Interactive comment on "Technical note: CO_2 is not like CH_4 — limits of and corrections to the headspace method to analyse $p\text{CO}_2$ 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

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 pf 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 headspace equilibration, and could have been contacted.

References

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3, 191 pp.

DOE. 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, A.G. Dickson and C. Goyet, Eds. ORNL/CDIAC-74