

Interactive comment on “Whole-lake spatial variability of organic matter molecular composition and elemental inorganic properties in a small boreal Swedish lake” by Julie Tolu et al.

Anonymous Referee #2

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A spatial geochemical study of a lacustrine environments is original and represents a largely unexplored aspect of biogeochemistry. Most studies reach directly to the coring equipment and retrieve a core which then becomes the focus of the study assuming we understand all those spatial details. Although the findings are perhaps not that surprising this is a valuable contribution which shows how OM and inorganic geochemistry varies in a relatively small but complex lake. These findings will stimulate thinking about the processes involved in other lake systems, but the paper could have had more impact if this concept would have been developed a bit more. Why not show a few sediment profiles from this lake in relation to these findings and show the implications. That would be really interesting and relatively easy to add. Now it remains

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just a hypothetical case. I have some criticism on how the results of the Py-GC/MS have been treated and would like to see some improvements made to the data that is derived from the Py-GC/MS.

Firstly, the title suggests that this study is characterising an entire lake. This is a bit misleading; I suggest to reword this to reflect more accurately the exact nature of this study.

The opening line of the abstract states: “The composition of organic matter (OM) exerts a strong control on biogeochemical processes in lakes, such as for carbon, nutrients and trace metals”. Carbon, nutrients and trace metals are not processes. . . I suggest to reword this.

L8 no hyphen between pyrolysis and gas

L15 no hyphen between source and pools

L24 Py-GC-MS = Py-GC/MS this is the accepted convention of abbreviated this technique.

L45 delete: C being the main constituent of OM (I think that is obvious) L65 “little work has been done to detail the compositional variability of the OM matrix as a whole”. Whilst I agree that in terms of spatial variation this is a virtually unknown territory, variation of the OM matrix in general is what many in the organic geochemistry community deal with. As such this is an overstatement and I believe the manuscript is doing an injustice to the many studies that have gone before. In Tolu et al 2015 a more robust overview is given of previous Py-GC/MS studies. I would like to see more such acknowledgement and brief detail about previous achievements on OM matter composition studies.

Method section. Pyrolysis GCMS is traditionally carried out at 650 degrees or there about and 450 is significantly lower than the conventional methods. Since this deviation may have consequences, more detail should be given here. I read Tolu et al 2015 which

is a very interesting paper. But I am not sure if for example it can be said that aliphatic signal in lacustrine sediments, that is often observed at 650 degrees can be dismissed as being an artefact of the pyrolysis process. Previous work from others has clearly shown that this is to be expected when algenan is present, there is no question about the fact that the aliphatic signal is an important constituent of lacustrine OM. . . The fact that this particular signal significantly lowers at 450 concerns me. As such, it may be that lowering the temperature to 450 may cause bias toward the terrestrial components. Have you considered an alternative approach such as TMAH pyrolysis? Also it is not clear to me if the authors can distinguish between thermal desorption and pyrolysis. A lot of the compounds listed could also be explained as thermally extracted and may not be pyrolysis products at all (this might also explain the difference between 650 and 450).

L185 "Because these sediment samples also contained too little OM for Py-GC-MS analysis." Py-GCMS normally should be able to detect extremely low amounts of OM even with the small sample size that is described here, I find it hard to believe that nothing could be detected. . . give the %TOC of these samples in the discussion. Is it really nothing or were the results unexpected? This might also be a 450 vs 650 problem. I would imagine there is more complex OM than material that can thermally desorb. Given the effort that has been put into analysing the geochemical data I think it would have been better to determine the %TOC using elemental analysis as was done in Tolu et al 2015. LOI is not a very precise way to determine TOC. the pyrolysis results could be expressed per TOC.

Table 2: Give references to the information that is underlying the grouping. This table looks a bit rushed. The compound classes are not always clear and confusingly grouped. I object against the terminology used to group the compounds and the way how the grouping is organised. The authors must decide how to group the compounds and stick to a very clear well explained system of doing so. What are "Big furans"? please improve. Maleimie = Maleimide Proteins as a class of pyrolysis compounds is

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not possible, I suspect protein derived is meant here. Lipids is the wrong term other compounds in the list are lipids too (eg hopanoids). Aliphatics is a better label.

Steroids and hopanoids have different biological origins, for a statistical approach such as what is presented here it would make a lot of sense to keep these separated. This would help with statistical analysis. A term such as lignin has a clear origin associated with it, a term such as “lipid” or “high mass compound” carries no such value.

The table as given in the supplement is much more useful. It is very important to see what contributes to these categories. Without it, the methodology becomes a black box. I suggest to combine table 2 and S1. This will avoid that the reader is wonders about what might be in a “big furan” category. I would suggest to rename some of the categories and rethink the groupings. This would mean that the PCA results are going to change.

I would like to see Retention Index values for each of the listed compounds in the table. This is very important as all compounds have been identified using the NIST database (according to the text) and this can be very unreliable. RI values together with the mass spectra (as have correctly been given) will give extra confidence. The mass spectra given are only a rough summary and do not have much value for a reader but with RI values it becomes much more solid. There are quite a few unknowns. I would like to challenge the authors: if they are not certain about the ID of a compound, how can you put a compound in a specific category?

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