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Hydrology and Earth System Sciences
Discussions

Interactive comment on "Analysis of oxygen isotopes of inorganic phosphate ($\delta^{18}O_p$) 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 (_18Op) in freshwater: A detailed method description" by Catharina Simone Nisbeth et al. Anonymous Referee #1 Received and published: 15 November 2019 Analysis of oxygen isotopes of inorganic phosphate (_18Op) in freshwater: A detailed method description by Nisbeth et al.

A) General comments The present manuscript submitted by Niesbeth et al. is supposed to be published as a technical note that provides a detailed description for the analysis of oxygen isotope ratios in inorganic phosphate obtained from freshwater sam-

ples. Such a detailed stepby-step guide is generally of great interest to the growing number of scientists usingthis approach to investigate sources and cycling of phosphorus in the environment. I have to admit this is the first time I review a technical note, but thanks to extensive lab experience, I have a good impression of what a sound technical note should look like. What I expect from a technical note is a clear, straight-forward, user-friendly stepby- step description of the method and its respective steps. Having said this, we are already at the major issue of this manuscript. In its present form, the manuscript is a) too long (technical notes in HESS should be "a few pages only"), and b) it carries characteristics that are typical for other manuscript types. For example, it appears to be more of a review then a technical note at some points, which include citations and lengthy discussions. While this approach is fine for a classical review paper, it does not belong into a technical note. If, for example, your technical method is not suitable for a certain type of water sample, so just say it and do not attempt to come up with lengthy discussions of why and how it could work (for example, see lines 300-302 or 312-315). In sum, the two general question the authors need to clarify is how should the manuscript should look like as a sound technical note, and what needs to be done to get it there.

Firstly, I would greatly wish to thank the reviewer for his insightful and helpful comments in relation to the need and compilation of such a technical note. We will endeavour to (a) cut down on the length of the technical note. (This request also comes from the two other reviewers). (b) We will endeavour to remove any deemed unnecessary further discussion as requested but just to clarify what we were trying to highlight here was the background and reasons for the steps, and it appears to us that including such background and reasons is accepted or even appreciated (e.g., R#3) by the other reviewers; although all reviewers note the length. Giving a reason as to the background of each step to some small degree is very important in our opinion as it helps the user estimate how their samples will behave and cut down on costly mistakes. Finally, we submitted this as a 'technical note' because we think it suits that category more than it would fit the (also more prestigious) 'original research' or 'review' categories, although

we also acknowledge that it is not the most typical example of a ‘technical note’.

-Getting the manuscript into the right form also involves a substantial shortening of the present text. By removing text, there is also the question how to keep the aspect of novelty and not just repeat what has been previously published in other original papers (e.g., by Tamburini et al.) or reviews (e.g., by Davies et al. 2014), because this would be just a repetition of what has already been published. I therefore suggest to use your “own experience” additions (i.e., the only truly new information provided to the reader) in order to provide a clear optimized method description. Finally, the revised manuscript would be entitled something like “Analysis of oxygen isotopes of inorganic phosphate (_18OPO4) in freshwater: Detailed description of an optimized method” or something similar in this direction.

We can take on this helpful advice and attempt to include our “own experience” sections as we go through the document. We can also change the title to something more similar to what has been suggested. R#4 propose a somewhat different title, though. Further, we plan to conduct new experiments to add new, validating, data to the paper (to concur to other of the reviewers’ valuable comments, cf. the next comment of R#1); when this is done and the paper is revised, the current title may be still valid, perhaps.

-What I also miss is a clear recommendation regarding quality control. How to assure your _ 18PO4 signal does not change during the numerous sample processing steps? As already laid out by the authors, there might be pronounced issues with high organic waters, bearing the risk that organic P becomes hydrolyzed to PO4, thereby altering the original _ 18PO4 signal.

The original description of the brucite step for the purification includes some discussion on the stripping out of organic matter (Colman thesis). There are two possible solutions: One is to use the suggested low molarity of NaOH and consequently low molarity of the acid (as suggested in Colman), or to monitor the possible DOP hydrolysis by using 18O labelled and unlabelled acids to hydrolyse the brucite floc (as we

do for the HCl extraction in soils, see my paper Tamburini 2010). The downside of this second approach is that you need duplicates of samples, thus, big amounts of water.

-I further suggest to include a schematic overview of all the processes involved, which would also act as a sort of graphical guideline (see for example Davies et al. 2014, Figure 4 for such an example).

We can accommodate this by constructing such a schematic as suggested.

-To conclude, the manuscript in its present form requires substantial revision to meet the criteria of a technical report. Considering the value of such an optimized method description for the growing numbers of researchers working on aquatic P cycling, I would like to encourage the authors to submit a revised version of their manuscript.

We appreciate that the reviewer acknowledges the subject and its timeliness. As authors we will endeavour to improve the document considerably if we are given the opportunity to correct and upgrade the manuscript based the good suggestions outlined in this review and the others.

Given the general and specific comments (see below), I end up with the recommendation “reject with suggestion of resubmission”; however, it appears that HESS does not provide this recommendation option for reviewers, so I leave the decision to handling editor if it is going to be a "major revision" or "rejection".

B) Specific comments -1.Introduction: We need to ask ourselves here the following question - do we really need a lengthy introduction regarding the application of _18OPO4 analysis in a technical note? I would strongly recommend to condense the entire 2-page long paragraph into a short paragraph of 3-5 sentences that refer to the common literature.

I agreed to some degree. However, in our opinion, we believe we need more of an introduction than 3-5 sentences in introducing this technical note. I think it would be more reasonable to edit the introduction down to approx. 1 page in order to do justice

relating to the motivations and importance in the difficulty of the method but also the positive motivation of the work.

-In accordance with Coplen's 2011 "Guidelines and recommended terms for expression of stableâËŸA ËĞ RisotopeâËŸA ËĞ Rratio and gasâËŸARËĞ ratio measurement results" (Rap. Comm. Mass Spectr.) , I would recommend the consistent use of the term _18OPO4throughout the text and avoid Pi and other non-conventional terms.

This is taken on-board and will be incorporated into the document.

-Keep consistency regarding chemical concentrations; there are molar concentrations but also mg/L in the text, this should be consistent.

We agree; this is a clear mistake and we will use consistent chemical concentrations in the revised manuscript.

-Chapter 2.2, Step I: I have great doubt that the described procedure will be suitable to prevent co-precipitation of dissolved PO4 by Fe-oxyhydroxides if you have high Fe2+ concentrations in your water samples. During pumping, subsequent storage and transportation, it is impossible to avoid diffusion of O2 through pumping hose and plastic materials. This will in turn quickly react (within minutes) with the Fe2+ and form Fe-oxides, which in turn co-precipitate dissolved PO4 from solution. Do the authors have prove for a successful application of their suggestion? If not I suggest to go for other ways to isolate the dissolved PO4 from solution. This also brings me to the question if you really need such a lengthy sampling description in general; but this depends on where you want to focus your technical note.

Well, we do not know to which extent freshwater from "normal" rivers have reduced conditions and contain a lot of Fe2+. We agree that even if the precautions proposed in 2.2 are taken, still PO4-iron-oxide co-precipitation may (will, to some degree) occur. In practice, however, the suggested steps in 2.2 are more precautious than what many field workers will have done so far. In the case we have such waters, we could co-

precipitate brucite and Fe-bound P. A step with a chelating or reducing agent could be added (either dithionite or Na-EDTA). Anyways – and this we will clarify in the revised manuscript's introduction – the paper's main objective is not to present a 'now finally completely validated 18Op-freshwater method'. Instead, the objective is to present a consensus for the current way to sample and isolate 18Op of freshwater samples (cf., the general comment of R#2).

Our wish for the scientific community is that the method description that the paper provides can be used as stepping stone for further development of the 18Op method. For example, the paper should clearly point out where validation exists (by reference) and where validation is still needed.

Nevertheless, we will shorten the text in 2.2; we admit it is too verbose.

-Line 188: This also applies to all previous steps, which means samples need to be processed immediately after sampling to avoid potential microbial alterations.

The main idea is that the water sample is treated right after sampling with the NaOH to precipitate brucite. In theory, brucite precipitate at high pH, a condition where most of microbial activity is prevented. In addition, whenever possible, the brucite sample should be stored in a cold room, if time is needed before centrifugation and further processing. Microbial alteration is minimized.

C) Purely technical corrections at the very end ("technical corrections": typing errors, etc.). line 248: There is no such section Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2019- 469, 2019. This is a typo and will be removed, there was no such section.

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