Technical note: CO$_2$ is not like CH$_4$ – limits of and corrections to the headspace method to analyse pCO$_2$ in fresh water

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Abstract. Headspace analysis of CO$_2$ frequently has been used to quantify the concentration of CO$_2$ in fresh water. According to basic chemical theory, not considering chemical equilibration of the carbonate system in the sample vials will result in a systematic error. By analysing the potential error for different types of water and experimental conditions, we show that the error incurred by headspace analysis of CO$_2$ is less than 5 % for typical samples from boreal systems which have low alkalinity (<900 µmol L$^{-1}$), with pH < 7.5, and high pCO$_2$ (>1000 µatm). However, the simple headspace calculation can lead to high error (up to ~300 %) or even impossibly negative values in highly undersaturated samples equilibrated with ambient air, unless the shift in carbonate equilibrium is explicitly considered. The precision of the method can be improved by lowering the headspace ratio and/or the equilibration temperature. We provide a convenient and direct method implemented in an R script or a JMP add-in to correct CO$_2$ headspace results using separately measured alkalinity.

1 Introduction

The analysis of dissolved CO$_2$ in water is an important basis for the assessment of the role of surface waters in the global carbon cycle (Raymond et al., 2013). Indirect methods like calculating CO$_2$ from other parameters like alkalinity and pH (Lewis and Wallace, 1998; Robbins et al., 2010) are affected by considerable random and systematic errors (Golub et al., 2017) caused for example by dissolved organic carbon, which may result in significant overestimation of the CO$_2$ partial pressure (pCO$_2$) (Abril et al., 2015), or by pH measurement errors (Liu et al., 2020). Thus, direct measurement of CO$_2$ is highly recommended, particularly in soft waters.

Headspace analysis is a standard method to analyse the concentration of dissolved gases in liquids (Kampbell et al., 1989). In principle, a liquid sample is equilibrated with a gaseous headspace in a closed vessel under defined temperature. The partial pressure of the gas in the headspace is analysed, in most cases either by gas chromatography or infrared spectroscopy. The concentration of the dissolved gas in solution is then calculated by applying Henry’s law after correction for the amount of gas transferred from the solution to the headspace.

In freshwater research this is the widely applied standard method to analyse the concentration of greenhouse gases such as CH$_4$ and N$_2$O (UNESCO/IHA, 2010). The method is handy, does not depend on sophisticated equipment in the field, and provides reliable results. Papers and protocols using this method have also been published to analyse dissolved CO$_2$ concentrations in fresh waters (UNESCO/IHA, 2010; Cawley, 2018; Lambert and Fréchette, 2005). However, CO$_2$ cannot be treated like CH$_4$ because CO$_2$ is in dynamic chemical equilibrium with other carbonate species in water while CH$_4$ is not (Stumm and Morgan, 1981; Sander, 1999). Depending on the CO$_2$ concentration and pH, reactions of the carbonate equilibrium will either produce or consume some CO$_2$ in the sample vessel (Cole and Prairie,
2 Methods

2.1 Theoretical considerations

If a water sample is equilibrated with a headspace initially containing a known \( p\text{CO}_2 \) (zero in case \( N_2 \) or another CO\(_2\)-free gas is used), some CO\(_2\) is exchanged between water and headspace, resulting in an altered dissolved inorganic carbon (DIC) concentration in the water of the sample, thereby altering the equilibrium of the carbonate system in the water. Depending on partial pressure of CO\(_2\) in the water relative to the headspace gas prior to equilibration, some CO\(_2\) will either be produced from HCO\(_3^-\) or converted to HCO\(_3^-\). The exact amount will depend on temperature, pH, total alkalinity (TA), and the original \( p\text{CO}_2 \) of the water sample. If a CO\(_2\)-free headspace gas was applied, the vessel will finally contain more CO\(_2\) than before equilibration, and consequently simply applying Henry’s law results in too high a \( p\text{CO}_2 \) value. If an ambient-air headspace is applied, the error becomes negative in undersaturated samples and the calculated \( p\text{CO}_2 \) an underestimate.

To calculate this error we implemented an R script that simulates the above-mentioned physical and chemical equilibration for a wide range of hypothetical \( p\text{CO}_2 \), alkalinity, temperature, and headspace ratio (HR = \( V_{\text{gas}}/V_{\text{liquid}} \)) values. As output, we then compared the corrected (for the chemical equilibration shift) and non-corrected \( p\text{CO}_2 \) values. All simulations were performed at 1 atm total pressure and results expressed as µatm.

2.2 Field data

As a further validation of our simulations, we used various datasets for which the \( p\text{CO}_2 \) was determined in multiple ways. We collated 266 observations from four reservoirs and three streams in Germany, 10 Canadian lakes, and a Malaysian reservoir exhibiting a wide range of TA between 0.03 and 1.9 mmol L\(^{-1}\) and pH between 5.2 and 9.8. Two independent techniques were used to measure water \( p\text{CO}_2 \) in each sampling site: the in situ non-dispersive infrared (NDIR) technique and the headspace equilibration technique. The same NDIR technique was used for all sites, while the headspace technique differed slightly between sites. First, for the in situ NDIR technique, the water was pumped through the lumen side of a membrane contactor (MiniModule, Membrana, USA) (Cole and Prairie, 2009), and the gas side was connected to a NDIR analyser (EGM4, PP Systems, USA; or LGR ultra-portable gas analyser) in a counterflow recirculating loop. Readings were taken when the CO\(_2\) mole fraction (mCO\(_2\), ppm) values of the NDIR analyser became stable (fluctuating ±3 ppm around the mean), at which point the gas loop was in direct equilibrium with the sampled water. Finally, \( p\text{CO}_2 \) of the water was calculated by multiplying the mCO\(_2\) by the ambient atmospheric pressure. Second, for the headspace technique, the methodology differed slightly among locations. In the German reservoirs, about 40 mL of water sample were taken in 60 mL syringes, and eventually occurring bubbles were pushed out by adjusting the sample volume to 30 mL. Samples were stored at 4 °C and analysed within 1 d. In the laboratory, 30 mL of pure \( N_2 \) gas was added to the syringes after the samples had reached laboratory temperature, and the syringes were shaken for 1 h at laboratory temperature. After headspace equilibration, the water was discarded from the syringes and the headspace was manually injected into a gas chromatograph equipped with a flame ionization detector (FID) and a methanizer (GC 6810C, SRI Instruments, USA). In the Canadian lakes, 20 mL samples were taken in 60 mL syringes and equilibrated with a 40 mL volume of atmospheric air by vigorously shaking the syringes for 2 min. In the Malaysian reservoir, 600 mL of water samples was taken in 1.2 L of glass bottles and equilibrated with 611.5 mL of atmospheric air in 2016. In consecutive years, diverse volumes of water samples were taken in 60 or 100 mL syringes and equilibrated with diverse volumes of calibrated air brought from the laboratory. The equilibrated air was immediately transferred to and stored in 12 mL pre-evacuated exetainer vials (Labco Ltd, UK) and returned to the laboratory where it was injected into a gas chromatograph (GC-2014, Shimadzu, Kyoto, Japan) equipped with a FID. The original water \( p\text{CO}_2 \) was then calculated according to the headspace ratio, temperature, and the measured headspace mCO\(_2\) as follows:
where \( m_{\text{CO}_2} \text{Before eq} \) and \( m_{\text{CO}_2} \text{After eq} \) are the \( \text{CO}_2 \) mole fractions in the headspace before and after equilibrium (ppm) respectively. \( K_{h,\text{Eq}} \) and \( K_{\text{Sample}} \) are the gas solubility at the equilibration temperature and at the sampling temperature (Henry coefficient, Sander, 2015) (mol L\(^{-1}\) atm\(^{-1}\)), \( P \) is pressure (atm), \( V_{\text{gas}} \) is the headspace volume, \( V_{\text{liquid}} \) is the sampled-water volume, and \( V_m \) is the molar volume (L mol\(^{-1}\)) (UNESCO/IHA, 2010). Results from Eq. (1) are reported as \( p_{\text{CO}_2} \) at 1 atm of barometric pressure and are corrected for ambient pressure at the time of sampling by multiplying with the in situ atmospheric pressure.

The difference between the headspace and NDIR method was divided by the \( p_{\text{CO}_2} \) measured by the in situ NDIR analysis and expressed as percent (\%) error. In addition, temperature and pH of the water were measured in situ by a CTD probe (Sea and Sun, Germany) or a portable pH meter (pH meter 913, Metrohm Ltd, Canada). In samples from Canada and Germany, TA was analysed by titration with 0.11 N HCl. In some systems, a single TA measurement was available for multiple dates and therefore assumes little temporal variability in the alkalinity of these systems. In the Malaysian samples, TA was derived from dissolved inorganic carbon (DIC) measurements and pH. Analysis of certified calibration gases showed that the analytical error of both the NDIR instrument and GC was <0.37 % at 1000 ppm. Analysis of seven replicate samples by our GC-headspace method gave a standard deviation of 6 %. This includes all random errors due to sampling, sample handling, and analysis.

To demonstrate the effect of our correction procedure, we used data from 377 lakes for which we had complete ancillary data and precise headspace measurements of \( \text{CO}_2 \) (<5 % error between duplicates) obtained from the pan-Canadian Lake Pulse sampling programme (Fig. B1a; see Huot et al., 2019 for details).

### 3 Results and discussion

#### 3.1 Simulations from chemical equilibrium

Applying a \( \text{CO}_2 \)-free gas as headspace always results in a positive error (overestimation of the real \( p_{\text{CO}_2} \), Fig. 1a). If ambient air is applied as headspace, the error becomes negative in case of undersaturated samples (Fig. 1b). In general, the error tends to be lower if ambient air is used for headspace equilibration (Fig. 1b) compared to equilibration with \( \text{CO}_2 \)-free gas (Fig. 1a), except in undersaturated conditions. This is because less \( \text{CO}_2 \) is exchanged between water and headspace during the equilibration procedure. The error will be below 5 % in supersaturated and low-alkalinity (>900 µmol L\(^{-1}\)) samples, which are typical for boreal regions. However, the error can be higher than 100 % if the samples are undersaturated. The magnitude of the error is predictable from pH. Because of the carbonate equilibrium reactions, high pH is necessarily accompanied by low \( p_{\text{CO}_2} \) for a given alkalinity. Consequently, the error is large at high pH, while it is below 10 % at pH < 8 (headspace gas–liquid ratio of 1 : 1).

Our field dataset is consistent with the theoretical predictions. While the fit between the simple headspace calculation and NDIR values over the whole range of values can be considered adequate overall (Fig. 2a, \( R^2 = 0.92 \)), it is clear that the deviations can become very large (up to about 300 %), particularly at water \( p_{\text{CO}_2} \) values <600 µatm (Fig. 2b). As expected from the simulations, the error in undersaturated samples was positive when using \( \text{CO}_2 \)-free gas as headspace and negative (sometimes impossible negative results) when
using ambient air (Fig. 2b). The error became negligible at \( \mathrm{pCO}_2 \) above 1000 µatm (Fig. 2b). Data scatter was considerable as was observed previously (Johnson et al., 2010), most probably because the analytical error of the applied methods was often in the same range as the absolute difference between both methods.

### 3.2 Error magnitude depends on the experimental procedure

The maximum error depends on how much \( \mathrm{CO}_2 \) is exchanged between water and headspace. The more gas is exchanged between water and headspace the higher the error is. Thus, the error increases with decreasing solubility coefficient or HR. In high-alkalinity samples, the error can be significantly reduced by using a smaller headspace-to-water ratio (Fig. 3). By lowering the headspace ratio from 1 to 0.2 at 20°C, the error can be reduced from about 50% to about 10%.

Since solubility of \( \mathrm{CO}_2 \) depends on temperature, the equilibration temperature also affects headspace equilibration. Due to lower solubility at higher temperature, more gas evades into the headspace, and thus the error increases with increasing temperature (Fig. 3a, b). At a HR of 1, the error increases from 97% at 20°C to 111% at 25°C in a high (1 mmol L\(^{-1}\)) alkalinity sample. Thus, the error can be significantly reduced by lowering the equilibration temperature. A possible way to take advantage of this is to perform headspace equilibration at in situ temperature in the field, as has been done in several studies. If in situ water temperature is lower than typical laboratory temperature, the error is thereby reduced. However, care must be taken to make sure that the exact equilibration temperature is known. For example, an error of 1 °C in the equilibration temperature results in a 2% different \( \mathrm{pCO}_2 \) value (\( \mathrm{TA} = 1 \) mmol L\(^{-1}\), \( \mathrm{pCO}_2 = 1000 \) µatm, HR = 1) (Fig. A1a). Both ambient air and \( \mathrm{N}_2 \) can be used as headspace gas. Using \( \mathrm{N}_2 \), however, eliminates the error associated with the exact quantification of \( \mathrm{pCO}_2 \) before.

### 3.3 What about kinetics?

\( \mathrm{CO}_2 \) reactivity with water would not cause a problem for headspace analysis if the reaction kinetics were slow compared to physical headspace equilibration. The slowest reaction of the carbonate system is the hydration of \( \mathrm{CO}_2 \), which has a first-order rate constant of 0.037 s\(^{-1}\) (Soli and Byrne, 2002), so that chemical equilibrium of \( \mathrm{CO}_2 \) in water is in the range of seconds (Zeebe and Wolf-Gladrow, 2001; Schulz et al., 2006). This means that chemical equilibrium reactions are faster than physical headspace equilibration, and the chemical system can be assumed to always be in equilibrium. Thus, the reactions of the carbonate system have to be fully considered in headspace analysis of \( \mathrm{CO}_2 \).

### 3.4 Correction of \( \mathrm{CO}_2 \) headspace data

If other information regarding the carbonate system of the sample is known (alkalinity or DIC), one can correct for the bias induced by simple headspace calculations. A procedure to correct headspace \( \mathrm{CO}_2 \) data using pH and alkalinity is already available in the standard operating procedure (SOP) no. 4 in Dickson et al. (2007) for marine samples and could...
be adapted to freshwater samples as well. For convenience, we provide here a modified procedure when the alkalinity of the sample is known by introducing an analytical solution to the equilibrium problem (iterative in SOP no. 4) and by using dissociation constants that may be more appropriate to fresh waters. The procedure essentially involves estimating the exact pH of the equilibrium solution before and after equilibration. If the alkalinity of the sample is known, the pH \((-\log_{10}[\text{H}^+])\) of the aqueous solution after equilibration can be obtained by finding the roots of the third-order polynomial:

\[
0 = [\text{H}^+]^3 + TA \cdot [\text{H}^+]^2 - ([\text{CO}_2] K_1 + K_w) [\text{H}^+] - 2K_1K_2[\text{CO}_2],
\]

where \([\text{CO}_2] = \rho \text{CO}_2 \cdot K_{hEeq}\) and from which one can obtain the ionization fraction for \text{CO}_2 \((\alpha_{\text{CO}_2})\) as

\[
\alpha_{\text{CO}_2} = \frac{1}{1 + \frac{K_1}{[\text{H}^+]^2} + \frac{K_2}{[\text{H}^+]^3}},
\]

where \(K_1\) and \(K_2\) are the temperature-dependent equilibrium constants for the dissociation reactions for bicarbonates and carbonates, respectively (Millero, 1979), and for estuarine conditions (Millero, 2010), as amended in Orr et al. (2015). \(K_w\) is the dissociation constant of water into \text{H}^+ and \text{OH}^- (Dickson and Riley, 1979). The total DIC contained in the original sample \(\text{DIC}_{\text{orig}}\) can then be calculated as

\[
\text{DIC}_{\text{orig}} = \frac{\text{CO}_2}{\alpha_{\text{CO}_2}} + (\text{CO}_2 \text{HS after} - \text{CO}_2 \text{HS before}),
\]

where \(\text{CO}_2\) is the amount of \text{CO}_2 in the equilibrated water (mol), and \(\text{CO}_2 \text{HS after}\) and \(\text{CO}_2 \text{HS before}\) are the amount of \text{CO}_2 in the headspace after and before equilibration (mol). Given the DIC concentration of the original solution from Eq. (4) \(\langle \text{DIC} \rangle = \text{DIC}_{\text{orig}}/V_{\text{liquid}}\), the pH of this solution prior to equilibration can be obtained by finding the roots of the fourth-order polynomial,

\[
0 = [\text{H}^+]^4 + (TA + K_1) \cdot [\text{H}^+]^3
\]

\[
+ (\text{TA} \cdot K_1 - K_w + K_1K_2 - [\text{DIC}]_{\text{orig}} K_1) \cdot [\text{H}^+]^2
\]

\[
+ (K_1 K_2 \cdot \text{TA} - K_1 K_w - 2[\text{DIC}]_{\text{orig}} K_1 K_2) \cdot [\text{H}^+] - K_1 K_2 K_w,
\]

(5)

to then estimate the corresponding ionization fraction \(\alpha'_{\text{CO}_2}\) as in Eq. (3) above and calculate the original \(\rho \text{CO}_2\) of the sample as

\[
\rho \text{CO}_2 = \frac{\alpha'_{\text{CO}_2} \cdot [\text{DIC}]_{\text{orig}}}{K_{h\text{Sample}}},
\]

where \(K_{h\text{Sample}}\) is the headspace dissociation constant of water in the sample headspace.

Figure 3. Error (%) when applying simple headspace calculation depending on headspace ratio and equilibration temperature for (a) 100 µmol L\(^{-1}\) and (b) 1000 µmol L\(^{-1}\) alkalinity. Panels (a) and (b) were constructed using highly undersaturated conditions (headspace \(p\text{CO}_2 = 50 \mu\text{atm}\) after equilibration and field water temperature of 20℃). The values of some isolines are added for reference. (c) Error (%) applying our complete headspace method when the alkalinity value supplied for calculations is off the real alkalinity of the sample by +50%. The results are for hypothetical water samples of different alkalinity and \(p\text{CO}_2\) in the headspace after equilibration using \text{CO}_2-free gas headspace, a headspace ratio of 1 : 1, and an equilibration and field temperature of 20℃. (d) Like panel (c) but with air headspace. All calculations assume a pressure of 1 atm.
where $K_{H, \text{Sample}}$ is determined for the water temperature during field sample collection (for simplicity, the equations above assume 1 atm pressure). We applied the above correction procedure to our samples, where $pCO_2$ was measured in several samples using both headspace and in situ NDIR methods together with measured alkalinity data. Figure 4 shows that the corrected values matched the in situ NDIR values nearly perfectly ($r^2 = 0.98$), whereas the simple headspace calculations resulted, as expected, in significant underestimation for undersaturated conditions, particularly for samples equilibrated with ambient air.

We examined the sensitivity of the correction procedure to the precision of the alkalinity measurements and found that the error associated with alkalinity determination does not severely impact the final $pCO_2$ estimate when using N$_2$ as a headspace gas. For example, the error in the corrected $pCO_2$ values is always below 20% even when the alkalinity is known only to within 50% error (Fig. 3c). However, more precise alkalinity values are required when using ambient air as a headspace gas in undersaturated conditions (Fig. 3d).

Lastly, our simulations (Figs. 2 and 4) provide a complete analysis of the effects of the environmental and methodological conditions on the error incurred when using the simple headspace technique for estimating $pCO_2$. However, they do not assess how often such problematic conditions occur in inland water systems. To address this question, we applied our correction procedure to a dataset from 377 Canadian lakes (Huot et al., 2019). These results show a significant deviation between corrected and uncorrected values, particularly in lakes with high alkalinity (> 900 µmol L$^{-1}$, Fig. B1b), and ignoring the correction would have resulted in errors > 20% in about 47% of the data. Furthermore, our analysis illustrates how a larger headspace ratio significantly exacerbates the magnitude of the error (Fig. B1b).

The correction calculations have been implemented in an R script and, for a user-friendly interface, as a JMP add-in (or JSL script) (https://github.com/icra/headspace, last access: 3 March 2021). Roots of the polynomials (Eqs. 2 and 5) can be solved using either standard analytical formulas or by iterative algorithms. For the analytical solution, our script uses a combined form of the computational steps described in Zwilinger (2018) for both the cubic and quartic polynomials to find their first real roots. Analytical solutions are faster than iterative algorithms but can suffer small numerical instabilities (SD ≈ 1 ppm) in extreme situations (alkalinity > 4000 µmol L$^{-1}$ and $pCO_2 < 100$ ppm) due to limitations inherent to double-precision numerical calculations. The provided scripts consider the barometric pressure and thus allow calculation of $pCO_2$ as well as CO$_2$ concentration (µmol L$^{-1}$) for in situ conditions.

4 Conclusions

The headspace method has been used in several studies about CO$_2$ fluxes from surface waters. Our error analysis shows that the usual headspace method can be used (error < 5%) if the pH is below 7.5 or $pCO_2$ is above 1000 µatm (TA < 900 µmol L$^{-1}$, air headspace), a typical situation in most boreal systems. However, the standard headspace method introduces large errors and cannot be used reliably for undersaturated samples, which are typical of eutrophic or low-DOC systems. In all other cases, not accounting for the chemical equilibrium shift leads to a systematic overestimation. The magnitude of the error can be reduced by increasing the water–headspace ratio or lowering the equilibration temperature. The magnitude of that error can be roughly estimated from Fig. 1. If alkalinity is known, $pCO_2$ obtained from headspace equilibration can be corrected by the provided scripts. We therefore recommend to always measure alkalinity if the headspace method is to be used for $pCO_2$ determinations. The procedure can also be used to correct historical $pCO_2$ data. Our field data showed that the correction works well even in highly undersaturated conditions and is not very sensitive to the precise determination of alkalinity if N$_2$ is used as a headspace gas. The precision of the corrected $pCO_2$ is similar to that obtained from direct $pCO_2$ measurement using a field NDIR analyser coupled to an online equilibrator (Cole and Prairie, 2009; Yoon et al., 2016).
Appendix A: Sensitivity analysis equilibration temperature and CO₂₇3

Figure A1. Error for a hypothetical sample with CO₂₇3_before_eq = 400 ppm, CO₂₇3_after_eq = 1000 ppm, equilibration temperature of 20 °C, and HR = 1 (a) depending on error in equilibration temperature and (b) depending on error in initial headspace gas composition.

Appendix B: Application of our correction to a large Canadian dataset

Figure B1. Field data from 377 lakes across Canada (a) for comparing pCO₂ derived from simple headspace calculation with that from the corrected headspace calculation according to this paper (Log₁₀ [TA (μmol L⁻¹)] colour coded). (b) Difference between the uncorrected and corrected pCO₂ expressed as error (%) as a function of TA (μmol L⁻¹) (the headspace ratio colour coded). Note that CO₂-free gas was used for headspace, and TA values were derived from DIC measurement and pH. More information about the dataset can be found in Huot et al. (2019).
Code availability. All codes are publicly available at https://github.com/icra/headscape (Marcé, 2020) and https://doi.org/10.5281/zenodo.4577401 (Marcé, 2021).

Data availability. All data can be found in the Supplement.

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/bg-18-1619-2021-supplement.

Author contributions. All authors conceived the story, performed calculations, and wrote the manuscript. JK, YTP, and RM wrote codes. MK and JK contributed field data.

Competing interests. The authors declare that they have no conflict of interest.

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