CO2} present in the headspace in equilibrium with the water. This approach works well in carbonate-dominated waters but overestimates the DIC concentration if non-carbonate alkalinity is present and can only be used in waters with alkalinity. Non-carbonate alkalinity may be present in the form of hydroxides, silicates, borates, sulfides, phosphates, ammonia, and organic compounds (Hem 1986; Stumm and Morgan 1996). The problem with using total alkalinity to estimate DIC is compounded by the difficulty in obtaining stable and reliable pH values for geochemically unstable waters such as those that undergo temperature change, outgassing (e.g., CO_2 evasion), in-gassing (e.g., O_2), or rapid mineral precipitation (Ritz and Collins 2008). Therefore, although pH and alkalinity data can be used to estimate DIC storage and export, they can also lead to biased results.

Recent advances have been made in the development of alternative methods to measure aqueous CO_2 directly. Nondispersive infrared (NDIR) CO_2 sensors measure dissolved CO_2 using a gas-permeable membrane or after a purging step to separate the CO_2 from water (Johnson et al. 2010; De Gregorio et al. 2011; Yasuda et al. 2012).

Such devices have been coupled to data loggers and used for in situ measurements in surface waters (Johnson et al. 2010) and volcano-associated springs (De Gregorio et al. 2011). Bass et al. (2012) and Yasuda et al. (2012) determined DIC concentrations directly in water by converting a sufficient mass of DIC to CO_2 through acidification and then measuring with an NDIR detector. NDIR sensors can be configured to obtain continuous data in situ for both CO_2 and DIC, but they usually measure over a fairly low range of DIC concentrations, require extensive calibration, and need at least 15 min for sensor equilibration prior to each measurement (Yasuda et al. 2012).

In this study, we developed a field-based method that can rapidly, precisely, and accurately quantify DIC in aqueous samples. In this method, DIC is determined by lowering the pH and increasing the ionic strength of an aqueous sample before directly measuring the resultant CO_2 using an industrial carbonation meter. This instrumental approach has previously been shown to be both accurate and precise in measuring dissolved CO_2 in natural waters and was robust under a variety field conditions (Vesper and Edenborn 2012).

2 Materials and Methods

2.1 Derivation of CM-DIC Calculation

The DIC determined using the carbonation meter method (CM-DIC) is calculated based on the dissolved CO_2 activity in combination with the associated pH. In samples with a pH greater than approximately 6, there is typically insufficient CO_2 present for direct measurement (Fig. 1), but when acid is added and the pH is lowered, DIC is converted into the CO_2 species. In the CM-DIC method, a low-pH, high ionic strength buffer used for pH adjustment also "fixes" the ionic strength in the samples. This effectively standardizes the activity-concentration relationship and simplifies the final calculation by eliminating the need to determine the activity-concentration correction factors (activity coefficients) for individual samples. Activity coefficients, estimates that define the relationship between chemical activities and concentrations, are necessary because the carbonation meter determines the CO_2 activity in water and the laboratory-prepared samples are expressed in terms of concentration.
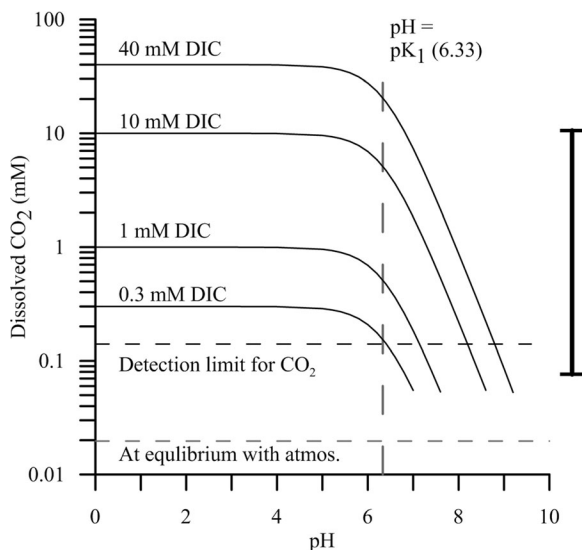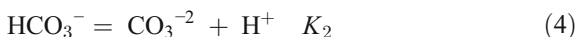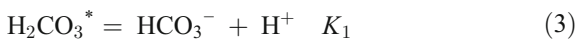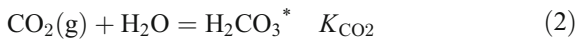
Fig. 1 The relationship between pH and dissolved CO_2 for up to 40 mM of DIC. When the pH of a sample is adjusted to a value less than the log of the first dissociation constant for carbonic acid ($K_1 = 10^{-6.33}$), HCO_3^- is converted into dissolved CO_2 for measurement. The detection limit (0.14 mM) for CO_2 on the carbonation meter is from Vesper and Edenborn (2012); the CO_2 in equilibrium with the atmosphere is based on a $P_{CO_2} = 10^{-3.5}$ atm. This figure was constructed for 25 °C using thermodynamic constants from Stumm and Morgan (1996) and assuming activity coefficients of 1

The calculation of CM-DIC is derived from the mass balance of DIC [Eq. 1] and carbonate equilibrium reactions:

$$DIC = \left[H_2CO_3^*\right] + \left[HCO_3^-\right] + \left[CO_3^{-2}\right] \quad (1)$$

where DIC is the total concentration in molar units and the brackets represent the molar concentrations of the three dominant carbonate species. The distribution of the concentrations between the three species is governed by the following chemical reactions and associated mass action equations:

$$CO_2(g) + H_2O = H_2CO_3^* \quad K_{CO2} \quad (2)$$

$$H_2CO_3^* = HCO_3^- + H^+ \quad K_1 \quad (3)$$

$$HCO_3^- = CO_3^{-2} + H^+ \quad K_2 \quad (4)$$

where K_{CO2} is the Henry's Law constant for CO_2 and K_1 and K_2 are the first and second dissociation constants for carbonic acid. The $H_2CO_3^*$ species, a combination of dissolved CO_2 gas and carbonic acid, has

approximately 3 orders-of-magnitude more dissolved gas than acid (Stumm and Morgan 1996); thus, $H_2CO_3^*$ can be used as a measure of the dissolved CO_2.

The mass balance and mass action equations are combined along with corrections for the activity-concentration relationships and the temperature dependency of the equilibrium constants:

CM-DIC

$$= \left[\frac{\alpha_{co_2}}{\gamma_{co_2}} + \left(\frac{K_1}{10^{-pH}\gamma_{HCO_3^-}}\right)\alpha_{co_2} + \left(\frac{K_1K_2}{10^{-2pH}\gamma_{CO_3^{-2}}}\right)\alpha_{co_2}\right] \times 1.1$$

$$(5)$$

where the CM-DIC is calculated in terms of mole/liter; α_{CO2} is the measured activity of CO_2 (in mol/L); γ is the activity correction coefficient for each solute; K_1 and K_2 are the first and second dissociation constants for carbonic acid (Eqs. 3 and 4), corrected for temperature (Plummer and Busenberg 1982); and 1.1 is a correction for the sample volume dilution introduced by the added buffer solution.

The activity coefficients (γ) used for CO_2, HCO_3^-, and CO_3^{-2} are 1.09, 0.72, and 0.27. These are the average values obtained from speciation calculations using the geochemical software Minteq and incorporating the Davies Equation for estimating activity coefficents (Allison et al. 1991). These calculations were completed for 126 prepared samples in which the complete sample composition is known (details below). The samples contained 0 to 40 mM DIC with corresponding ionic strengths in the buffered samples from 0.307 to 0.384. When activity coefficients from all three individual species were used in the calculation, there was less than 1.5 % variance in the final DIC concentration. Therefore, we concluded that average values of the activity coefficients can be used for further calculations without introducing significant error.

An alternative approach is to assume that all activity coefficients are equal to 1 for this calculation. This approach results in a slightly more accurate determination of the known concentrations because the errors in doing so partially cancel each other out: using 1 instead of 1.09 for γ_{CO2} slightly overestimates the DIC and using 1 instead of 0.72 for γ_{HCO3} slightly underestimates the DIC (the γ_{CO3} has negligible impact at these pH levels). The difference in the error of measurement between the two approaches is within 5 % over the CM-DIC concentration range tested. Ideally, any extensive use of this method would incorporate a sensitivity

analysis for the specific type of water being tested; in that case the activity coefficients could be adjusted for use as calibration parameters to maximize accuracy.

The method detection limit (MDL) for CM-DIC was calculated using Eq. 5 and the previously determined 0.14 mM MDL for CO_2 on the carbonation meter (Vesper and Edenborn 2012). Unlike the MDL for CO_2, the MDL for CM-DIC increases with pH as the bicarbonate ion becomes more important in solution. However, the addition of the citrate buffer in this method controls the final pH of the mixture. Based on the standard solutions prepared in this study, the pH levels of the citrate-sample mixtures varied between 5.1 and 5.6 which correspond to MDLs for CM-DIC of 1.4 to 1.6 mM C. The higher value is illustrated on the graphs.

2.2 Test Solutions

Standard solutions of known DIC concentrations were prepared in the laboratory using $NaHCO_3$ (Sigma Aldrich, St. Louis, MO) in N_2-bubbled deionized water. Solutions were prepared over a concentration range of 0–40 mM by adding moisture-free $NaHCO_3$ to pre-weighed volumes of N_2-bubbled deionized water with minimal headspace in 750 mL green-glass spring water bottles (Perrier) with screw-on caps. Six sets of standard solutions were independently prepared and three aliquots from each bottle were analyzed. For two complete sets of standards, aliquots were also taken for measurement using a laboratory DIC analyzer (see below).

Additional samples were tested in the laboratory and in the field. Laboratory samples included a seawater sample and several commercially bottled spring waters. The seawater sample was an Atlantic Seawater Standard (Ocean Scientific International Ltd., Havant, Hampshire, UK), a filtered North Atlantic ocean water sample with a salinity of 35‰. Two bottled spring waters were selected for their potential use as practical and readily available standards in the field: Evian Natural Spring Water (Source Cachat, Evian-Les-Bains, France) and FIJI Natural Artesian Water (Yaqara Valley, Viti Levu, Fiji Islands; Fiji Water Company, Los Angeles, CA, USA). These waters are widely available and are reportedly bottled from single-source locations.

Data and water samples were obtained from several carbonate springs and abandoned coal mine discharges for this study. Temperature and pH were measured in situ using a YSI meter (YSI, Inc., Yellow Springs, OH); pH was calibrated daily using pH 4 and 7 buffers prior to

the first field measurement. No additional laboratory pH data were obtained. Total alkalinity was measured using a two-endpoint Gran titration (to pH levels 4.2 and 3.9) on a raw (unfiltered) sample following the method of Thomas and Lynch (1960). The titration was conducted using a digital titrator (Hach Company, Loveland, CO) and completed immediately after sample collection. Water samples for laboratory analysis were filtered through 0.45-μm syringe filters. Samples for cation analyses were preserved with trace-metal grade nitric acid and analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer Optima, Waltham, MA) following the US EPA method 200.7. Samples for sulfate analysis were kept cold and analyzed using ion chromatography (IC, Dionex, Sunnyvale, CA). All laboratory analyses were completed at the Department of Energy, National Energy Technology Laboratory in Pittsburgh, PA.

2.3 Carbonation Meter DIC Method (CM-DIC)

The use of a beverage carbonation meter (CarboQC; Anton Paar GmbH, Graz, Austria) to measure dissolved CO_2 in natural waters has been described previously (Vesper and Edenborn 2012). Briefly, approximately 10 mL of water is injected into a chamber on the meter which is automatically sealed when the analysis begins. Changes in temperature and pressure in the chamber are measured while a motor-driven piston expands the chamber volume twice (by 10 % and then 30 %). The CO_2 is calculated based on the difference in the temperature and pressure for the two different volumes. This method assumes that the only gases present are less soluble than CO_2; this is generally true for natural waters except when H_2S is present (Vesper and Edenborn 2012). Each measurement is complete in approximately 2 min.

The carbonation meter is operated using its default setting for mineral water. Inflow tubing (30 cm, 2.5× 4 mm transparent polyurethane; Fisher Scientific, Pittsburgh, PA) is attached to the meter and is also fitted with a nylon Luer-Lok fitting (female Luer thread style to 200 series barb, 1.6 mm ID, FTLL220-1; Value Plastics, Inc., Fort Collins, CO). Outflow tubing of the same diameter and composition leads to an appropriate waste container. In field settings, water is typically sampled using a 140-mL syringe (w/Luer-Lok; e.g., Kendall Monoject, Covidien, Mansfield, MA), ideally by

disassembling and assembling the syringe under water to avoid gas exchange with the atmosphere.

The syringe containing the sample is inverted so that any air bubbles are expelled, and the volume is adjusted to 100 mL, excluding air bubbles. A 10-mL syringe (w/Luer-Lok; e.g., Becton Dickinson, Franklin, NJ) attached to a nylon Luer-Lok fitting (female thread style to 200 series barb, 3.2 mm tubing, FTLL210-1; Value Plastics, Inc.) and connected to a 5-cm length of PVC vinyl tubing (3.2 mm ID, 6.4 OD; Fisher Scientific) is filled with a buffer of 1 M sodium citrate dihydrate, pH 4.3 (Orion Ionic Strength Adjustment Buffer 950210, Thermo Fisher Scientific, Waltham, MA) to the 10-mL mark. The two syringes are then attached (Fig. 2a) and the CO_2 buffer is injected into the larger syringe, whose plunger extends as the buffer is added. The tubing is removed from the large syringe, the Luer-Lok tip is covered with a gloved fingertip, and the syringe is rocked (ca. one 90° rotation per second) for 20 s. This period of mixing is required to ensure complete mixing of the two solutions and was confirmed by pH and dye dissolution analyses (data not shown).

The sample syringe is firmly connected to the Luer-Lok fitting on the input tubing to the carbonation meter. The plunger thumb rest is placed on a firm surface and pressure is applied, the "RINSE" button is pressed on the carbonation meter, and pressure is continuously supplied to the syringe. After ca. 10 s, the meter valve opens and sample flows through the meter chamber and exits to a waste container. Pressure is continuously applied to ensure that all gas bubbles have been purged

Fig. 2 Connecting the small buffer-containing syringe with the 140-mL sample-containing syringe; carbonation meter set-up in the field

from the chamber. When approximately 80 mL has passed through the meter, the "START" button is pressed and pressure is still applied to the syringe, using less pressure if it appears that it will be emptied before the meter valve closes (ca. 2 s). After the valve closes and the measurement procedure begins, the syringe is disconnected from the input tube, the contents (ca. 5–10 mL) are expelled into a small beaker, and the pH measured (e.g., Orion Star A214 meter with Orion 9107 BN electrode and temperature probe; Thermo Orion). The final pH of the mixture is a function of the alkalinity of the initial sample and is incorporated into the DIC calculation to account for the speciation of carbonate species in the buffered sample. Recorded values include CO_2 (g/L) and temperature (C) from the carbonation meter and pH and temperature of the excess volume of the buffer-sample mixture. In this study, samples were analyzed in replicate ($n=3$ to 12). The pH of the replicate buffer-sample mixtures is monitored as an indication of complete mixing with buffer; the pH of the replicate sample mixtures agrees within approximately 0.05 units if all samples are well-mixed. A degassed deionized water blank sample is introduced between DIC samples to rinse the meter chamber of residual buffer and sample. This rinsing step is repeated until the measured CO_2 is below the instrument detection limit of 0.14 mM (Vesper and Edenborn 2012).

2.4 Laboratory Analysis of DIC ("Lab-DIC")

DIC ("Lab-DIC") was determined on a laboratory-based Shimadzu TOC-V-CPH wet-oxidation Carbon Analyzer (Shimadzu Corporation, Kyoto, Japan). This instrument determines DIC by acidification with phosphoric acid to convert DIC to CO_2 and measuring the evolved gas using an NDIR detector. Reagents included 1,000 ppm (88 mM) DIC standard, 25 % ACS (weight %) reagent-grade phosphoric acid (Ricca Chemical, Arlington, TX), and 2 M Omnitrace hydrochloric acid and Milli-Q Type I water (EMD Millipore, Billerica MA). Two calibration curves were used to account for the concentration range of the prepared samples (0–17 mM and 0–42 mM DIC); dilutions for the curves were prepared internally by the instrument.

The samples for Lab-DIC were collected in 40-mL glass vials with septa tops and kept cold prior to analysis. Field samples were collected by filling and capping the bottle under water.

2.5 Statistical Analysis

Statistical analyses were conducted using SAS 9.3 and JMP 10 (SAS, Cary NC). SAS procedures used included PROC UNIVARIATE, PROC CORR, and PROC GLM. Analyses included regression analysis, residual analysis, and analysis of variance (ANOVA) to determine if the date, bottle selection, or temperature influenced the final results for the prepared samples.

3 Results

3.1 Assessment of Standard DIC Solutions

The standard solutions contained between 0 and 40 mL DIC. After the addition of the citrate buffer, the mixtures had a mean pH of 5.19 (3.4 % RSD) and a temperature of 22.5 °C (3.2 % RSD). Blank samples of degassed deionized water contained between 0 and 0.045 mM CO_2; this is below the MDL for CO_2 (0.14 mM).

The distributions of the measured CM-DIC concentrations in the prepared standards were approximately normal for each concentration of DIC, except for the zero (0) concentration, which exhibited mild departure from normality. Based on the average relative standard error (RSE), the CM-DIC concentrations agreed within 4.5 % of the prepared concentrations (Fig. 3, Table 1). The standard error (SE) increased with concentration and the RSE decreased (Fig. 3b, c). The larger SE at higher concentrations may be due to minor losses of CO_2 at higher CO_2 partial pressures. Based on the entire dataset, the CM-DIC values were biased slightly low in the middle range of concentrations and slightly higher at the extremes. The highest RSE obtained (15.8 %) was for a 1-mM DIC solution; RSEs greater than 6 % were only observed for samples containing 1 or 5 mM DIC. All other RSEs were less than 5.8 %.

The Pearson correlation coefficient between prepared DIC samples and CM-DIC measured concentrations indicated a strong positive relationship ($r > 0.999$, $p < 0.001$). The linear regression between CM-DIC and prepared-DIC concentrations had a slope that was not statistically different than 1 ($p = 0.884$), with an intercept equal to −0.255. The negative intercept indicates that the CM-DIC concentrations were slightly lower than expected.

A repeated-measures ANOVA was completed using CM-DIC as the dependent variable. Independent variables included in the model were the date on which the
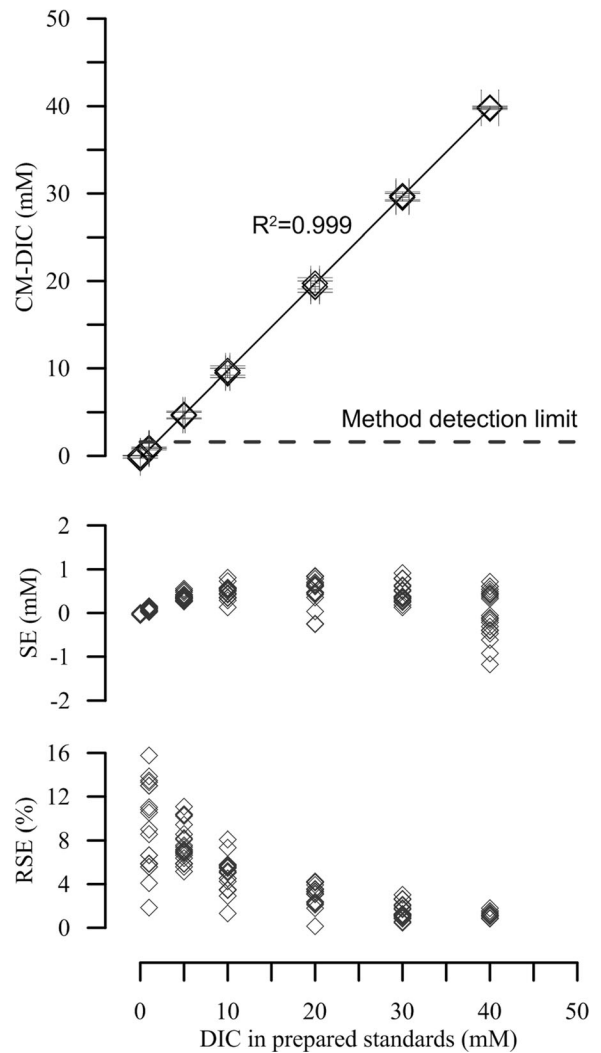

Fig. 3 CM-DIC measured in prepared standard solutions, as calculated by Eq. 5 with standard and relative standard errors. *Symbols* are for the average concentrations measured over six different days ($n = 18$ per concentration); the *vertical error bars* are for the average standard error for each concentration; the *horizontal error bars* represent 5 % of the concentration

analysis was performed, the bottle from which the sample was obtained, and the temperature. Because CM-DIC was computed based on the CO_2 concentration and the pH of the buffer-sample mixture, these parameters were not used in the model. Temperature was included in the analysis to determine if it had an impact beyond adjustment of the thermodynamic constants. After accounting for all other independent variables in the model (TYPE III analysis), we found that none of these variables was statistically significant to the final CM-DIC concentration (model R-square was >0.999). An

Table 1 Statistical assessment of standard DIC solutions

Parameter		CM-DIC (mM)	Lab-DIC (mM)
Number of data points	n	126	13
Standard error (mM)[a]	$\bar{x}$	0.312	0.300
	min; max	0.025; 0.646	0.025; 0.608
Relative standard error (%)[b]	$\bar{x}$	4.42	9.73
	min; max	0.32; 8.58	0.18; 53.5
Linear regression[c]	Intercept	−0.255	0.333
	Slope	1.00	0.981
	R	0.999	0.999

Seven concentrations of DIC (0–40 mM) were measured

[a] Absolute value of the difference between the known and the measured concentrations

[b] Error divided by the known concentration

[c] Regression of measured concentrations on known values

Table 2 Comparison of CM-DIC and Lab-DIC concentrations for commercial bottled waters, North Atlantic seawater, and degassed deionized water blanks

Source	n[a]	CM-DIC			Lab-DIC		
		Mean (mM)	Stdev[b] (mM)	RSD[c] (%)	Mean (mM)	Stdev[b] (mM)	RSD[c] (%)
Evian bottled water	45	6.11	0.045	0.74	6.46	0.094	1.46
FIJI bottled water	54	2.64	0.040	1.52	2.82	0.050	1.77
North Atlantic seawater	6	2.17	0.019	0.88	2.19	0.064	2.92
Deionized water	9	0.056	0.012	21.4	0.011	0.009	81.8

[a] Number of sample replicates

[b] Standard deviation

[c] Relative standard deviation expressed as a percent

analysis of the residuals from the initial model identified eight outliers (n=126); all of the statistical calculations included these outliers. To summarize, no significant effects on CM-DIC of the prepared samples due to bottle (p>0.999), date (p>0.98), or temperature (p=0.406) were observed.

The Lab-DIC concentrations for the prepared solutions agreed within 10 % of the expected concentrations (Table 1), slightly higher than the 4.5 % agreement for the CM-DIC for the same samples. For both methods, the greatest RSEs were for 0 and 1 mM DIC concentrations. Similar to the CM-DIC results, the linear regression for the Lab-DIC concentrations against the expected values yielded a fit-line with a slope of approximately 1. However, the intercept of the Lab-DIC regression was positive (0.333), indicating that this method slightly overestimated the DIC concentrations, while the CM-DIC slightly underestimated the standard concentrations.

3.2 Measurement of Commercial Bottled Water and Seawater Samples

Commercial bottled spring waters were purchased locally for testing. In total, 54 samples of Fiji water and 45 samples of Evian water were analyzed (Table 2). Using the CM-DIC method, the Fiji water contained a mean of 2.64 mM DIC (RSD 1.5 %) and the Evian water contained a mean of 6.11 mM DIC (RSD <1 %). We measured similar concentrations using the Lab-DIC (Fig. 4). Both methods of analysis produced RSEs of

less than 2 % for the DIC concentrations in the bottled water samples. Raw water samples from the two bottled waters had similar initial pH values: Evian had an average pH of 7.32 (n=6, RSD of 1.8 %) and the Fiji water had an average pH of 7.34 (n=6, RSD=2.25).

The North Atlantic seawater sample contained 2.14± 0.02 mM CM-DIC and 2.19±0.06 Lab-DIC (Fig. 4, Table 2). Deionized water "blanks" contained 0.06± 0.01 mM CM-DIC and 0.01±0.01 mM Lab-DIC, well below the 1-mM concentration in the lowest prepared standard solution (Table 2). Determination of low DIC in the deionized water confirmed that it did not add to the mass of DIC when it was used in the preparation of the standard solutions.

Overall, CM-DIC and Lab-DIC concentrations were comparable for prepared standard solutions, the sea water sample, and the bottled spring waters (Fig. 4). The linear regression between CM-DIC and Lab-DIC for this combined data set had a slope of 0.984 and a model R-square of >0.999 (n=126).

3.3 Field Measurement of DIC in Carbonate Springs and Coal Mine-Impacted Waters

The spring waters sampled for this study have comparable chemical characteristics to each other and are typical of waters influenced by carbonate rock dissolution. The waters contained an average of 250 mg/L as $CaCO_3$ hardness, <0.2 mg/L of iron, <100 mg/L of sulfate, and had field pH levels from 6.5 to 7.3.
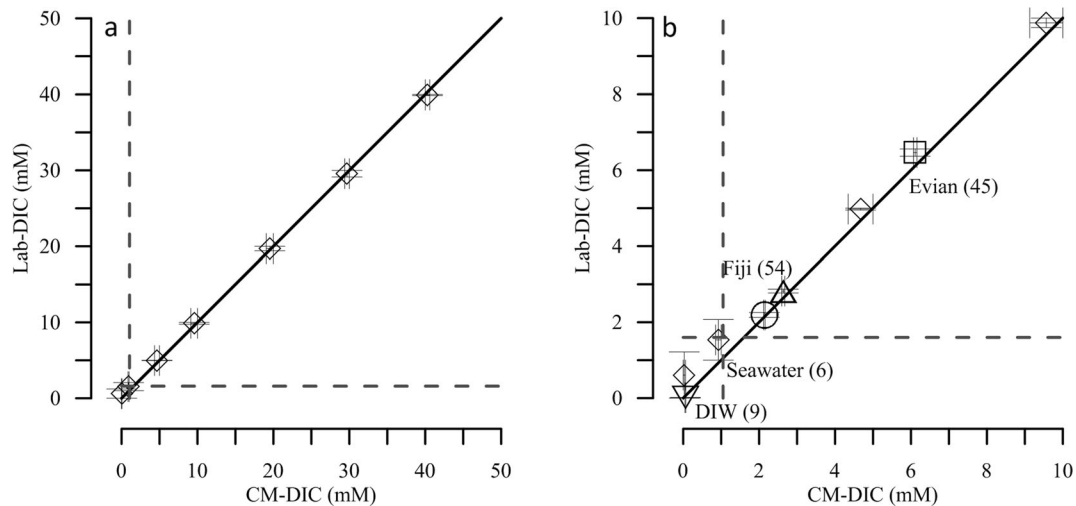
Fig. 4 **a** Comparison of prepared standard DIC solutions determined using the carbonation meter and laboratory instrumentation. **b** Additional test samples (bottled waters, seawater standard, deionized water (DIW)) plotted with the standards over a lower concentration range. *Error bars* are standard deviations for replicate analyses; $n=8$ unless noted otherwise in parentheses. *Dashed lines* provided for the method detection limits; the *solid line* has a slope of 1

Alkalinity was measured in the field for some of the samples and ranged from 1.52 to 4.66 meq/L (76 to 233 mg/L as $CaCO_3$, respectively, Table 3). The springs range in size from a localized seep along a river bank (discharge undetermined) to a much larger spring that discharges from the base of a limestone cliff (ca. 350 m³/day). The underlying geology at and nearby the springs includes limestones, dolomites, and mixed carbonate-clastic sequences. The field CM-DIC and Lab-DIC concentrations obtained for the spring waters agreed within 25 % for all samples with an average difference of 11 % (Table 3). The Lab-DIC was slightly higher than the CM-DIC for six of the seven spring water samples in this comparison (Fig. 5a).

The mine water samples included the discharge from four abandoned coal mine sites and associated water samples collected downstream of the discharge source. Two of the locations were at abandoned bituminous mines and two were at abandoned anthracite mines. At the source locations, the mine waters contained an average of 210 mg/L as $CaCO_3$ hardness, 23 mg/L of iron, 520 mg/L of sulfate, and had pH levels from 4.2 to 6.0. Total alkalinity was determined in the field for some of the samples and ranged from 0 to 0.74 meq/L (0 to 37 mg/L as $CaCO_3$, respectively, Table 3). The downstream samples generally had higher pH levels (up to 7.02), lower iron concentrations (below detection at some sites), and relatively constant hardness and sulfate concentrations (RSD <10 %). The Lab-DIC

concentrations were less than the CM-DIC concentrations for 10 of the 13 samples (Table 3); the difference between the values ranged from 9.6 to 85 %. The sample with the greatest difference between the CM-DIC and Lab-DIC measurements was from the most acidic mine drainage sample collected (pH 4.2).

The agreement between CM-DIC and Lab-DIC was better for the carbonate spring water samples than for the coal mine drainage waters (Fig. 5a). The samples with the greatest percent difference between the CM-DIC and the Lab-DIC were the samples with the highest concentration of CO_2 in the water based on the CM-CO_2 measurements (Fig. 5b).

4 Discussion

The ability to collect large datasets in the field—either spatially or over time—aids researchers in understanding the dynamics between inorganic carbon species, degassing, and pH. The CM-DIC method allows for the collection of accurate and precise DIC at the sample source location. The beverage carbonation meter is easily transported into the field and has been used successfully under extreme environmental conditions and in rugged terrain.

In theory, the carbonation meter requires no further field calibration or use of CO_2 standards provided that the temperature and pressure readings have been

Table 3 Comparison of CM-DIC and Lab-DIC concentrations for field samples

Source type	Location (are at sources[a])	Field pH	Raw alkalinity		CM-DIC				Lab-DIC				ABS % Diff[e]
			meq/L	as mg/L CaCO$_3$	n[b]	Mean (mM)	Stdev[c] (mM)	RSD[d] (%)	n[b]	Mean (mM)	Stdev[c] (mM)	RSD[d] (%)	
Carbonate springs	Carter[a]	6.48	4.66	233	3	5.70	0.02	0.34	1	6.64	–	–	16.4
	CRIM[a]	–[f]	2.21	110	3	2.79	0.56	20	3	2.19	0.01	0.40	21.7
	Hundred[a]	7.38	2.80	140	3	2.54	0.02	0.74	1	3.12	–	–	22.9
	PR1T01[a]	7.04	–[e]	–	3	7.17	0.06	0.90	3	7.42	0.35	4.7	3.53
	PR1T27	7.98	–	–	3	5.39	0.11	2.0	3	5.66	0.19	3.3	4.89
	PR1T80	8.10	–	–	3	5.07	0.12	2.4	3	5.29	0.04	0.74	4.41
	Tytoona[a]	6.82	1.52	76	3	1.93	0.09	47	1	2.04	–	–	5.57
Coal mine drainage waters	F000[a]	5.99	–	–	3	6.39	0.08	1.30	3	2.16	0.06	2.9	66.1
	F005	6.09	–	–	3	5.77	0.04	0.69	3	3.03	1.01	33.4	47.5
	F021	6.59	–	–	3	2.69	0.05	1.78	3	2.43	0.65	26.6	9.6
	F136	6.58	–	–	3	2.62	0.06	2.36	3	2.18	0.35	16.3	16.8
	F180	6.09	–	–	4	2.02	0.09	4.64	3	2.24	0.53	23.6	10.7
	LRM000[a]	5.28	–	–	3	5.22	0.18	3.50	3	2.22	0.41	18.6	57.4
	LRM010	5.47	0.74	37	3	5.22	0.06	1.24	3	1.83	0.14	7.6	65.0
	LRM050	5.65	0.14	7.0	3	2.99	0.06	2.02	3	1.54	0.07	4.7	48.5
	LRM078	6.17	0.59	30	3	1.99	0.11	5.74	3	1.78	0.03	1.5	10.4
	LRM138	7.02	0.73	36	3	1.21	0.07	5.95	3	1.62	0.01	0.3	34.2
	LRM172	6.82	1.13	56	3	1.20	0.02	2.07	3	1.63	0.03	1.7	35.5
	SCAR15[a]	4.22	0	0	3	1.66	0.02	1.09	3	0.24	0.02	6.5	85.8
	SCARPS[a]	5.74	–	–	3	3.08	0.06	1.95	3	1.90	0.86	45.1	38.3

Although the raw alkalinity is reported in units of CaCO$_3$, the concentration is for the total alkalinity and may include non-carbonate as well as carbonate contributions

[a] Source locations

[b] Number of sample replicates

[c] Standard deviation

[d] Relative standard deviation expressed as a percent

[e] ABS %Diff=absolute value [(Mean CM-DIC−Mean Lab-DIC)/(Mean CM-DIC)*10]

[f] Not measured

accurately calibrated by the manufacturer. The DIC standards prepared for this study were prepared in commercial spring water bottles; freshly purchased commercial spring waters could also be easily used as standards under field conditions as a check on instrument stability. We found that commercial spring and lab-prepared waters stored in glass containers, and those naturally low in CO_2, resulted in the most accurate and precise CM-DIC concentration measurements.

The CM-DIC method proposed here has similarities to methods reported by Bass et al. (2012) and Yasuda et al. (2012) in incorporating an acidification step to convert DIC into CO_2, but the CM-DIC method uses an industrial carbonation meter that measures CO_2 directly in water; the other methods use an NDIR detector that requires that the CO_2 species first be partitioned from the dissolved phase into the gas phase. Unlike the NDIR sensor methods, the CM-DIC approach does not require adjustment for the volume of sample in the apparatus, regular calibration with CO_2, or the need to wait for equilibration between the water and gas phases.

Field data may be particularly helpful when sampling chemically unstable waters that can change in composition between collection and analysis. For example, coal mine waters, which may be under sub-oxic conditions in the subsurface, can undergo rapid chemical change after
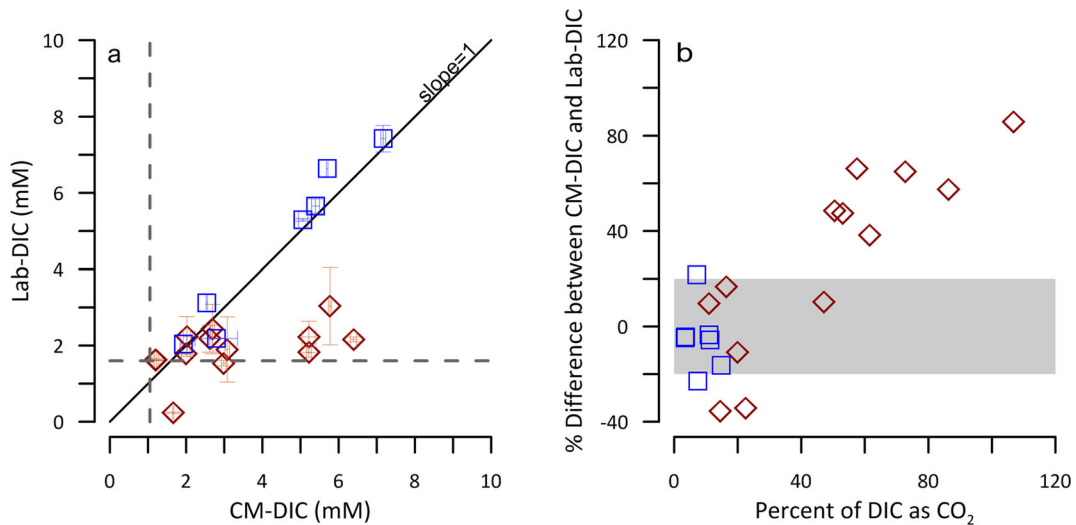
Fig. 5 a Comparison between field-measured DIC concentrations determined by CM-DIC and Lab-DIC for carbonate waters (*blue squares*) and mine drainage waters (*brown diamonds*). *Dashed lines* provided for the method detection limits; the *solid line* has a slope of 1. **b** Relationship between percent different and the CO_2 concentration in the samples. The region with less than 20 % error is *shaded*

discharge. Documented changes in mine water chemistry downstream from source locations include the oxidation of ferrous iron, precipitation of solids, and degassing (Kirby et al. 1999; Younger et al. 2002; Vesper and Smilley 2010; Geroni et al. 2012; Cravotta et al. 2014). The interplay of these components is complex and typically controlled by kinetics rather than equilibrium chemistry (Geroni et al. 2012; Cravotta et al. 2014). In this study, the mine water samples analyzed using both CM-DIC and Lab-DIC nearly always had lower concentrations of DIC using the Lab-DIC method (Table 3). Degassing of the water following

sample collection may account for this difference given that (1) the CM-DIC concentrations exceeded the Lab-DIC value in 77 % of the samples (Table 3), and (2) the greatest difference between the methods was for the samples with the highest percentage of DIC in the dissolved CO_2 form (Fig. 5b). In these mine waters, the collection of DIC data in the field may help eliminate error that arises from chemical changes in the samples post-collection and thereby provide more representative data of the actual field conditions.

The principal human error associated with the proposed method lies in the potential for incomplete mixing

Fig. 6 Estimation of error in CM-DIC relative to error in the pH measurement. Over the pH range of the buffered samples (*shaded box*), the CM-DIC error is less than 5 % of its concentration. The 5 % error is illustrated by the *open box*. As pH increases, the error in pH measurement results in a greater error in CM-DIC
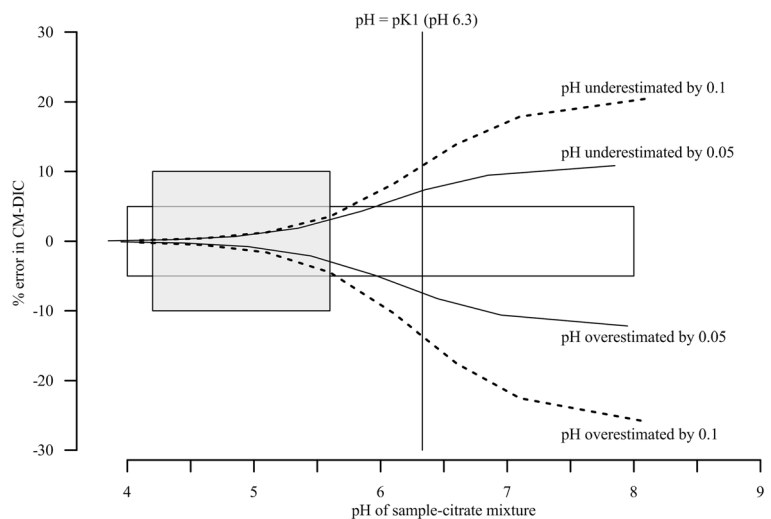
of the added buffer and the water sample. In practice, replicate samples of the same source water should have pH values within ca. 0.01 after complete mixing with the buffer.

The inclusion of pH in the calculation (Eq. 5) means that an error associated with pH will propagate through to an error in the CM-DIC. This error is minimized at pH levels that are less than the pK_1 for carbonic acid and will be greater at higher pH levels (Fig. 6). At the lower pH levels (<6.3), most of the DIC is present as dissolved CO_2 and can be accurately measured on the carbonation meter. So although the negative log scale for pH means that lower pH levels should mathematically propagate through to higher errors, the error is limited by the importance of CO_2 being the dominant carbonate species at low pH. The use of the acidic and high ionic strength buffer in the CM-DIC method not only converts the DIC into the measurable form but decreases the error in the measurement by altering the pH into the low-error range. Therefore, although the CM-DIC method is dependent on pH, the error is minimized through the addition of a strong buffer.

DIC field data can be obtained faster (<2 min per sample) and with greater ease using the carbonation meter than by titrating for alkalinity. The CM-DIC method also avoids possible bias that can occur due to the presence of non-carbonate alkalinity. When Vesper and Edenborn (2012) compared CO_2 data obtained on the carbonation meter with those obtained from alkalinity and pH data, the CO_2 concentrations calculated from the titrations were typically higher for coal-mine drainage and thermal-mineral spring waters, likely to do the presence of non-carbonate alkalinity (Kirby and Cravotta 2005). Furthermore, the CM-DIC method allows for field measurement of CO_2 and DIC in acidic waters that contain no measurable alkalinity.

5 Conclusions

The ability to measure DIC in the field allows researchers to rapidly collect DIC data, work with chemically unstable waters, and to avoid errors related to degassing in the sampling and transport processes. The accuracy and precision of CM-DIC were determined by the measurement of prepared DIC standards and supported by the statistical analysis of the data. A comparison with a standard laboratory technique of analysis indicated that the CM-DIC method was as least as

accurate as the laboratory method (Tables 1 and 2), but could be accomplished in the field in a short period of time. The collection of DIC data in the field may result in more accurate and representative data for some samples, most notably in chemically dynamic/unstable or acidic waters. In summary, the CM-DIC method fulfills the need for easy, rapid, and field-deployable, means of DIC analysis and may enable researchers to obtain more representative concentrations of DIC in water samples.

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