Technical note: CO₂ is not like CH₄ – limits of and corrections to the headspace method to analyse pCO₂ in water

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Abstract. Headspace analysis of CO₂ frequently has been used to quantify the concentration of CO₂ in freshwater. According to basic chemical theory, not considering chemical equilibration of the carbonate system in the sample vials will result in a systematic error. In this paper we provide a method to quantify the potential error resulting from simple application of Henry’s law to headspace CO₂ samples. By analysing the potential error for different types of water and experimental conditions we conclude that the error incurred by headspace analysis of CO₂ is less than 5% for samples with pH < 7.5. However, the simple headspace calculations can lead to high error (up to -800%) or even impossible 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 and use of a CO₂ free gas for headspace creation. We provide a direct method to correct CO₂ 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 alkalinity and pH (Lewis and Wallace, 1998; Robbins et al., 2010) are affected by considerable random and systematic errors (Golub et al., 2017) caused e.g. by dissolved organic carbon which may result in significant over estimation of the CO$_2$ partial pressure (pCO$_2$) (Abril et al., 2015). Thus, direct measurement of CO$_2$ is highly recommended, particularly in softwaters.

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 infra-red 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 the 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. Surprisingly, papers and protocols have been published which use this method also to analyse dissolved CO$_2$ concentrations in freshwaters (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, 2009). Although this is textbook knowledge and has been considered in numerous papers (Golub et al., 2017; Gelbrecht et al., 1998; Rantakari et al., 2015; Aberg and Wallin, 2014; Horn et al., 2017), especially in marine research (Dickson et al., 2007), a practical evaluation of the systematic error when applying simple headspace analysis on CO$_2$ on typical freshwaters is missing. The underlying assumption is that “the effect is likely small” (Hope et al., 1995). In this paper we aim to quantify the error associated with the simple application of Henry’s law on headspace CO$_2$ data, present practical guidelines describing conditions under which the simple headspace analysis of CO$_2$ can give acceptable results, and offer a tool for exact CO$_2$ calculation using a complete headspace method that accounts for the carbonate equilibrium in the sample vessel, which can also be used for correcting results obtained by simple headspace analysis of CO$_2$ using additional information regarding the carbonate system (i.e. alkalinity or DIC). Lastly, we tested the proposed correction procedure to a set of field measurements where pCO$_2$ was determined with independent methods (with and without headspace equilibration).
2. Methods

2.1 Theoretical considerations

If a water sample is equilibrated with a headspace containing a given pCO₂ (zero in case N₂ or other CO₂-free gas is used), some CO₂ is exchanged between water and headspace resulting in an altered dissolve inorganic carbon (DIC) concentration in the water of the sample thereby altering the equilibrium of the carbonate system in the water. Depending on partial pressures of CO₂ in the water relative to the headspace gas prior to equilibration, some CO₂ will either be produced from HCO₃⁻ or converted to HCO₃⁻. The exact amount will depend on temperature, pH, alkalinity, and the original pCO₂ of the water sample. If an N₂ headspace was applied, the vessel will finally contain more CO₂ than before equilibration and consequently simply applying Henry’s law results in a too high pCO₂ value. If an air headspace is applied, the error becomes negative in undersaturated samples.

To calculate this error we implemented an R-script that simulates the above mentioned physical and chemical equilibration for a wide range of hypothetical pCO₂, alkalinity, temperature, and headspace ratio (HR = V_gas / V_liquid) values. As output, we then compared the corrected (for the chemical equilibrium shift) and non-corrected pCO₂ values.

2.1 Field data

We routinely sampled water in 4 German reservoirs and 11 Canadian lakes exhibiting a wide range of total alkalinity (TA) between 0.2 and 2.4 meq L⁻¹. Two techniques were used to measure water pCO₂ in each sampling site: in situ NDIR technique and headspace equilibration technique. First, for the in situ NDIR technique, the water is pumped through the lumen side of a membrane contactor (mini module, Membrana, U.S.A.) (Cole and Prairie, 2009) and the gas side is connected to a NDIR analyser (EGM4, PP-Systems, U.S.A. or LGR ultra-portable gas analyser) in a counter-flow recirculating loop. Readings were taken when the CO₂ [ppmv] values of the NDIR analyser became stable (usually less than a minute) at which point the gas loop is in direct equilibrium with the sampled water. Final pCO₂ of the water was calculated by multiplying the CO₂ mixing ratio by the ambient atmospheric pressure. Second, for the headspace technique, the water samples were taken in 60 mL syringes. In the German reservoirs, about 40 mL of water sample were taken 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 day. In the laboratory, 30 mL of pure N₂ gas was added to the syringes after the samples had reached laboratory temperature and the syringes were shaken for one hour at laboratory temperature. After headspace equilibration 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, SR1 Instruments, U.S.A.). In the Canadian lakes, 20 mL of the water samples were taken and equilibrated with 40 mL volume of atmospheric air by vigorously shaking the syringes for 2 minutes. The equilibrated air was immediately transferred to and stored in 12 mL pre-evacuated extetainer 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 pCO₂ was then calculated according to the headspace ratio, temperature, and the measured headspace pCO₂ as follows:
\[ p_{CO_2} = \frac{\left( p_{CO_2\ after\ eq} \times K_h\ eq \right)}{K_h\ sample} \left( \frac{V_{liquid}}{V_{gas}} \times \frac{\left( p_{CO_2\ after\ eq} - p_{CO_2\ before\ eq} \right)}{V_m} \right) \]

**Eq. 1**

with \( p_{CO_2\ before\ eq} \) and \( p_{CO_2\ after\ eq} = CO_2 \) mixing ratio in the headspace before and after equilibrium [ppm], \( K_h\ eq \) and \( K_h\ sample \) = gas solubility at the equilibration temperature and at the sampling temperature (Henry coefficient (Sander, 2015) [mol L\(^{-1}\) atm\(^{-1}\)], \( V_{gas} \) = headspace volume, \( V_{liquid} \) = sampled-water volume, and \( V_m \) = molar volume [L mol\(^{-1}\)] (UNESCO/IHA, 2010).

The difference between the two methods was divided by the pCO\(_2\) measured by the in situ NDIR analysis and expressed as % 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 12 samples from Canadian lakes, total alkalinity (TA) was analysed by titration with 0.11N HCl.

### 3. Results and Discussion

#### 3.1 Simulations from chemical equilibrium

Applying a CO\(_2\)-free gas as headspace always resulted in a positive error (over-estimation of the real pCO\(_2\), Figure 1a). If air is applied as headspace the error becomes negative in case of under saturated samples (Figure 1b). The error tends to be lower if ambient air is used for headspace equilibration (Figure 1b) compared to equilibration with CO\(_2\)-free gas (Figure 1a). This is because less CO\(_2\) is exchanged between water and headspace during the equilibration procedure. The error will be quite low in high CO\(_2\), low alkalinity samples which are typical for boreal regions. However, the error can be higher than 100% if the samples are under saturated. The magnitude of the error is predictable from pH. Because of the carbonate equilibrium reactions, high pH is necessarily accompanied by low pCO\(_2\) for a given alkalinity. Consequently, the error is large at high pH while it is below 10 % at pH < 8 (headspace ratio 1:1).

Our field dataset is consistent with the theoretical predictions. The fit between both methods is rather good (Figure 2a, \( R^2 = 0.96 \)) showing that the absolute error was in an acceptable range. However, the relative error reached values up to 200 %. A large error was observed at low pCO\(_2\) while the error approached zero at pCO\(_2\) above 1000 µatm (Figure 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. In under-saturated samples the difference between N\(_2\) and air headspace became apparent, in line with theoretical predictions the error became negative when air was applied as headspace (Figure 2b).

#### 3.2 Error magnitude depends on the experimental procedure

The maximum error (\( error_{max} \)) depends on how much gas 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 larger headspace to water ratio (Figure 3). By raising the headspace ratio from 1 to 5 at 20°C the error can be reduced from about 50% to about 10%.

Since solubility of CO₂ 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 (Figure 3). At a HR of 1, the error increases from 97% at 20°C to 111% at 25°C in a high (1 meq 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 have 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.

### 3.3 What about kinetics?

CO₂ 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 CO₂ which has a first order rate constant of 0.037 s⁻¹ (Soli and Byrne, 2002) so that chemical equilibration of CO₂ 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 always to be in equilibrium. Thus, the reactions of the carbonate system have to be fully considered in headspace analysis of CO₂.

### 3.4 Correction of CO₂ 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. The procedure involves estimating the exact pH of the equilibrium solution before and after equilibration. Here, we develop the procedure when the alkalinity of the sample is known, in addition to the usual parameters required for headspace calculations: water temperature of equilibration and in the field, pCO₂ after equilibration, pCO₂ of the headspace gas before equilibration, and headspace ratio.

After equilibration, the pH (-\log_{10}[H⁺]) of the aqueous solution can be obtained by finding the roots of the 3rd polynomial

\[
0 = [H⁺]^3 + TA \cdot [H⁺]^2 - (\{CO₂\}K₁ + K_w[H⁺]) - 2K₁K₂[CO₂] \quad \text{Eq. 2}
\]

where \([CO₂] = pCO₂ \cdot K_h[n] \) and from which one can obtain the ionisation fraction for CO₂ (\(α_{CO₂}\)) as

\[
α_{CO₂} = \frac{1}{1 + \frac{K₅}{[H⁺]} + \frac{K₆}{[H⁺]^2}} \quad \text{Eq. 3}
\]

Where K₁ and K₂ are the temperature -dependent equilibrium constants for the dissociation reactions for bicarbonates and carbonates, respectively (Millero, 1979). K_w is the dissociation constant of water into H⁺ and OH⁻ (Millero, 1979). The total DIC contained in the original sample (DIC_{orig}) can then be calculated as
Given the DIC concentration of the original solution from Eq. 4, the pH of this solution prior to equilibration can be obtained by finding the roots of the 4th order polynomial

\[ 0 = [H^+]^4 + (TA + K_1) \cdot [H^+]^3 + (TA \cdot K_1 - K_w + K_1 K_2 - [DIC]_{orig} K_1) \cdot [H^+]^2 + (K_1 K_2 \cdot TA - K_1 K_w - 2 [DIC]_{orig} K_1 K_2) \cdot [H^+] - K_1 K_2 K_4 \]  

Eq. 5

to then estimate the corresponding ionization fraction \( a'_{\text{CO}_2} \) as in Eq. 3 above and calculate the original pCO2 of the sample as

\[ pCO_2 = \frac{a'_{\text{CO}_2} [DIC]_{orig}}{K_{h, \text{Sample}}} \]  

Eq. 6

where \( K_{h, \text{Sample}} \) is determined for the water temperature during field sample collection. We applied the above correction procedure to the Canadian samples where pCO2 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 (\( r^2=0.997 \)) whereas the simple headspace calculations resulted, as expected, in significant underestimation for undersaturated 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 pCO2 estimate when using N2 as a headspace gas. For example, the error in the corrected pCO2 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).

The correction calculations have been implemented in an R script and, for a user-friendly interface, as an JMP add-in (or JSL script) (https://github.com/icra/headspace). Roots of the polynomials (Eqs. 2 and 5) can be solved using either standard analytical formulas (e.g. Zwillinger (2018)) or by iterative algorithms. Analytical solution are faster than iterative algorithms but can suffer small instabilities (SD\( \approx 1 \) ppmv) in extreme situations (alkalinity >4000 \( \mu \text{eq L}^{-1} \) and pCO2 <100 ppmv) due to limitations inherent to double precision numerical calculations.

4. Conclusions

The headspace method has been used in several studies about CO2 fluxes from surface waters. Our error analysis shows that the usual headspace method can be used (error\( \approx 5\% \)) if the pH is below 7.5 or pCO2 is above 1000 \( \mu \text{atm} \) (TA\( \approx 1700 \), air headspace), a typical situation in most boreal systems. However, the standard headspace introduces large errors and cannot be used reliably for under saturated 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 over estimation. The magnitude of the error can be reduced by increasing the water/headspace ratio, lowering the equilibration temperature, and/or using air instead of N2 as headspace. The
magnitude of that error can be roughly estimated from Figure 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 on-line equilibrator (Cole and Prairie, 2009; Yoon et al., 2016).

5. Code availability

All codes are publicly available at https://github.com/icra/headspace

6. Data availability

All data can be found in the supplemental information file.

7. Supplement link (will be included by Copernicus)

8. Author contribution

All authors conceived the story and wrote the manuscript. JHK, YP, and RM wrote codes and performed calculations. MK and JHK contributed field data.

9. Competing interests

The authors declare that they have no conflict of interest.

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Figure 1: Error [%] when applying simple headspace calculations of pCO₂ on hypothetical water samples of different alkalinity and pCO₂ in the headspace after equilibration for (a) N₂ headspace and (b) air headspace. The resulting pH and pCO₂ of the samples are depicted as full and dashed lines, respectively. Headspace ratio 1:1, equilibration and field temperature 20°C. Note the log scale in all axes. In b) results for pCO₂ in headspace after equilibration lower than 215 µatm are masked, because they would imply negative pCO₂ in the sample.

Figure 2: (a) Field data from 4 German reservoirs and 11 Canadian lakes comparing pCO₂ derived from headspace analysis with direct pCO₂ measurements by NDIR analysis (pH colour coded). (b) Difference between both methods expressed as percentage of the NDIR value as a function of pCO₂. Open symbols: air headspace, closed symbols: N₂ headspace applied.
Figure 3: Error [%] when applying simple headspace calculation depending on headspace ratio and equilibration temperature for a) 100 µmol/L and b) 1000 µmol/L alkalinity. Panels a and b were constructed using highly undersaturated conditions (headspace pCO2=50 µatm after equilibration and field water temperature of 20°C). The value 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 pCO2 in the headspace after equilibration using N2 headspace, headspace ratio 1:1, and equilibration and field temperature of 20°C. d) like c) but with air headspace.
Figure 4: Comparison of uncorrected and corrected data (using measured alkalinity) with pCO₂ measured by NDIR analysis. Blue dots indicate samples with negative concentrations if not corrected.

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