Comment: Freshwater CO_2 Headspace Equilibration Calculations

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Koschorreck et al. describe a method for calculating the original CO_2 concentration of a water sample when using a headspace equilibration to extract dissolved CO_2 from water. This manuscript contributes a correction to the final measured CO_2 concentration to account for the near-instantaneous equilibration between CO_2 and HCO_3^- in water during equilibration with the headspace. While the HCO_3^- equilibration correction exists in the chemical oceanography literature (e.g., Dickson et al. 2007), this correction is used less frequently in the freshwater literature. We have multiple ongoing projects in freshwater streams involving data using headspace equilibrations for estimating CO_2 concentrations, and until reading this work, we had not considered correcting CO_2 concentrations for the HCO_3^- equilibrium despite always having a copy of Dickson et al. (2007) nearby. Thus, we believe this manuscript is a welcome addition to the literature. Given the importance of accurate calculations for estimating CO_2 concentrations and our previous experience with these calculations, our objectives in this comment are to:

1. Use a different mathematical formulation than in Koschorreck et al. to estimate the HCO_3^- equilibrium correction, and compare the magnitude of correction between the two approaches.

2. Evaluate the correction magnitude with samples where headspace equilibration may bias estimates of pCO_2: high alkalinity and a large volume CO_2-free headspace relative to the water volume.

We used our own grab sample data to compare the full set of headspace equilibration calculations as presented by Koschorreck et al. with the same calculations derived from our group. We note that in parts of our calculations we use different equations than Koschorreck et al. but the approaches are based on the same theory. Our code and a detailed comparison of our calculations with that of Koschorreck et al. are available at https://github.com/jrblaszczak/CO2_headspace_code. First, we added the HCO_3^- equilibrium correction

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to our existing headspace equilibration calculations using equations 4 and 5 in Dickson et al. (2007) (SOP 4). We then compared the calculated CO_2 concentration from the code provided by Koschorreck et al. with our code using diel grab sample data (sampled every 2-4 hr over a 24 hr period) from streams in northwestern Montana and central Arizona. For these samples, we performed headspace equilibrations in the field using 40 mL of streamwater and 70 mL of injected CO_2-free air in 140 mL syringes. We equilibrated the headspace by shaking the syringes for 3 minutes, after which we flushed the water from the syringe and stored the remaining gas sample in the syringe until analysis within 48 hours on a Picarro G2131-i analyzer (Picarro, Santa Clara, CA, USA). We measured stream temperature and barometric pressure at the time of water sampling and collected an unfiltered streamwater sample for total alkalinity, which was measured by titration to a pH of 4.5. Stream temperature of our samples was between 7 and 22 °C and the total alkalinity was between 1440 and 2060 μeq L^{-1}.

There was minimal variation of the HCO_3^- equilibrium corrections and corrected CO_2 concentrations between the calculations provided by Koschorreck et al. and the calculations we independently compiled. The HCO_3^- equilibrium corrections between the approaches were similar to the hundredth decimal place (expressed as μmol L^{-1} DIC), which we consider to be functionally the same. The average percent deviation of corrected CO_2 concentrations between approaches was 0.9% (SD $\pm$ 0.6%) which is likewise a small difference. As noted above, the code we provide for this comparison uses different calculations than Koschorreck et al., but is based on the same theory. Thus, we see this comparison as an independent verification of their calculations.

The deviation of HCO_3^- equilibrium corrected and uncorrected CO_2 concentrations for our samples ranged between (2-23%, reported in ppmv). The error in our samples is not surprising given the relatively high total alkalinity, low headspace ratio (1.75), and that we used a CO_2-free headspace. We are limited in our ability to change our methods to reduce this error given our protocol for measuring gases on the Picarro G2131-i analyzer requires 70 mL of gas per sample, and using CO_2-free headspace is logistically easier than adding a measurement of air for each sample during a diel. Additionally, equilibration air containing CO_2 would bias estimates of δ^{13}C-DIC. By adding the HCO_3^- equilibrium correction we can increase the accuracy of our grab sample CO_2 concentrations without altering our sampling protocol.

While our approaches result in the same outcome we note one difference that is worth mentioning by Koschorreck et al.. This difference involves assumptions we make about calculating the H$^+$ concentration (eqn. 2, Koschorreck et al.) from the equation for total alkalinity (A_T, eqn. 1) that leads to an algebraically simpler equation and therefore may enable more efficient computation and incorporation of these calculations into larger process models.

$$A_T = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+] \tag{1}$$

We assume that the H^+ and OH^- concentrations are zero in eqn. 1 for two reasons. First, these concentrations are tiny compared to HCO_3^- and CO_3^{-2}, and likely within the range of the error associated with the measured alkalinity via titration or charge balance. Thus, we contend that assuming H^+ and OH^- concentrations are zero will have a negligible effect on the calculation of the overall H^+ concentration. Second, this assumption allows us to solve a 2nd-order polynomial rather than a 3rd-order polynomial equation. While the authors incorporate an elegant solution to solve the 3rd-order polynomial using the *polyroot* function in R, the use of this function may limit downstream incorporation of these calculations in stochastic simulations. For example, we use adaptations of Markov chain Monte Carlo methods (e.g., the general purpose Bayesian modeling software Stan, Carpenter et al. 2017) to simulate posterior distributions in Bayesian hierarchical models to estimate stream metabolism from diel patterns of CO_2. In this case, the simpler mathematical solution for solving for the H^+ concentration will facilitate computational speed without sacrificing accuracy. Given the occasional need for mathematically simpler solutions, we suggest the authors discuss the complexity of their approach, and note that the calculations can be simplified by assuming $[H^+]$ and $[OH^-] \approx 0$.

Overall, we feel that Koschorreck et al. provide an useful contribution to the literature that will lead to more accurate measurements of CO_2 concentrations, particularly in freshwaters. The extensive analyses by Koschorreck et al. of the deviation of corrected and uncorrected CO_2 concentrations across geochemical and methodological scenarios provide necessary context to this issue. Likewise, Koschorreck et al. are the first group to our knowledge to combine calculations for CO_2 concentrations from headspace equilibrations into a streamlined and publicly available R script. We commend the authors for pointing out a commonly neglected correction and for providing the code with which the community can easily overcome this additional step to estimating accurate dissolved CO_2 concentrations.

We have a few minor comments on the manuscript:

1. We suggest that the authors carefully re-examine and edit the text in the abstract and conclusion sections that highlights the general importance of factors that may impact the deviation between corrected and uncorrected CO_2 concentrations for consistency. For example, in the conclusion it is noted that samples with pH below 7.5 and pCO_2 above 1000 μatm will have a small error, but in the abstract only the pH is noted. We also note that the abstract and conclusion sections differ in the suggested content of gas used in the headspace to reduce error. The abstract states CO_2 free gas should be used while the conclusion states that air should be used instead of an N_2 headspace. Consistency of the messaging of these factors would provide more clarity to the manuscript.

2. We suggest the authors use more consistent notations, particularly for pCO_2. The authors could note both the 'location' of the pCO_2 measurement (i.e., headspace vs. water) as well as before or

after equilibrium in their notation. This caused some confusion for us when evaluating the text and code. A few examples include: line 141- pCO_2 is used while in line 87 pCO_{2water} is used, line 87- $pCO_{2Aftereq}$ is used while in line 146 $pCO_{2HSafter}$ is used. We believe consistent annotation will improve understanding of these calculations.

3. Many researchers, including our group, prefer to report our data in units of μmol L^{-1}, especially when we compare data of different molecules (e.g., CO_2 vs O_2 for metabolism). Thus, we suggest that the authors include in the R code the reporting of CO_2 concentrations in μmol L^{-1}. This should not be much trouble given the calculations are already conducted in molar units.

References

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