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

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Abstract. Headspace analysis of CO$_2$ frequently has been used to quantify the concentration of CO$_2$ 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. 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 under saturated 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 a 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 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), or by pH measurement errors (Liu et al., 2020). Thus, direct measurement of CO_2 is highly recommended, particularly in softwaters.

Headspace analysis is a standard method to analyse the concentration of dissolved gasses 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_2O (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 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 some recent papers (Golub et al., 2017; Gelbrecht et al., 1998; Rantakari et al., 2015; Aberg and Wallin, 2014; Horn et al., 2017), and is standard practice in marine research (Dickson et al., 2007), a practical evaluation of the systematic error when applying simple headspace analysis to CO_2 on typical freshwaters is missing, presumably because it is widely assumed 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 convenient tool for the exact CO_2 calculation that accounts for the carbonate equilibrium shifts in the sample equilibration vessel. The approach can also be used for correcting previous results obtained by simple headspace analysis of CO_2 using additional information regarding the carbonate system (i.e. alkalinity or DIC), a procedure we tested on a set of field measurements where pCO_2 was determined with independent methods (with and without headspace equilibration). Lastly, we evaluated how likely this correction may be required using a large data set from 337 diverse Canadian lakes.

2. Methods

2.1 Theoretical considerations

If a water sample is equilibrated with a headspace initially containing a known pCO_2 (zero in case N_2 or other 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 pressures 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 pCO_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 a too high pCO_2 value. If ambient air headspace is applied, the error becomes negative in under-saturated samples and the calculated pCO_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 pCO_2, 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 pCO_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 data sets for which the pCO_2 was determined in multiple ways. We collated 266 observations from 4 reservoirs and 3 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 pCO_2 in each sampling site: *in situ* NDIR technique and 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 (mini module, Membrana, U.S.A.) (Cole and Prairie, 2009) and the gas side was 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 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 is in direct equilibrium with the sampled water. Final pCO_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 day. 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 one hour 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, U.S.A.). In the Canadian lakes, 20 mL of the water samples were taken in 60 mL syringes and equilibrated with 40 mL volume

89   of atmospheric air by vigorously shaking the syringes for 2 minutes. In the Malaysian reservoir, 600 mL of water samples

90   were taken in 1.2 L of glass bottles and equilibrated with 611.5 mL of atmospheric air in 2016. In consecutive years, diverse

91   volumes of water samples were taken in 60 mL or 100 mL syringes and equilibrated with diverse volumes of calibrated air

92   brought from the laboratory. The equilibrated air was immediately transferred to and stored in 12 mL pre-evacuated exetainer

93   vials (Labco Ltd., UK) and returned to the laboratory where it was injected into a gas chromatograph (GC-2014, Shimadzu,

94   Kyoto, Japan) equipped with a FID. The original water pCO_2 was then calculated according to the headspace ratio, temperature,

95   and the measured headspace mCO_2 as follows:

96    $$pCO_{2\ water} = \frac{(mCO_{2\ After\ eq} \times K_{h\ Eq} \times P) + \left\{(\frac{V_{gas}}{V_{liquid}}) \times \left(\frac{mCO_{2\ After\ eq} - mCO_{2\ Before\ eq}}{V_m}\right)\right\}}{K_{h\ Sample}}$$ **Eq. 1**

97   with $mCO_{2\ Before\ eq}$ and $mCO_{2\ After\ eq}$ are respectively the CO_2 mole fractions in the headspace before and after equilibrium

98   [ppm], $K_{h\ Eq}$ and $K_{h\ Sample}$ = gas solubility at the equilibration temperature and at the sampling temperature (Henry coefficient

99   (Sander, 2015)) [mol L^{-1} atm^{-1}], P = pressure [atm], V_{gas} = headspace volume, V_{liquid} = sampled-water volume, and V_m = molar

100   volume [L mol^{-1}] (UNESCO/IHA, 2010). Results from Eq. 1 are reported as pCO_2 at one atmosphere of barometric pressure

101   and are corrected for ambient pressure at the time of sampling by multiplying with the in situ atmospheric pressure.

102   The difference between headspace and NDIR method was divided by the pCO_2 measured by the *in situ* NDIR analysis and

103   expressed as % error. In addition, temperature and pH of the water were measured *in situ* by a CTD probe (Sea and Sun,

104   Germany) or a portable pH meter (pH meter 913, Metrohm Ltd, Canada). In samples from Canada and Germany, TA was

105   analysed by titration with 0.11N HCl. In some systems, a single TA measurement was available for multiple dates and therefore

106   assumes little temporal variability in the alkalinity of these systems. In the Malaysian samples, TA was derived from dissolved

107   inorganic carbon (DIC) measurements and pH. Analysis of certified calibration gases showed that the analytical error of both

108   the NDIR instrument and GC was <0.37% at 1000 ppm. Analysis of 7 replicate samples by our GC-headspace method gave a

109   standard deviation of 6%. This includes all random errors due to sampling, sample handling and analysis.

110   To demonstrate the effect of our correction procedure, we used data from 377 lakes for which we had complete ancillary data

111   and precise headspace measurements of CO_2 (<5% error between duplicates) obtained from the pan-Canadian Lake Pulse

112   sampling program (Figure B1a, see Huot et al. (2019) for details).

113   **3.   Results and Discussion**

114   **3.1 Simulations from chemical equilibrium**

115   Applying a CO_2-free gas as headspace always results in a positive error (over-estimation of the real pCO_2, Figure 1a). If

116   ambient air is applied as headspace the error becomes negative in case of undersaturated samples (Figure 1b). In general, the

117   error tends to be lower if ambient air is used for headspace equilibration (Figure 1b) compared to equilibration with CO_2-free

118   gas (Figure 1a), except in undersaturated conditions. This is because less CO_2 is exchanged between water and headspace

119   during the equilibration procedure. The error will be below 5% in supersaturated and low alkalinity (<900 $\mu mol\ L^{-1}$) samples

120   which are typical for boreal regions. However, the error can be higher than 100% if the samples are undersaturated. The

121   magnitude of the error is predictable from pH. Because of the carbonate equilibrium reactions, high pH is necessarily

122   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

123   (headspace gas:liquid ratio of 1:1).

124   Our field dataset is consistent with the theoretical predictions. While the fit between the simple headspace calculation and

125   NDIR values over the whole range of values can be considered adequate overall (Figure 2a, $R^2 = 0.92$), it is clear that the

126   deviations can become very large (up to about 300%), particularly at water pCO_2 values <600μatm (Figure 2b). As expected

127   from the simulations, the error in undersaturated samples was positive when using CO_2-free gas as headspace and negative

128   (sometimes impossible negative results) using ambient air (Figure 2b). The error became negligible at pCO_2 above 1000 μatm

129   (Figure 2b). Data scatter was considerable as was observed previously (Johnson et al., 2010), most probably because the

130   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

132   The maximum error depends on how much CO_2 is exchanged between water and headspace. The more gas is exchanged

133   between water and headspace the higher the error is. Thus, the error increases with decreasing solubility coefficient or HR. In

134   high alkalinity samples, the error can be significantly reduced by using a smaller headspace to water ratio (Figure 3). By

135   lowering the headspace ratio from 1 to 0.2 at 20°C the error can be reduced from about 50% to about 10%.

136   Since solubility of CO_2 depends on temperature, the equilibration temperature also affects headspace equilibration. Due to

137   lower solubility at higher temperature, more gas evades into the headspace and thus, the error increases with increasing

138   temperature (Figure 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})

139   alkalinity sample. Thus, the error can be significantly reduced by lowering the equilibration temperature. A possible way to

140   take advantage of this is to perform headspace equilibration at *in situ* temperature in the field, as has been done in several

141   studies. If *in situ* water temperature is lower than typical laboratory temperature, the error is thereby reduced. However, care

142   must be taken to make sure that the exact equilibration temperature is known. For example, an error of 1°C in the equilibration

143   temperature results in a 2 % different pCO_2 value (TA=1 mmol L^{-1}, $pCO_2 = 1000$ μatm, HR = 1) (Figure A1a). Both ambient

144   air and N_2 can be used as headspace gas. Using N_2, however, eliminates the error associated with the exact quantification of

145   $pCO_{2\ Before}$. Using the same example, an unlikely error of 100 ppm in the headspace gas ($mCO_{2\ Before\ eq}$) results in a 6.4%

146   different pCO_2 result (Figure A1b).

3.3 What about kinetics?

148   CO_2 reactivity with water would not cause a problem for headspace analysis if the reaction kinetics were slow compared to

149   physical headspace equilibration. The slowest reaction of the carbonate system is the hydration of CO_2 which has a first order

rate constant of 0.037 s^{-1} (Soli and Byrne, 2002) so that chemical equilibration of 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 always to be in equilibrium. Thus, the reactions of the carbonate system have to be fully considered in headspace analysis of CO_2.

3.4 Correction of 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 CO_2 data using pH and alkalinity is already available in the SOP N∘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 N∘4) and by using dissociation constants that may be more appropriate to freshwaters. 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 ($-\log_{10}[H^+]$) of the aqueous solution after equilibration can be obtained by finding the roots of the 3rd order polynomial

$$0 = [H^+]^3 + TA \cdot [H^+]^2 - ([CO_2]K_1 + K_w)[H^+] - 2K_1K_2[CO_2] \qquad \text{Eq. 2}$$

where $[CO_2] = pCO_2 \cdot K_{h\,Eq}$ and from which one can obtain the ionisation fraction for CO_2 (α_{CO2}) as

$$\propto_{CO_2} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}} \qquad \text{Eq. 3}$$

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 H^+ and OH^- (Dickson and Riley, 1979). The total DIC contained in the original sample (DIC$_{orig}$) can then be calculated as

$$DIC_{orig} = \frac{CO_2}{\alpha_{CO_2}} + (CO_{2\,HS_{after}} - CO_{2\,HS_{bef}}) \qquad \text{Eq. 4}$$

where CO_2 is the amount of CO_2 in the equilibrated water [mol], CO_{2HS} after + before the amount of CO_2 in the headspace after and before equilibration [mol]. Given the DIC concentration of the original solution from Eq. 4 ([DIC] = DIC$_{orig}$ / V$_{liquid}$), the pH of this solution prior to equilibration can be obtained by finding the roots of the 4th order polynomial

$$0 = [H^+]^4 + (TA + K_1) \cdot [H^+]^3 + (TA \cdot K_1 - K_w + K_1K_2 - [DIC]_{orig}K_1) \cdot [H^+]^2 + (K_1K_2 \cdot TA - K_1K_w - 2[DIC]_{orig}K_1K_2) \cdot [H^+] - K_1K_2K_w \qquad \text{Eq. 5}$$

to then estimate the corresponding ionization fraction α'_{CO_2} as in Eq. 3 above and calculate the original pCO$_2$ of the sample as

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180 $$pCO_2 = \frac{\alpha'_{CO_2} \cdot [DIC]_{orig}}{K_{h\,Sample}}$$ **Eq. 6**

181 where $K_{h\,Sample}$ is determined for the water temperature during field sample collection (for simplicity, the equations above

182 assume a 1 atm pressure). We applied the above correction procedure to our samples where pCO$_2$ was measured in several

183 samples using both headspace and in situ NDIR methods together with measured alkalinity data. Figure 4 shows that the

184 corrected values matched the in situ NDIR values nearly perfectly (r^2=0.98) whereas the simple headspace calculations

185 resulted, as expected, in significant underestimation for undersaturated conditions, particularly for samples equilibrated with

186 ambient air.

187 We examined the sensitivity of the correction procedure to the precision of the alkalinity measurements and found that the

188 error associated with alkalinity determination does not severely impact the final pCO$_2$ estimate when using N$_2$ as a headspace

189 gas. For example, the error in the corrected pCO$_2$ values is always below 20% even when the alkalinity is known only to within

190 50% error (Fig. 3c). However, more precise alkalinity values are required when using ambient air as a headspace gas in

191 undersaturated conditions (Fig. 3d).

192 Lastly, our simulations (Figs. 2 and 4) provide a complete analysis of the effects of the environmental and methodological

193 conditions on the error incurred when using the simple headspace technique for estimating pCO$_2$. However, they do not assess

194 how often such problematic conditions occur in inland water systems. To address this question, we applied our correction

195 procedure to a dataset from 377 Canadian lakes (Huot et al., 2019). These results show a significant deviation between

196 corrected and uncorrected values, particularly in lakes with high alkalinity (>900 μmol L^{-1}, Figure B1b) and ignoring the

197 correction would have resulted errors >20% in about 47% of the data. Furthermore, our analysis illustrates how a larger

198 headspace ratio significantly exacerbates the magnitude of the error (Figure B1b).

199 The correction calculations have been implemented in an R script and, for a user-friendly interface, as an JMP add-in (or JSL

200 script) (https://github.com/icra/headspace). Roots of the polynomials (Eqs. 2 and 5) can be solved using either standard

201 analytical formulas or by iterative algorithms. For the analytical solution, our script uses a combined form of the computational

202 steps described in Zwillinger (2018) for both the cubic and quartic polynomials to find their first real roots. Analytical solutions

203 are faster than iterative algorithms but can suffer small numerical instabilities (SD ≈1 ppm) in extreme situations (alkalinity

204 >4000μmol L^{-1} and pCO$_2$<100ppm) due to limitations inherent to double precision numerical calculations. The provided scripts

205 consider the barometric pressure and thus, allow calculation of pCO$_2$ as well as CO$_2$ concentration [μmol L^{-1}] for *in situ*

206 conditions.

207 **4. Conclusions**

208 The headspace method has been used in several studies about CO$_2$ fluxes from surface waters. Our error analysis shows that

209 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},

210 air headspace), a typical situation in most boreal systems. However, the standard headspace method introduces large errors

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211 and cannot be used reliably for under saturated samples, which are typical of eutrophic or low DOC systems. In all other cases,
212 not accounting for the chemical equilibrium shift leads to a systematic over estimation. The magnitude of the error can be
213 reduced by increasing the water/headspace ratio or lowering the equilibration temperature. The magnitude of that error can be
214 roughly estimated from Figure 1. If alkalinity is known, pCO_2 obtained from headspace equilibration can be corrected by the
215 provided scripts. We therefore recommend to always measure alkalinity if the headspace method is to be used for pCO_2
216 determinations. The procedure can also be used to correct historical pCO_2 data. Our field data showed that the correction works
217 well even in highly undersaturated conditions and is not very sensitive to the precise determination of alkalinity if N_2 is used
218 as a headspace gas. The precision of the corrected pCO_2 is similar to that obtained from direct pCO_2 measurement using a field
219 NDIR analyser coupled to an on-line equilibrator (Cole and Prairie, 2009; Yoon et al., 2016).

5. Appendices

Appendix A: Sensitivity analysis equilibration temperature and CO₂ Before eq
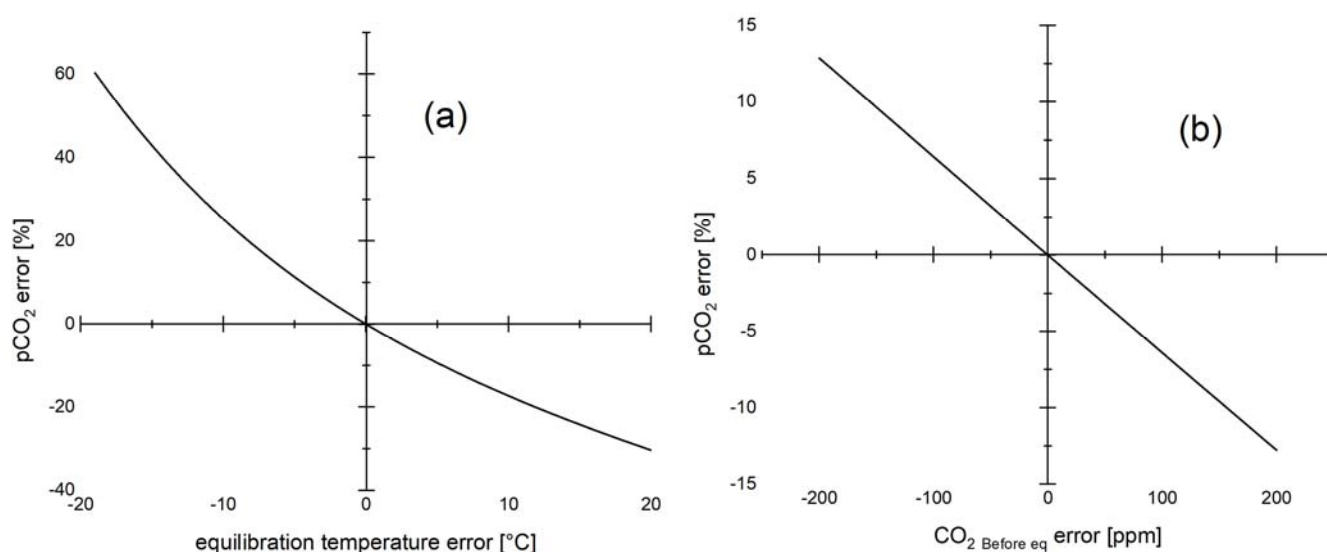
222
223 **Figure A1: Error for a hypothetical sample with CO₂ Before eq = 400 ppm, CO₂ after eq = 1000 ppm, equilibration**
224 **temperature 20°C, HR = 1 (a) depending on error in equilibration temperature (b) depending on error in initial**
225 **headspace gas composition.**

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Appendix B: Application of our correction to a large Canadian dataset
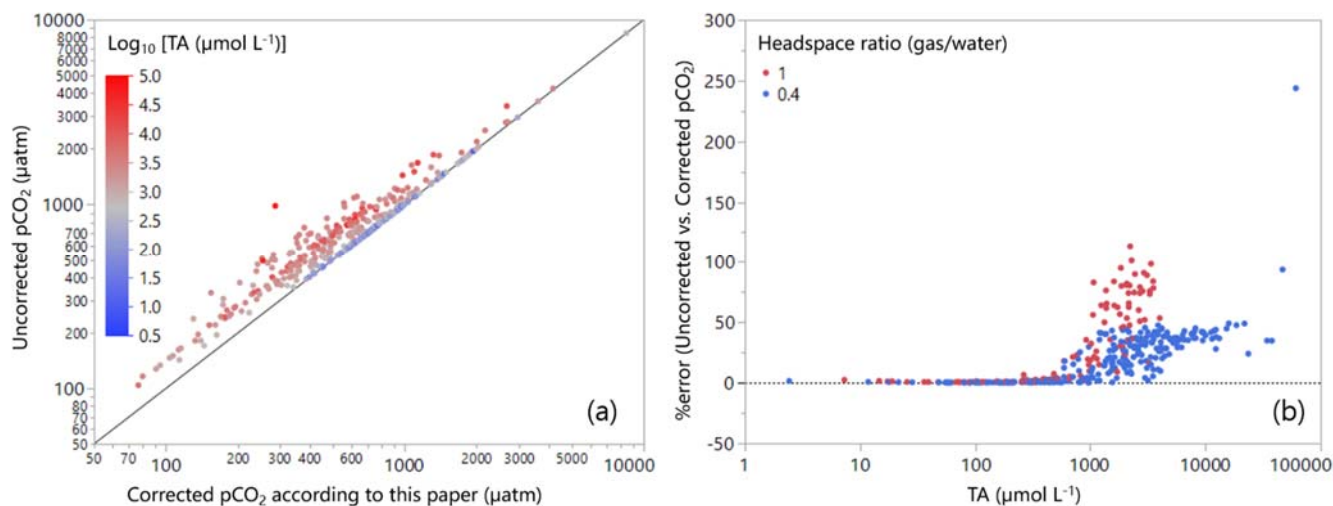
Figure B1: Field data from 377 lakes across Canada (a) for comparing pCO_2 derived from simple headspace calculation with that from the corrected headspace calculation according to this paper (Log_{10} [TA (μmol L^{-1})] colour coded). (b) Difference between the uncorrected and corrected pCO_2 expressed as error (%) as a function of TA (μmol L^{-1}) (The headspace ratio colour coded). Note that CO_2-free gas was used for headspace, and TA values were derived from DIC measurement and pH. More information about the dataset in Huot et al. (2019).

6. Code availability

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

7. Data availability

All data can be found in the supplemental information file.

8. Supplement link (will be included by Copernicus)

9. Author contribution

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

10. Competing interests

The authors declare that they have no conflict of interest.

11. Acknowledgements

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257 **Figure 1: Error [%] when applying simple headspace calculations of pCO_2 on hypothetical water samples of different alkalinity and**
258 **pCO_2 in the headspace after equilibration for (a) CO_2-free gas headspace and (b) ambient-air headspace assuming a pressure of 1**
259 **atm. The resulting pH and pCO_2 of the samples are depicted as full and dashed lines, respectively. Headspace ratio 1:1, equilibration**
260 **and field temperature 20°C. Note the log scale in all axes. In b) results for pCO_2 in headspace after equilibration lower than 215**
261 **µatm are masked, because they would imply negative pCO_2 in the sample.**

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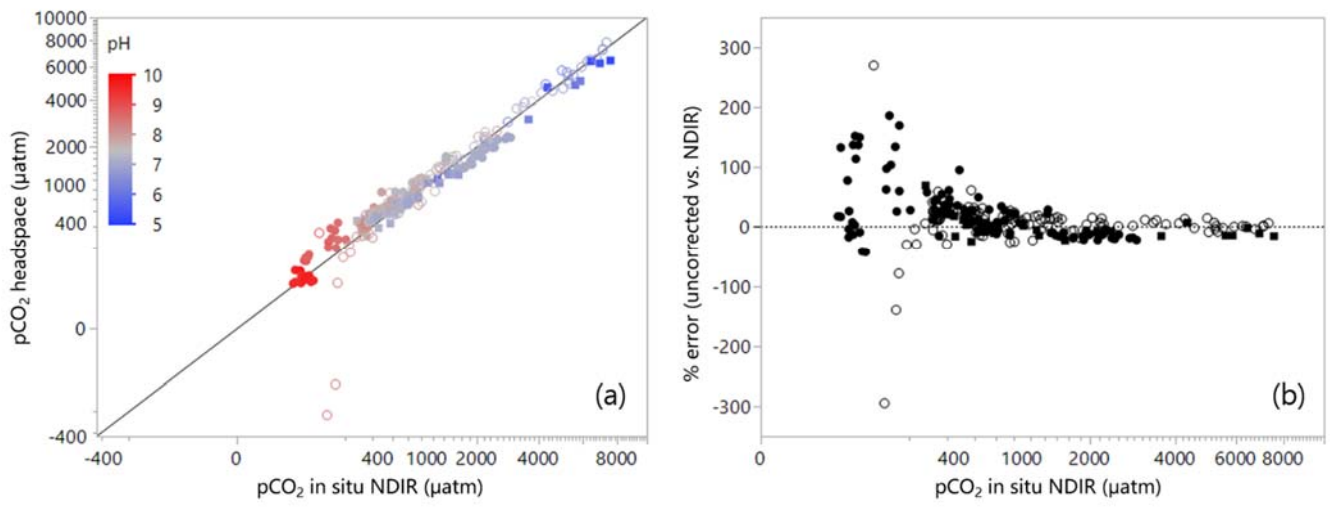
Figure 2: (a) Field data from 11 lakes, 5 reservoirs, and 3 streams in Germany, Canada, and Malaysia comparing pCO_2 derived from simple headspace analysis with direct pCO_2 measurements by NDIR analysis (pH colour coded). Note the cube-root scale in both axes. (b) Difference between the pCO_2 derived from the simple headspace analysis and the direct pCO_2 measurements by NDIR analysis expressed as error (%) as a function of the directly measured pCO_2 by NDIR analysis. Note the cube-root scale in x axis. Open-circle symbols: ambient-air headspace, closed-circle symbols: CO_2-free gas headspace, and closed-square symbols: premeasured-CO_2 gas (between 150 to 250 ppm) headspace applied.

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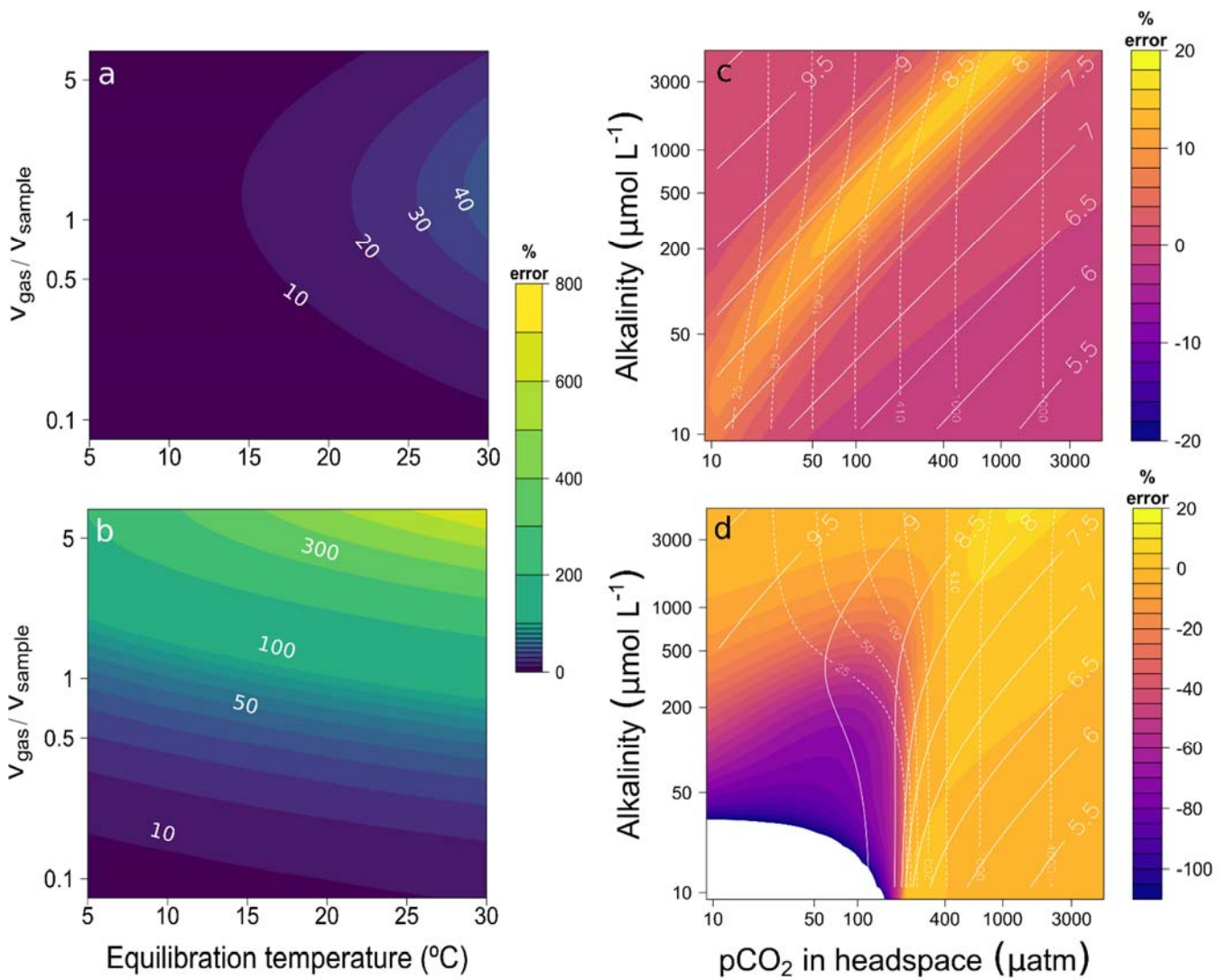
Figure 3: Error [%] when applying simple headspace calculation depending on headspace ratio and equilibration temperature for a) 100 µmol L^{-1} and b) 1000 µmol L^{-1} alkalinity. Panels a and b were constructed using highly undersaturated conditions (headspace pCO$_2$=50 µatm after equilibration and field water temperature of 20ºC). 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 pCO$_2$ in the headspace after equilibration using CO$_2$-free gas headspace, headspace ratio 1:1, and equilibration and field temperature of 20°C. d) like c) but with air headspace. All calculations assume a pressure of 1 atm.

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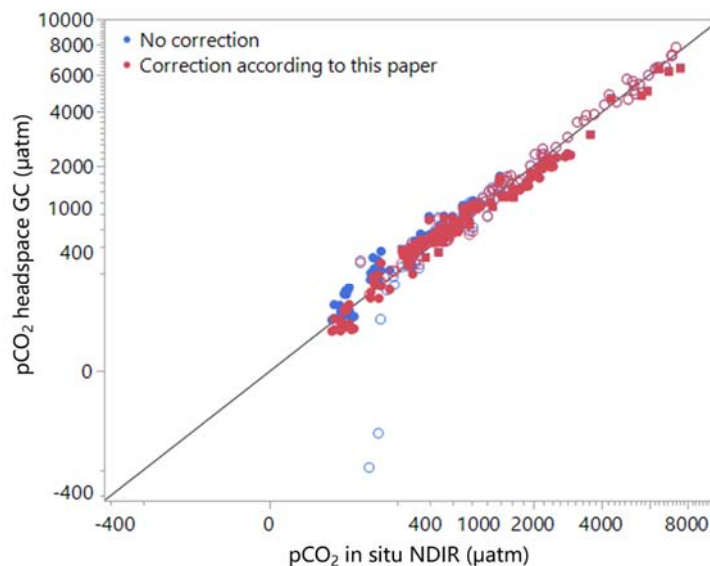
Figure 4: Comparison of uncorrected and corrected data with direct pCO_2 measurements by NDIR analysis. Note the cube-root scale in both axes. Open-circle symbols: ambient-air headspace, closed-circle symbols: CO_2-free gas headspace, and closed-square symbols: premeasured-CO_2 gas (between 150 to 250 ppm) headspace applied.

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