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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 water

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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 that the error incurred by headspace analysis of CO_2 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 CO_2 free gas for headspace creation. We provide a direct method to correct CO_2 headspace results using separately measured alkalinity.

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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 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, 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 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 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 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, alkalinity, and the original pCO_2 of the water sample. If an N_2 headspace 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 air headspace is applied, the error becomes negative in under-saturated 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 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.

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 pCO_2 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 CO_2 [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 pCO_2 of the water was calculated by multiplying the CO_2 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 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 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 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 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 pCO_2 as follows:

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

with $pCO_{2\,Before\,eq}$ and $pCO_{2\,After\,eq}$ = 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° 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 3). At a HR of 1, the error increases from 97 % at 20° 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?

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 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. 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, pCO_2 after equilibration, pCO_2 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

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

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

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

Where K_1 and K_2 are the temperature -dependent equilibrium constants for the dissociation reactions for bicarbonates and carbonates, respectively (Millero, 1979). 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

$$DIC_{orig} = \frac{CO_2}{\alpha_0} + (CO_{2\,HS_{after}} - CO_{2\,HS_{bef}})$$ **Eq. 4**

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

$$0 = [H^+]^4 + (TA + K_1) \cdot [H^+]^3 + \left(TA \cdot K_1 - K_w + K_1K_2 - [DIC]_{orig}K_1\right) \cdot [H^+]^2 + \left(K_1K_2 \cdot TA - K_1K_w - 2[DIC]_{orig}K_1K_2\right) \cdot [H^+] - K_1K_2K_w$$ **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

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

where $K_{h\,Sample}$ is determined for the water temperature during field sample collection. We applied the above correction procedure to the Canadian 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=0.997) 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 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).

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≈ 1 ppmv) in extreme situations (alkalinity >4000 µeq L-1 and pCO_2 <100 ppmv) due to limitations inherent to double precision numerical calculations.

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<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 N_2 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.

10. Acknowledgements

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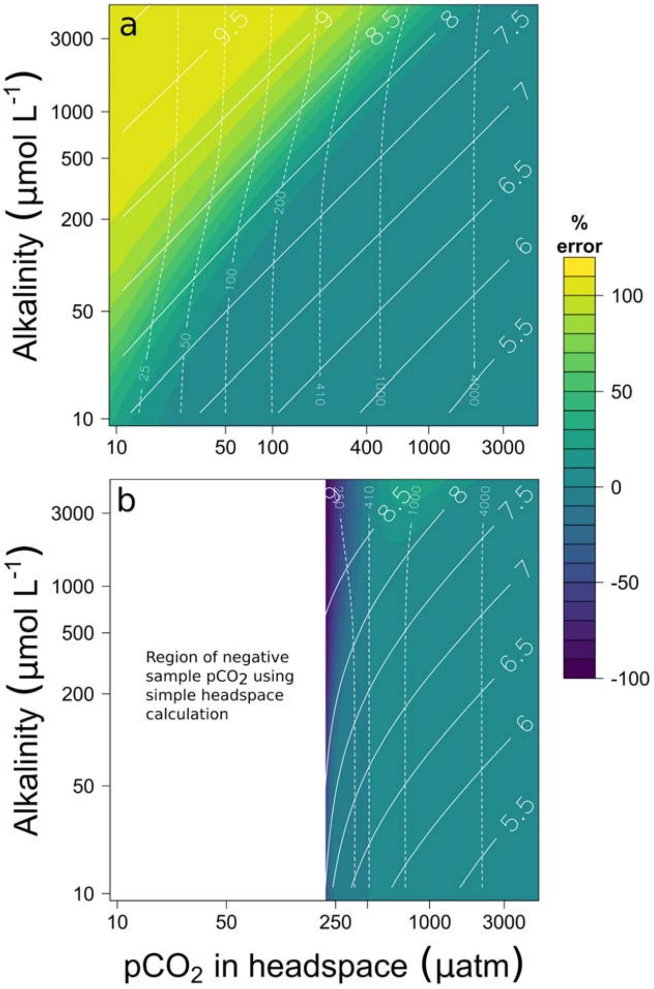

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Figure 1: Error [%] when applying simple headspace calculations of pCO_2 on hypothetical water samples of different alkalinity and pCO_2 in the headspace after equilibration for (a) N_2 headspace and (b) air headspace. The resulting pH and pCO_2 of 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 pCO_2 in headspace after equilibration lower than 215 µatm are masked, because they would imply negative pCO_2 in the sample.

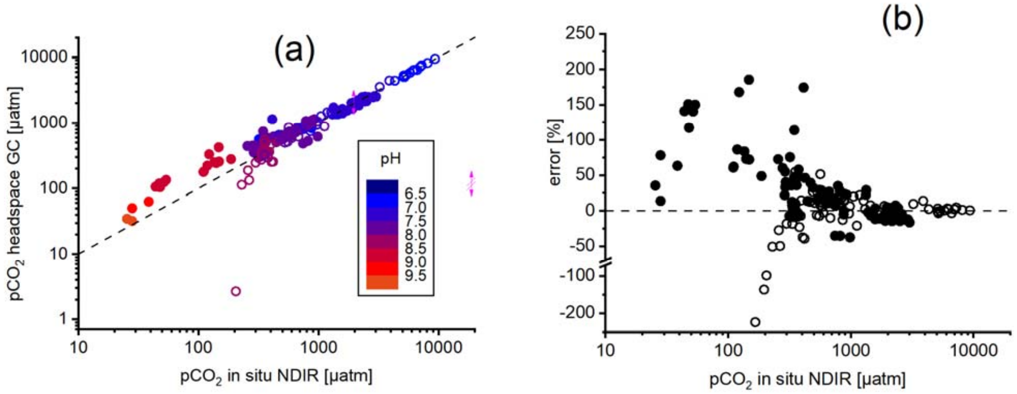

Figure 2: (a) Field data from 4 German reservoirs and 11 Canadian lakes comparing pCO_2 derived from headspace analysis with direct pCO_2 measurements by NDIR analysis (pH colour coded). (b) Difference between both methods expressed as percentage of the NDIR value as a function of pCO_2. Open symbols: air headspace, closed symbols: N_2 headspace applied.

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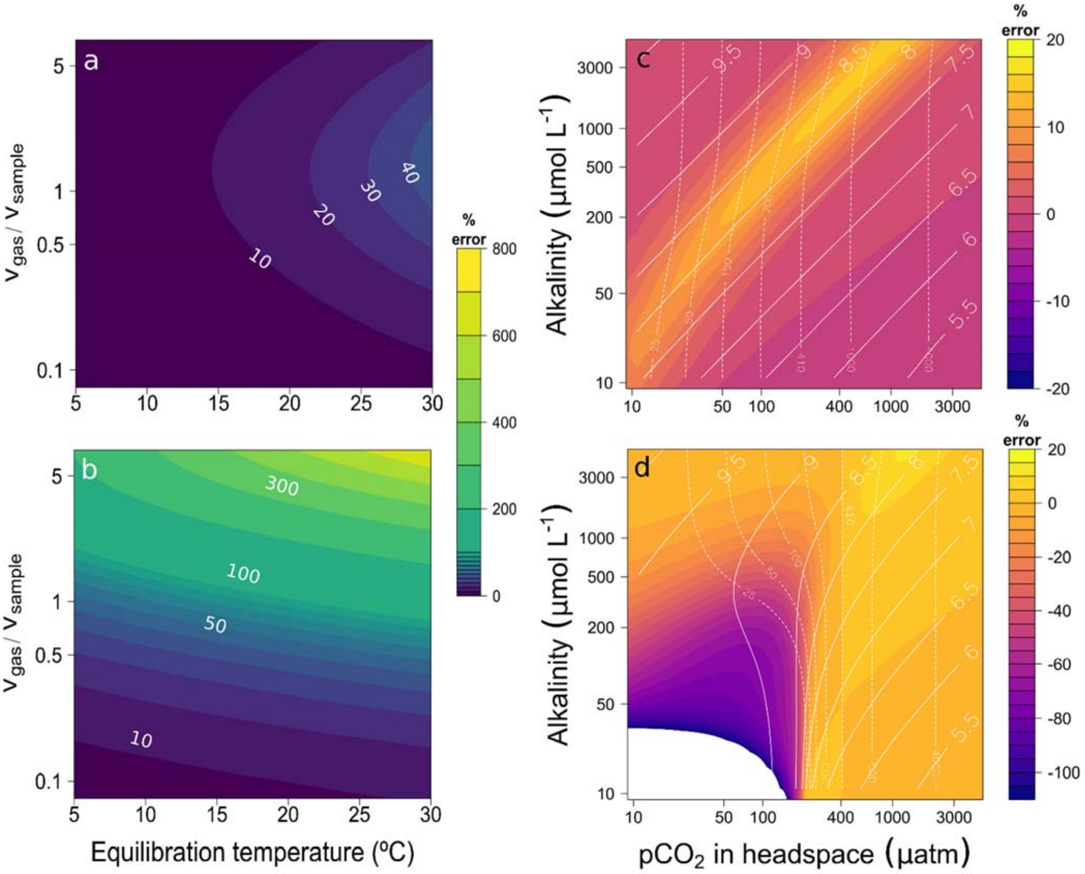

Figure 3: Error [%] when applying simple headspace calculation depending on headspace ratio and equilibration temperature for a) 100 µmol/L and b) 1000 µmol/L alkalinity. Panels a and b were constructed using highly undersaturated conditions (headspace pCO_2=50 µatm after equilibration and field water temperature of 20ºC). The 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 pCO_2 in the headspace after equilibration using N_2 headspace, headspace ratio 1:1, and equilibration and field temperature of 20°C. d) like c) but with air headspace.

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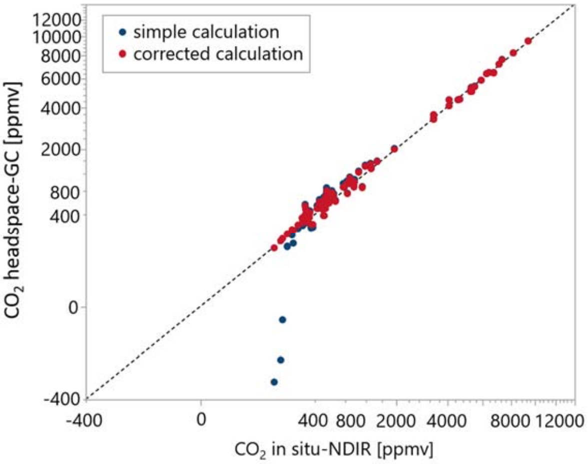

Figure 4: Comparison of uncorrected and corrected data (using measured alkalinity) with pCO$_2$ measured by NDIR analysis. Blue dots indicate samples with negative concentrations if not corrected.

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