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Biogeosciences Discussions

Interactive comment on "Technical Note: Comparison between a direct and the standard, indirect method for dissolved organic nitrogen determination in freshwater environments with high dissolved inorganic nitrogen concentrations" *by* D. Graeber et al.

Anonymous Referee #1

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This is the second time I have been asked to review this paper. It is very discouraging that the authors largely ignored my early suggestions for improvement. As a result, the paper still suffers from a number of issues. I realize that some might not be correctable but they need to be discussed regardless.

This manuscript describes the use of size exclusion chromatography to measure DON concentrations and then compares it to more traditional approaches. The method looks

very interesting and it would be a wonderful addition to out analytical toolbox. The writing is a bit confusing in places so I suggest improvements below. I also found the apparently random use of different sample sizes curious, which I again provide comments. This reads like a study that evolved haphazardly as it went along, rather than starting with a well thought out plan. Things evolve and that is understandable but sentence or two of explanations of choices would help here and there.

The most substantive issue, and for me it is a deal breaker, is the complete lack of discussion of blanks as I note below.

Specific comments 1. Abstract – I think few analysts would call 2.5 hours per sample fast. Presumably samples can be staggered or run in batches. I think indicating an average number of samples that can be run in 8 hours (or some other time unit) would be more useful to the reader.

2. Abstract – Specify that this method is for freshwater systems unless you provide evidence that it can be used in marine systems.

3. Section 2.1 – Why acidify and sparge for a TDN analysis? If this if for the DOC side of things, than this should be stated.

4. Page 7028, lines 16-21 – Expand on the residual within the column. How much is retained? What is the range of effects this can produce in the final concentrations measured?

5. Page 7030, top of page – The volumes of water used to rinse the filters seem excessive to me. Are these filters prone to contamination? If yes, why were they used when there are so many other good alternatives?

6. Section 2.4.1 – Only one natural sample was tested for the more extensive trials. This strikes me as very odd for a method paper. I would have loved to see several natural samples with different characteristics used. What was the rationale here?

7. Section 2.4.1 – Why were model substances tested at 2 mg N/L while the natural

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sample was only 1.5 mg N/L? What was the rationale?

8. Section 2.4.1 – Why was NH4+ not measured in the model substance samples? Amino acid standards can often have relatively high NH4+ concentrations depending on how the standards are prepared. If there is any sample left, I suggest checking the NH4+ concentration as it could explain some of the deviations in DON values.

9. As I said in my earlier review, it strikes me that a summary table of the various treatments and sample sizes would be useful. As written it is this seemingly endless list of things that sound the same but are not. It makes the reader work too hard.

10. Tables 1 and 2 – Here I am baffled. The point of the manuscript is to test the SEC-DON method and yet they don't report measures of error. This is standard for any study but it is particularly important when one is establishing the limitations of a new method.

11. Section 4.1 – The authors state that the main reason DON concentrations are overestimated was an overestimation of HTCO-TDN. There are also recoveries far in excess of 100. Is this a blank issue? There are no data provided for blanks and no discussion of how blank issues could impact the results or whether the data presented were corrected for blanks. I'm sorry but a method paper that doesn't have a thorough description and discussion of blanks associated with the analysis is not publishable in my view.

12. Figure 4 – I am completely baffled by how the standard method could be off by this much at the concentrations being measured. Were samples diluted? Could this be a calculation problem somewhere? Something seems very wrong to me.

13. Page 7035, top of paragraph – The issue of nitrogen remaining in the column comes up again. The authors assume the retention must be low because of the high recovery rates but as a reader I can't have much confidence in the recoveries when I have no information on the blanks. I myself have had beautiful recoveries ruined by an

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ugly blanks on a number of occasions. All may be well but with the data provided the reader can't know for sure.

To close I found this paper very frustrating. The technique looks promising and there is a real need in the community for new approaches. Too many basic questions are left unanswered, however. What were the blanks of the standard and SEC method? This can have a huge impact on the calculation of final concentrations and percent recoveries. I brought this up in an earlier review. The fact that it is still left unaddressed suggests that the authors don't have blank estimates they can present, the blanks are something they don't want to show, or they didn't appreciate the time a overworked reviewer took to try to help them improve their paper.

Unfortunately with the outstanding questions listed above I must recommend that the paper be rejected.

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