

***Interactive comment on* “Technical note: CO₂ is not like CH₄ — limits of and corrections to the headspace method to analyse *p*CO₂ in water” by Matthias Koschorreck et al.**

Anonymous Referee #1

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The importance of this paper is to point out a major problem in the processing of CO₂ measurements made by headspace equilibration due to the equilibration of CO₂ with HCO₃⁻ to the wider community working on CO₂ dynamics in freshwater.

This has been known for decades by the marine CO₂ community, related to the buffering capacity of water due to the presence of HCO₃⁻ that in fact strongly affects all aspects of CO₂ dynamics in marine and freshwater environments.

This problem was possibly less acknowledged by the freshwater CO₂ community due to the dominance of soft-water lakes in northern North America and Scandinavia where the very large majority of studies of inland water CO₂ studies have been carried out so

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far.

That said, the authors reinvent the wheel by proposing a “tool for exact CO₂ calculation” because the marine CO₂ community has established for decades a method to correct the CO₂ data from measurements of headspace. This is the SOP N°4 (“Determination of pCO₂ in air that is in equilibrium with a discrete sample of sea”) of the two versions of the “CO₂ Handbook” (DOE 1994; Dickson et al. 2007).

This method can be also applied to the type of data reported by the authors by computing DIC from TA and pCO₂_After_eq, correcting DIC for the CO₂ loss or gain during equilibration in the headspace (based on pCO₂_After_eq and pCO₂_Before_eq and using the law of perfect gases), and re-computing “correct” pCO₂ (pCO₂_water) from TA and corrected DIC.

The SOP4 method also allows to correct for water temperature changes between in-situ water and water sample after equilibration. This change of temperature can be substantial (depending on the difference between air temperature and in-situ water temperature) and will lead to a strong bias of pCO₂ values. For the first step of the computation of DIC the water temperature of sample after equilibration is used. For the final step of the computation of pCO₂ (from corrected DIC) the in-situ temperature is used giving corrected pCO₂ at in-situ temperature.

I suggest that the authors should mention SOP4 in the ms and compare both “tools”.

Finally, I find it regretful that the authors did not reach out to the community for additional data-sets that would have made their case more compelling by extending the range of pCO₂ and Total alkalinity values, and thus more representative of lakes globally. Several groups have obtained similar data-sets of direct pCO₂ measurements by equilibration coupled to NDIR detectors in parallel with pCO₂ measurements based on headspace equilibration, and could have been contacted.

References

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