

Interactive comment on “Analysis of oxygen isotopes of inorganic phosphate ($\delta^{18}\text{O}_p$) in freshwater: A detailed method description” by Catharina Simone Nisbeth et al.

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Interactive comment on “Analysis of oxygen isotopes of inorganic phosphate ($\delta^{18}\text{O}_p$) in freshwater: A detailed method description” by Catharina Simone Nisbeth et al.

Anonymous Referee #3 Received and published: 9 December 2019 This MS essentially reads as a long protocol on a method to process freshwater samples to recover sufficient phosphate to allow for isotopic analysis of ^{18}O : ^{16}O ratios. While there are a number of published approaches to do so for soils, marine waters, vegetation and other P bearing compounds, the lack of an approach for freshwaters has challenged researchers interested in developing a better understanding of P sources and cycling in

C1

freshwater systems. While I find the MS a bit long and perhaps dry in terms of discussion, I note that many of the observations documented within are similar to experiences that myself and others have observed when trying various approaches. Importantly, commentary on what does not work within a given step is a valuable contribution, particularly when one considers time and financial costs to go from large sample C1 volumes to a few grains of silver phosphate. For those of us working on small budgets, such information is extremely important. In the interests of shortening the MS, perhaps the authors might consider a tabular format which links agreement/disagreement with prior literature support as well as known issues with P recovery? Specific comments

Firstly I would like to thank the reviewer for their helpful comments and their appreciation of our primary motivations in putting together a paper such as this in order to attempt to save researchers considerable time, money and effort in processing and analyzing samples for analysis of oxygen isotopes of inorganic phosphate.

Lines 40-52 – given that in freshwaters, P is most often limiting, some indication of the range of P found in freshwaters might be useful for readers. Further, some discussion of the relative likelihood of where ^{18}O - PO_4 could be expected to function as a tracer (i.e. low light, eutrophic) vs simply an indication of probably P-recycling pathways (high light, oligotrophic) might also be useful.

Good point, we will include this in the corrected version of the manuscript.

Line 145-6 – we have used volumes of up to 200 L for low P lakewater samples as typical concentrations are ~ 0.05 μM . 0.4 μM is very high for many freshwaters in the northern hemisphere unless significantly affected by human activity or high natural sources of P.

Line 173-75 While in principle this is impractical, we have used sequences of 1 μm and 0.2 μm polypropylene cartridge filters under low pressure to filter >150 L down to 0.2 μm with little problem.

C2

I agree, this is often quite impractical and a filter of nylon polymer 10 micron pore size screen is often useful to act as an initial screen to separate some particles and agglomerated particles. We will include your suggestion as you outlined as an alternative approach (see also R#2 in filtration).

Lines 180-82 – we have found that NaOH loading (as % v:v) has a strong influence on recovery of DOP/DOM. Step V – In our experience, working in high C:P waters, NaOH loadings of ~ 1 % v:v are required to completely remove Pi from supernatant in presence of highly colored brucite floc. Furthermore, once we have reduced to a working volume (ca 250 mL) the flocs become more intensely colored rather than less intensely colored as described here. Further, as described in Step VI, after acid dissolution at this stage, there is a darkly colored precipitate that does not dissolve. While we have not determined the nature of this precipitate, loss on ignition when combusted after lyophilisation is near 80% suggesting some acid insoluble organics. We have used columns (similar to Coleman 2002) to “clean” this brownish color from samples with good success. C2

If the final solution from the last dissolution of the brucite is colored, many times I have filtered before proceeding on the next step.

Lines 287-302 – It should be worth adding that significant work on MAGIC in freshwaters has been done with respect to quantitation of Pi (i.e. Anagnostu and Sherrell 2008) and has identified other interfering compounds worth mentioning. Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2019-469>, 2019.

Certainly, we will include this in the corrected manuscript and it will be a very useful resource for researchers.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., <https://doi.org/10.5194/hess-2019-469>, 2019.