

Interactive comment on “Technical note: CO₂ is not like CH₄ — limits of and corrections to the headspace method to analyse pCO₂ in water” by Matthias Koschorreck et al.

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We thank the reviewer for the quick assessment of our work and the constructive comments it includes.

The reviewer is correct that this topic is well-known in marine science. However, for multiple reasons, the potential impact of the carbonate equilibrium on headspace CO₂ calculation never percolated to a good portion of the freshwater community. There are many examples in the freshwater literature where pCO₂ was determined from headspace equilibration without any consideration of the altered chemical equilibrium during the equilibration process. Perhaps this should be more clearly stated. As the

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reviewer points out, one of the main reason is that most of the freshwater literature deals with very soft waters and many scientists intuitively recognize the problem but simply consider its effect to be small and therefore neglect it. So, our impetus was not to “re-invent the wheel” but simply to draw attention that the issue is not always negligible, even in soft waters. This is the reason we wrote this manuscript as a small technical note in a journal widely read by the freshwater community.

The reviewer is also quite right to point out that we should have made more direct references to the marine literature and its SOPs (although the marine SOP4 was cited already, Dickson et al. 2007). This will be further amended in the revision process. Nevertheless, there are some differences between the SOP4 of the marine community and what we propose. For example, the equations used for temperature-dependence of the equilibrium constants in marine SOPs are not the most suitable for freshwater samples (even when Sal is set to zero) and our code provides alternative equation sets for different environments (freshwater, estuarine, marine). Also, while the procedure in Annex 2 of SOP4 reproduces the same logic, the solution we provide does not require an iterative solution-finding algorithm but are instead exact solutions and therefore do not require an initial H⁺ estimate. In freshwaters, pH is much more variable than in the ocean (pH of lakes typically between 5 and 9.5). Nevertheless, we also provide an iterative procedure. We will modify the paper accordingly to clarify these subtle differences and will include a comparison between our tool and the SOP4 protocol as suggested by the reviewer.

While it is true that SOP4 (with some modifications to account for the low salinity typical of many inland waters) would provide a viable alternative to calculate CO₂ using the headspace method also in freshwater, the fact remains that its use within the freshwater community is rare and considered largely anecdotal despite its existence for decades. We feel that this is reason enough to alert the freshwater community of its potential significance and more importantly, identify when and where it is particularly relevant. Our intention was not to claim that we have developed something completely

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novel, but to draw attention of this issue to the freshwater community, and offer a tool specifically targeted to freshwater researcher. In our opinion, an easy to use tool may boost the adoption of the same procedural principles adopted in marine sciences but that are not used by the freshwater community. Further, the codes we provide to do corrections in an easy way should encourage its wider use. This makes our manuscript especially suited as a “technical report” and will hopefully help to improve data quality in freshwater carbon research.

As for the effect of temperature changes during equilibration, we will revise our wording in the manuscript because in fact this is considered in our calculations. We will make sure that this is clear in a revised version of the manuscript.

We will consider the reviewer’s comment on the necessity of contacting other groups to obtain more coupled NDIR and headspace data but felt that the pool of our own relevant data was sufficient to exemplify our point.

We are happy to keep discussing these or other aspects of our manuscript.

Regards,

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