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. ~~In this paper we provide a method to quantify the potential error resulting from simple application of Henry´s law to headspace CO_2 samples.~~ By analysing the potential error for different types of water and experimental conditions we ~~conclude~~ 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~~1700~~ µmol~~mol~~ L^{-1}), with pH (<7.5), and high pCO_2 (>1000 µatm). However, the simple headspace calculation~~s~~ can lead to high error (up to -3~~8~~00%) or even impossibl~~y~~e 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. ~~and use of a CO_2 free gas for headspace creation.~~ 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 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. Surprisingly, pPapers and protocols using this method have also 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 some recent papers (Golub et al., 2017; Gelbrecht et al., 1998; Rantakari et al., 2015; Aberg and Wallin, 2014; Horn et al., 2017), especially and is standard practice in marine research (Dickson et al., 2007), a practical evaluation of the systematic error when applying simple headspace analysis on to CO_2 on typical freshwaters is missing, presumably because it is widely . The underlying assumed ption 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 convenient tool for the exact CO_2 calculation using a complete headspace method that accounts for the carbonate equilibrium shifts in the sample equilibration vessel. The approach , which 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). . Lastly, we tested the proposed correctiona procedure we tested on to 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 ~~given~~ 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 ~~n N_2~~ 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 ~~an~~ 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.

2.1 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 ~~took~~collated 266 observations ~~70 water samples~~ from ~~routinely sampled water in~~ 4 ~~German~~ reservoirs and 3 streams in Germany, ~~and~~ 10~~1~~ Canadian lakes, and a Malaysian reservoir exhibiting a wide range of ~~total alkalinity (~~TA~~)~~ between 0.0~~3~~2 and 1.9~~2.4~~ mmol~~eq~~ 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. First, for the *in situ* NDIR technique, the water ~~is~~was pumped through the lumen side of a membrane contactor (mini module, Membrana, U.S.A.) (Cole and Prairie, 2009) and the gas side ~~is~~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 mCO_2 [ppm~~v~~] values of the NDIR analyser became stable (fluctuating $\pm$ ~~5~~3 ppm around the mean~~usually less than a minute~~) 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 CO_2 ~~mixing ratio~~mole fraction (mCO_2) by the ambient atmospheric pressure. Second, for the headspace technique, the methodology differed slightly among locations. ~~Ithe water samples were taken in 60 mL syringes. I~~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

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lakes, 20 mL of the water samples were taken in 60 mL syringes and equilibrated with 40 mL volume of atmospheric air by vigorously shaking the syringes for 2 minutes. In the Malaysian reservoir, 600 mL of water samples were 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 mL 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 pCO_2 was then calculated according to the headspace ratio, temperature, and the measured headspace mpCO$_2$ as follows:

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

with $mCO_{2\ Before\ eq}$ and $mCO_{2\ After\ eq}$ are respectively the = CO$_2$ mole fractions 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}], P = pressure [atm], V$_{gas}$ = headspace volume, V$_{liquid}$ = sampled-water volume, and V$_m$ = molar volume [L mol^{-1}] (UNESCO/IHA, 2010). Results from Eq. 1 are reported as pCO$_2$ at one atmosphere of barometric pressure and are corrected for ambient pressure at the time of sampling as described previously.

The difference between headspace and NDIR method 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, and Germany, total alkalinity (TA) was analysed by titration with 0.11N HCl. In some systems, a single Assuming little variability of TA measurement was available for multiple dates and therefore assumes little temporal variability in the alkalinity of these systems. within the surface water of particular lakes we used one TA value for all samples from a respective lake or reservoir. In the Malaysian samples, TA was derived calculated 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 or 7 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.

3. Results and Discussion

3.1 Simulations from chemical equilibrium

Applying a CO$_2$-free gas as headspace always resultesd in a positive error (over-estimation of the real pCO$_2$, Figure 1a). If ambient air is applied as headspace the error becomes negative in case of under saturated samples (Figure 1b). In general, The 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), except in undersaturated conditions. This is because less CO$_2$ is exchanged between water and headspace

during the equilibration procedure. The error will be ~~below 10%quite low~~ below 10% in ~~high CO₂super-saturated and,~~ high CO_2 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 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 gas:liquid ratio of 1:1).

Our field dataset is consistent with the theoretical predictions. While ~~The the~~ the fit between the simple headspace calculation and NDIR values over the whole range of values can be considered ~~both methods is~~ adequate overall ~~rather good~~ (Figure 2a, $R^2 =$ 0.9~~28~~86), it is clear that the deviations can become very large (up to about 300%), particularly at water pCO_2 values <600µatm (Figure 2b). ~~the difference was 12 ± 43 % which is clearly higher than the errors of the analytical instruments, showing that the absolute error was in an acceptable range. However, t~~The relative error reached values up to 2~~3~~00 %. As expected from the simulations, ~~large error was observed at low pCO₂ while~~ the error in undersaturated samples was positive when using CO_2-free gas as headspace and negative (sometimes impossible negative results) using ambient air (Figure 2b). The error became negligible ~~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 N₂ 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~~ 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 ~~larger~~ smaller headspace to water ratio (Figure 3). By lowering~~raising~~ the headspace ratio from 1 to 0.2~~5~~ at 20°C the error can be reduced from about 50% to about 10%.

Since solubility of 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 (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 m~~eq~~mol 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 ha~~ve~~s 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 pCO_2 value (TA=1 mmol L^{-1}, pCO_2 = 1000 µatm, HR = 1) (Figure A1a). Both ambient air and N_2 can be used as headspace gas. Using N_2, however, eliminates the error associated with the exact quantification of

154 pCO2 Before. For theUsing the same example, sample an unlikely error of 100 ppm in the headspace gas (mpCO2 Before eq) results

155 in a 6.4% different pCO2 result (Figure A1b).

3.3 What about kinetics?

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

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

159 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

160 (Zeebe and Wolf-Gladrow, 2001; Schulz et al., 2006). This means that chemical equilibrium reactions are faster than physical

161 headspace equilibration and the chemical system can be assumed always to be in equilibrium. Thus, the reactions of the

162 carbonate system have to be fully considered in headspace analysis of CO_2.

3.4 Correction of CO_2 headspace data

164 If other information regarding the carbonate system of the sample is known (alkalinity or DIC), one can correct for the bias

165 induced by simple headspace calculations. A procedure to correct headspace CO_2 data using pH and alkalinity is already

166 providedavailable in the SOP N∘4 in Dickson et al. (2007) for marine samples and could be adapted to freshwater samples as

167 well. For convenience,The procedure involves estimating the exact pH of the equilibrium solution before and after

168 equilibration. Here, we develop provide here a improvedmodified the procedure when the alkalinity of the sample is known

169 by introducing an analytical solution to the equilibrium problem (iterative in SOP N∘4) and by using dissociation constants

170 that may be more appropriate to freshwaters. The procedure essentially involves estimating the exact pH of the equilibrium

171 solution before and after equilibration., in addition to the usual parameters required for headspace calculations: water

172 temperature of equilibration and in the field, pCO2 after equilibration, pCO2 of the headspace gas before equilibration, and

173 headspace ratio.

174 If the alkalinity of the sample is known, After equilibration, the pH ($-\log_{10}[H+]$) of the aqueous solution after equilibration

175 can be obtained by finding the roots of the 3rd order polynomial

177 $$0 = [H^+]^3 + TA \cdot [H^+]^2 - ([CO_2]K_1 + K_w)[H^+] - 2K_1K_2[CO_2]$$ **Eq. 2**

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

179 $$\propto_{CO_2} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$ **Eq. 3**

180 wWhere K_1 and K_2 are the temperature -dependent equilibrium constants for the dissociation reactions for bicarbonates and

181 carbonates, respectively (Millero, 1979), and for estuarine conditions, Millero (2010) as amended in Orr et al. (2015). K_w is

182 the dissociation constant of water into H^+ and OH^- (Dickson and Riley, 1979)Millero. The total DIC contained in the original

183 sample (DIC_{orig}) can then be calculated as

184 $$DIC_{orig} = \frac{CO_2}{\alpha_{CO_2}\alpha_u} + (CO_{2\,HS_{after}} - CO_{2\,HS_{bef}}) \qquad \textbf{Eq. 4}$$

185 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

186 and before equilibration [mol]. Given the DIC concentration of the original solution from Eq. 4 ([DIC] = DIC_{orig} / V_{liquid}), the

187 pH of this solution prior to equilibration can be obtained by finding the roots of the 4th order polynomial

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189 $$0 = [H^+]^4 + (TA + K_1) \cdot [H^+]^3 + (TA \cdot K_1 - K_w + K_1 K_2 - [DIC]_{orig} K_1) \cdot [H^+]^2 + (K_1 K_2 \cdot TA - K_1 K_w - 2[DIC]_{orig} K_1 K_2) \cdot [H^+] -$$

190 $$K_1 K_2 K_w \qquad\qquad \textbf{Eq. 5}$$

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

192 as

193 $$pCO_2 = \frac{\alpha'_{CO_2} \cdot [DIC]_{orig}}{K_{h\,Sample}} \qquad \textbf{Eq. 6}$$

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

195 assume a 1 atm pressure). We applied the above correction procedure to the Canadianour samples where pCO$_2$ was measured

196 in several samples using both headspace and in situ NDIR methods together with measured alkalinity data. Figure 4 shows

197 that the corrected values matched the in situ NDIR values nearly perfectly (r^2=0.98397) whereas the simple headspace

198 calculations resulted, as expected, in significant underestimation for undersaturated conditions, particularly for samples

199 samples equilibrated with ambient air.

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

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

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

203 50% error (Fig. 3c). However, more precise alkalinity values are required when using ambient air as a headspace gas in

204 undersaturated conditions (Fig. 3d).

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

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

207 how often such problematic conditions occur in inland water systems. To address this question, we used data from 377 lakes

208 for which we had complete ancillary data and precise headspace measurements of CO$_2$ (<5% error between duplicates)

209 obtained from the pan-Canadian Lake Pulse sampling program (Figure B1a, see Huot et al. (2019) for details). These results

210 show a significant deviation between corrected and uncorrected values, particularly in lakes with high alkalinity (>900 μmol

211 L^{-1}, Figure B1b) and ignoring the correction would have resulted errors >20% in about 47% of the data. Furthermore, our

212 analysis illustrates how a larger headspace ratio significantly exacerbates the magnitude of the error (Figure B1b).

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

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

216 analytical formulas (e.g. Zwillinger (2018)) or by iterative algorithms. ~~Analytical solution are faster than iterative algorithms~~
217 ~~but can suffer small instabilities (SD≈ 1 ppmv) in extreme situations (alkalinity >4000 µeq L-1 and pCO₂ <100 ppmv)~~
218 ~~due to limitations inherent to double precision numerical calculations.~~Analytical solutions are faster than iterative algorithms
219 but can suffer small numerical instabilities (SD $\approx$1 ppm) in extreme situations (alkalinity >4000μmol L^{-1} and pCO_2<100ppm)
220 due to limitations inherent to double precision~~s~~ numerical calculations. The provided skripts consider the barometric pressure
221 and thus, allow calculation of pCO_2 as well as CO_2 concentration [μmol L^{-1}] for *in situ* conditions.
222
223

4.   Conclusions

225 The headspace method has been used in several studies about CO_2 fluxes from surface waters. Our error analysis shows that
226 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^{-}
227 ^{1}~~1700~~, air headspace), a typical situation in most boreal systems. However, the standard headspace method introduces large
228 errors and cannot be used reliably for under saturated samples, which are typical of eutrophic or low DOC systems. In all other
229 cases, not accounting for the chemical equilibrium shift leads to a systematic over estimation. The magnitude of the error can
230 be reduced by increasing the water/headspace ratio or~~,~~ lowering the equilibration temperature~~, and/or using air instead of N₂~~
231 ~~as headspace~~. The magnitude of that error can be roughly estimated from Figure 1. If alkalinity is known, pCO_2 obtained from
232 headspace equilibration can be corrected by the provided scripts. We therefore recommend to always measure alkalinity if the
233 headspace method is to be used for pCO_2 determinations. The procedure can also be used to correct historical pCO_2 data. Our
234 field data showed that the correction works well even in highly undersaturated conditions and is not very sensitive to the
235 precise determination of alkalinity if N_2 is used as a headspace gas. The precision of the corrected pCO_2 is similar to that
236 obtained from direct pCO_2 measurement using a field NDIR analyser coupled to an on-line equilibrator (Cole and Prairie,
237 2009; Yoon et al., 2016).

4.5. Appendices

Appendix A: Sensitivity analysis equilibration temperature and CO_2 Before eq
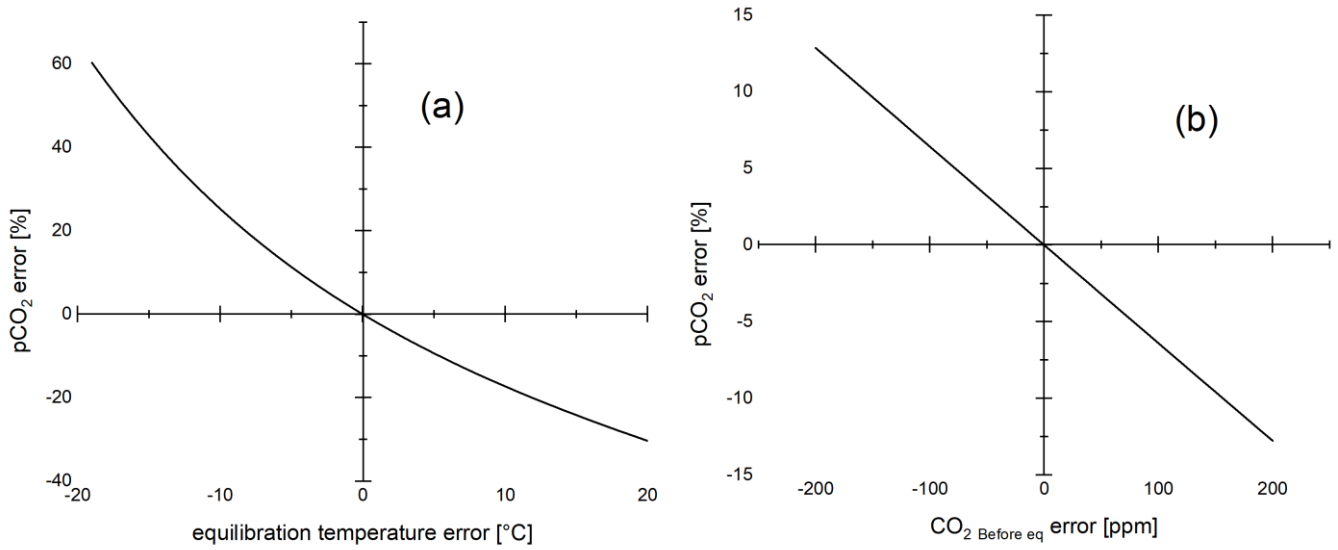
Figure A1: Error for a hypothetical sample with CO_2 Before eq = 400 ppm, CO_2 after eq = 1000 ppm, equilibration temperature 20°C, HR = 1 (a) depending on error in equilibration temperature (b) depending on error in initial headspace gas composition.

Appendix B: Application of our correction to a large Canadian dataset
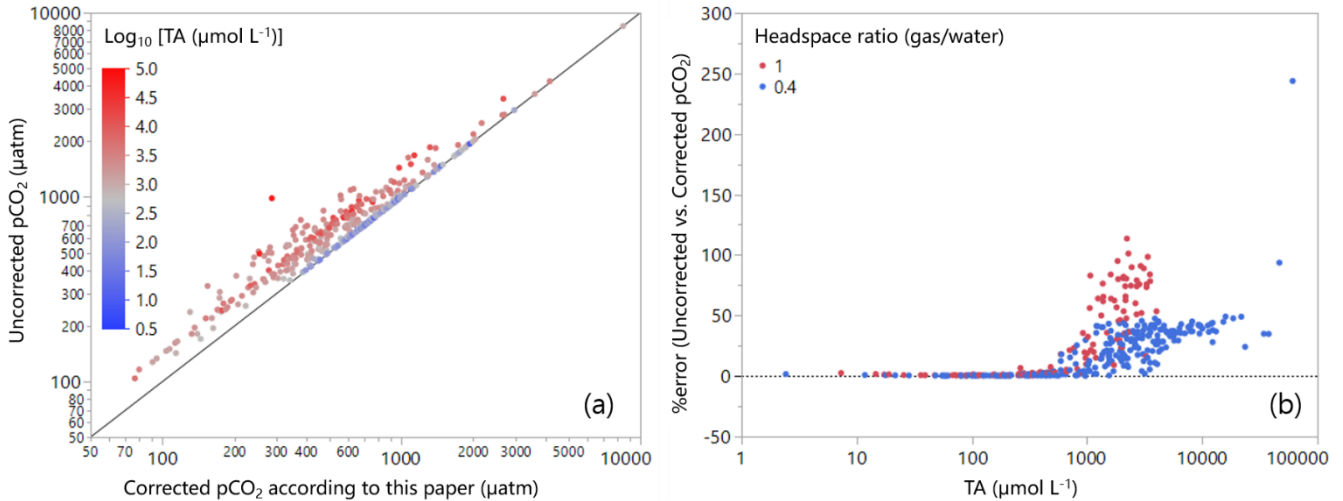
Figure B1: Field data from 377 lakes across Canada (a) for comparing pCO_2 derived from simple headspace calculation with that from the corrected headspace calculation according to this paper (Log_10 [TA (µmol L^-1)] colour coded). (b) Difference between the uncorrected and corrected pCO_2 expressed as error (%) as a function of TA (µmol L^-1) (The

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250 **headspace ratio colour coded). Note that CO$_2$-free gas was used for headspace, and TA values were derived from DIC**
251 **measurement and pH.** **More information about the dataset in** **Huot et al. (2019).**

5.6. Code availability

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

6.7. Data availability

All data can be found in the supplemental information file.

7.8. Supplement link (will be included by Copernicus)

8.9. 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.

9.10. Competing interests

The authors declare that they have no conflict of interest.

10.11. Acknowledgements

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278 **Figure 1: Error [%] when applying simple headspace calculations of pCO_2 on hypothetical water samples of different alkalinity and**
279 **pCO_2 in the headspace after equilibration for (a) CO̶N̶₂̶-̶free gas headspace and (b) ambient-air headspace assuming a pressure of**
280 **1 atm. The resulting pH and pCO_2 of the samples are depicted as full and dashed lines, respectively. Headspace ratio 1:1,**
281 **equilibration and field temperature 20°C. Note the log scale in all axes. In b) results for pCO_2 in headspace after equilibration lower**
282 **than 215 µatm are masked, because they would imply negative pCO_2 in the sample.**
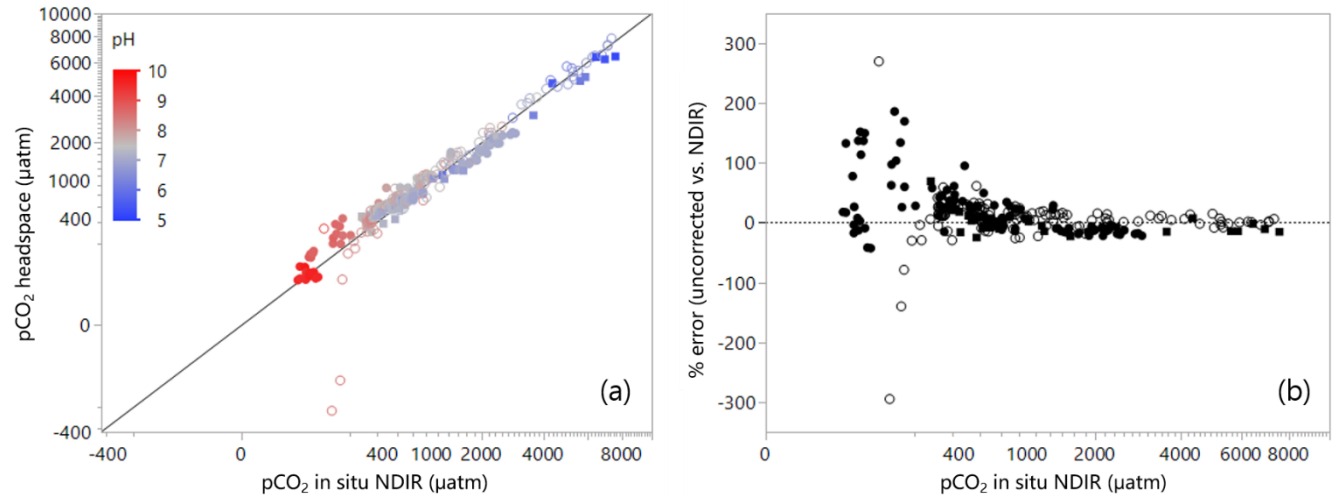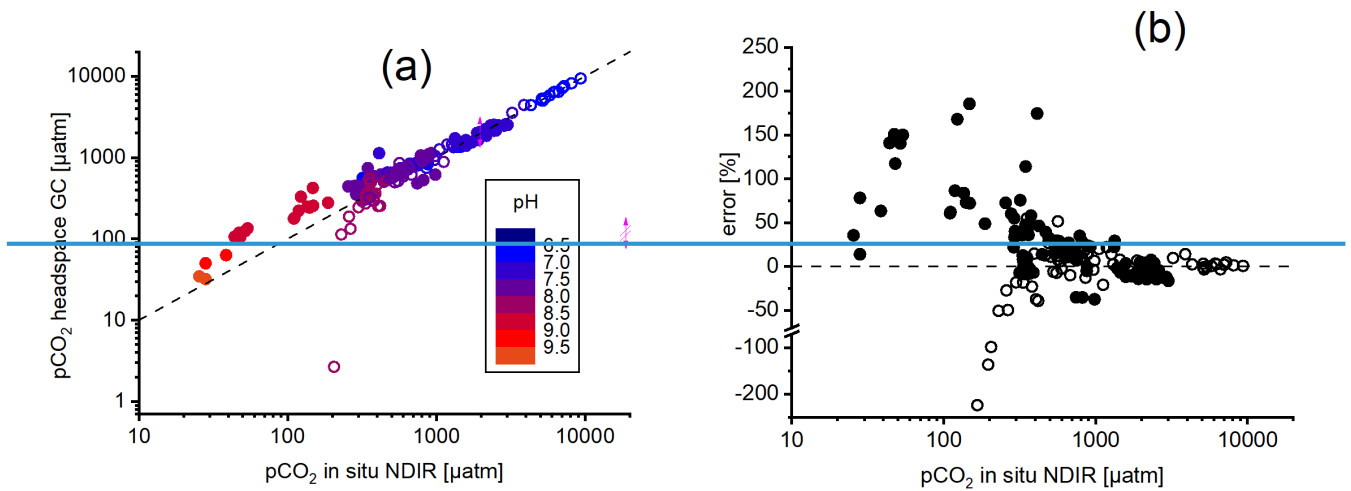
Figure 2: (a) Field data from 11 lakes, 5 reservoirs, and 3 streams in Germany, Canada, and Malaysia4 German reservoirs and 11 Canadian lakes comparing pCO_2 derived from simple headspace analysis with direct pCO_2 measurements by NDIR analysis (pH colour coded). Note the cube-root scale in both axes. (b) Difference between the pCO_2 derived from the simple headspace analysis and the direct pCO_2 measurements by NDIR analysis expressed as percentage error (%) of the NDIR valueas 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.Open symbols: air headspace, closed symbols: N_2 headspace applied.

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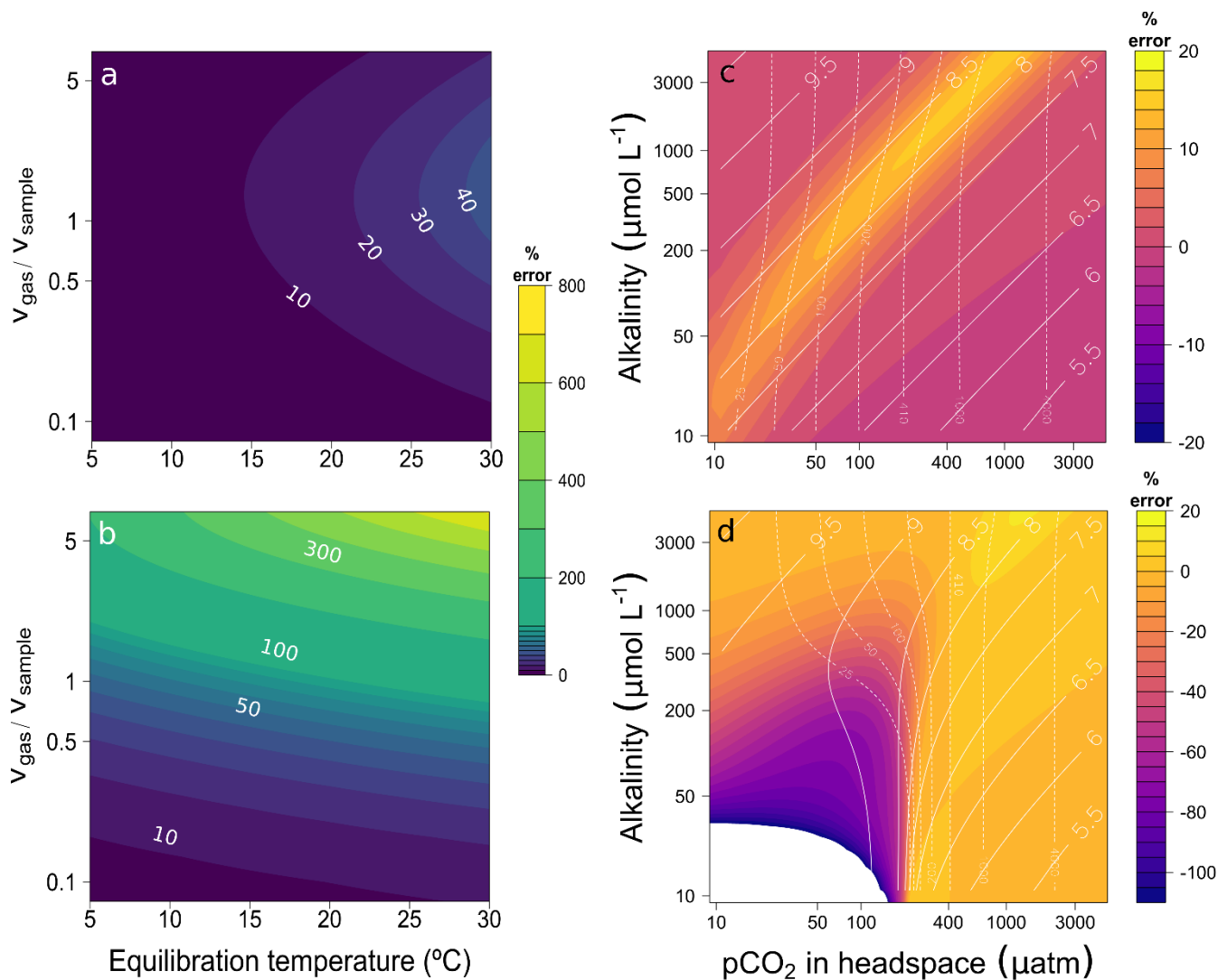
Figure 3: Error [%] when applying simple headspace calculation depending on headspace ratio and equilibration temperature for a) 100 µmol L^{-1} and b) 1000 µmol L^{-1} alkalinity. Panels a and b were constructed using highly undersaturated conditions (headspace pCO_2=50 µatm after equilibration and 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~~N_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.
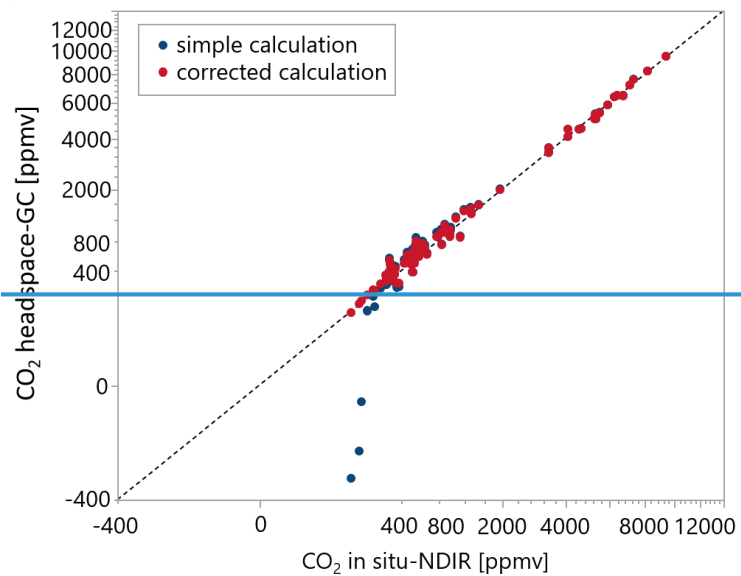
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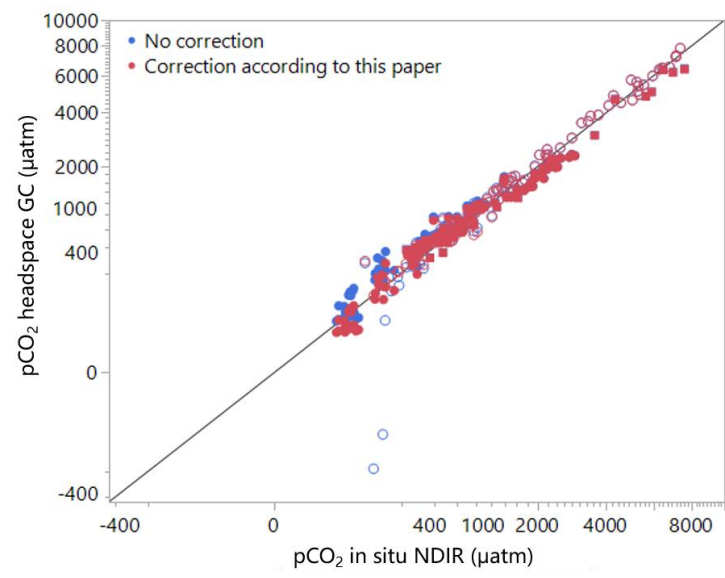
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Figure 4: Comparison of uncorrected and corrected data (using measured alkalinity) **with direct pCO₂ measuredments by NDIR analysis. Note the cube-root scale in both axes. Open-circle symbols: ambient-air headspace, closed-circle symbols: CO₂-free gas headspace, and closed-square symbols: premeasured-CO₂ gas (between 150 to 250 ppm) headspace applied.**

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~~11.~~12.   References

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382