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Biogeosciences Discussions

Interactive comment on "Lability of natural organic matter in freshwater: a simple method for detection using hydrogen peroxide as an indicator" *by* Isabela Carreira Constantino et al.

Anonymous Referee #1

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General comments:

The method presented in this paper appears to have potential to be a useful method for quantifying labile organic matter in environmental water samples. The quantification of labile organic matter can provide very meaningful information about the biogeochemical conditions in a particular environment and is useful across a wide range of scientific studies. However, the presentation of the method and interpretation of results in this paper are generally unclear and in places the interpretations appear flawed (more on this later). Furthermore, many of the decisions/approaches made by the authors lack sufficient justification/support and thus it is not possible to assess the validity of these

decisions. The authors should also provide more background on other methods of quantifying labile organic matter (e.g. incubations with native microbes) and the advantages and disadvantages of their method compared to existing ones. I think there may be some real advantages to their method but these need to be discussed by the authors. In addition, it is not made completely clear that the method the authors present here is new. I am under the impression that it is, but if it is in fact completely new they should state that more clearly. If the method is not new then they should make it clear how they have improved upon previous work. The authors should also discuss exactly what the method is measuring and how the model organic substances used (in particular pyruvate) compare to labile organic matter (more on this below). In particular, we see that pyruvate is more labile than the other model compounds (fulvic acid and lignin) though this in no way implies that pyruvate is a good model for LOM. It may be true that pyruvate is a reasonable model for LOM, however the authors need to explain what constitutes a "good" model for LOM and why pyruvate meets these criteria. Overall, I feel that the method described in the paper may provide a useful approach to quantifying labile organic matter. However, the paper currently lacks clarity and provides insufficient justification/support to allow for a full assessment of the significance of this work. As the paper currently stands there are a number of very significant issues that need to be addressed. The paper will require substantial revisions and reworking to allow for a full assessment of the potential scientific contributions.

Specific comments:

Note: Numbers in parenthesis are line numbers

(42) "...and the biogeochemical processes involved" Involved in what? Are you referring to the processes generation NOM?

(44) "According to some studies nearly 80% of NOM is composed of recalcitrant fractions..." Is this a general consensus or only something that a few studies agree upon?

(47) “important for several environmental reactions. . .” such as?

(48-49) “HS are considered recalcitrant compounds if their resistance to chemical and microbiological degradation is taken into consideration” (my emphasis added). Isn’t this how recalcitrant is defined? You might want to change “if their resistance” to “as they are resistant to” and remove “is taken into consideration”. This would make more sense.

(63-64) “. . .that is more biodegradable”. More relative to what? Maybe rewrite as “LOM is operationally defined as the fraction of NOM that is biodegradable under a set of defined conditions”

(64-65) “...by the photodegradation of organic compounds”. Provide citations here.

(65-67) Is it always (or generally) true that allochthonous material is more recalcitrant? If so provide citations.

(70-76) This paragraph is awkwardly written and unclear.

(77-79) These sentences are awkward/unclear. Maybe say something like “NOM can be measured by (state method), however this method only provide information about bulk concentration and does not provide info about the relative amounts of LOM and ROM”

(84-87) Very unclear. You write “we hypothesize that LOM is fresh and reactive. . .” By definition LOM is reactive so as stated it is an awkward hypothesis and needs to be reworded or reworked.

(86-87) “. . .transforming them into NOM oxidizing.” This sentence does not make sense.

Section 2.2.2 Microcosms experiments is not clearly presented. It is not obvious from reading whether you are describing the method that is then used in section 2.2.4 or if you are describing a separate set of experiment from section 2.2.4. You should make

this more clear by possibly renaming section 2.2.2 to “Microcosm experiments: Model organic compounds”.

(116-117) “Some organic compounds were chosen to represent models of LOM and ROM.” Which compounds for LOM and which for ROM? I realize that pyruvate is for LOM and the others for ROM but it is awkward to write “some organic compounds” as opposed to stating which ones. Also you should provide a discussion justifying why you chose these compounds as model compounds. You obviously had some reason for selecting these but need to justify the decision and provide citations supporting the decision where applicable.

Section 2.2.3 Data treatment. There are essentially no details provided about the kinetic models used and how you fit your data to these models. You need to provide more details and justification of your approach.

(136) “Considering the previously evaluated results”, what results are you referring to?

(136-137) “the best model compounds were determined to be fulvic acid and sodium pyruvate”. Best how? What was your criteria for best? Presumably fulvic acid and lignin were tested to see which was a better ROM model. However, you only tested one potential LOM (i.e. pyruvate) so it is not fair to say it was the best model. You could potentially say it was a suitable model. This raises a more general issue, that there needs to be better justification/support for your choices. In particular, pyruvate appear (based on your data) to be more labile that fulvic acid. This is reasonable, but it does not necessarily mean that it is a good model for LOM. It is conceivable that another model compound may be even more labile than pyruvate. Thus, while pyruvate may be labile, it might not be nearly as labile as other compounds. Therefore, when you use pyruvate data in your kinetic modeling it becomes unclear exactly what your quantification of LOM means. More discussion and justification is needed here.

(143) Any reason why 0.45 um filter was used? A 0.2 um filter would have been more ideal for removing microbes. This may not really have affected your results, but you

should explain/justify your choice here.

(156-159) You state that the data follow a zero-order law. Is there any theoretical reason why this would be true? Even if the data follow this law, you should provide some discussion/justification as to why it follows a zero-order law.

Section 3.1. You state that H2O2 consumption is virtually non-existent until 1400 minutes after the start of the experiment. Why is this the case? You should provide conceptual/theoretical discussion explaining this.

(163) the numbers reported here do not agree with the numbers in Table 1.

Figure 1. The data do not all appear to follow a zero-order law. If the data fit a zero-order law, then C/Co vs. time should be linear (at least the portion following the 1400 minute lag should be). However, the data do not appear linear in many cases and thus your contention that they follow a zero-order relationship does not appear to be completely reasonable. This issue is part of a broader issue here where there is often insufficient justification for the statements made in the paper. As the paper is currently presented you do not explain how model parameters were fit (e.g., was a least squares fitting approach used) or how models were chosen. For example, was a zero-order model used because it fit better than a 1st-order model? Or was the model chosen for theoretical considerations. Discussion on these issues is required.

Table 1: Similar comments as for Figure 1. Also the number of significant figures for the "Lignin" column" differs from the other columns. Also you should include discussion and information showing how good the fits are for the estimated parameters (K). Currently there is no way to assess if the parameters reported in Table 1 are good fits. This is very important as it is presently not possible to assess if the kinetic models chosen to fit the experimental data are reasonable models. As I have mentioned above the zero-order fit for fulvic acid and lignin appears that it might not be all that reasonable. Furthermore, you should provide any available justification as to why the pyruvate data should fit a 1st-order model.

In section 3.1 you mention that pyruvate was oxidizing (as indicated by consumption of H2O2). However, you provide no indication of the extent of oxidation (did it completely oxidize to CO2 or did it go to an simpler organic compound)? Did you measure changes in TOC during these experiments? If so it would be useful to include and discuss this data for both the pyruvate and fulvic acid experiments. This issue comes back to the previously stated issue that you do not explain exactly what you are measuring by using pyruvate as a model for LOM. It is totally conceivable that other model substances for LOM might oxidize more (and thus consume more H2O2) or less (and consume less H2O2) than pyruvate. Thus, had you used those substances you would have gotten completely different rate constants and your equations 2 and 3, which you use to estimate LOM in natural samples would have been different. A full and discussion of these issues, and presentation of data that might help to resolve this questions is crucial to demonstrating the utility of the method presented in your paper. Resolving/addressing these issues is crucial to demonstrating the validity/utility of your method.

(178) The numbers here do not agree with the table.

Equation 1: Justification for choosing this model should be discussed.

(249-250) You state that the results are in agreement with a zero-order model. If there was LOC in the samples wouldn't you expect (at least based on your earlier conclusions) that the samples would follow a 1st-order model. Recall that you stated your pyruvate data followed a 1st-order model and your fulvic data a zero-order model.

(255-275) Your conclusions/statements here are unclear and do not seem valid. You conclude that "these results indicate that freshwater from the Preto River predominantly consists of ROM". I would expect the freshwater only experiment to have very similar behavior to the freshwater with fulvic acid (since the fulvic acid adds only ROM). I would also expect the freshwater+pyruvate samples to consume H2O2 faster than the only freshwater sample, since the addition of pyruvate adds LOM. Thus, I do not believe that you can conclude from these results that the Preto River water consists predomi-

nantly of ROM based on your experimental results. In fact if the Preto River water was predominantly composed of ROM, then wouldn't you expect the data from the freshwater only experiment to be very similar to the control (Figure 3)? Since the freshwater only data is very different from the control, then I do not believe you can make the conclusions that you have made here. Thus, this section is very unclear and it is not obvious what exactly you mean to show with the data in Figure 3 and Table 2. Again, you will also need to justify the model choices in Table 2 and provide goodness-of-fit data/discussion for the K values estimated in Table 3.

(300-301) You mention that similar behavior of H2O2 consumption has been observed in Jardim et al. 2010. Was the same or similar method used in this paper? If so is your method new/modified? If Jardim et al. (2010) were doing something different from your current paper, then please make this clear.

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