Biogeosciences
Discussions

Interactive comment on "Mineralization of organic matter in boreal lake sediments: Rates, pathways and nature of the fermenting substrates" *by* François Clayer et al.

Anonymous Referee #1

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The manuscript is a modification of previous work published by Clayer et al 2018 in Geochimica et Cosmochimica Acta. It builds on the hypothesis that the degradation of organic material under anaerobic conditions has two ultimate sinks – CO2 or CH4, the most reduced and oxidized states of carbon. The relative abundance of these two should therefore provide information on the average oxidation state of the degraded organic material accounting for transport and other sources of CO2. This principal approach has been presented in Clayer et al (2018) GCA. The current paper is very similar to this published work and contains many data that are shared. It was not obvious to me where this work is a significant novel contribution beyond what has also ready been published. The authors use a simple steady state reaction transport model

for diffusive and advective transport to determine microbial process rates based on sediment porewater concentration gradients. Furthermore, the isotope composition of DIC is used to improve the mass balance calculations. Below I question the validity of this approach to obtain a meaningful mass balance using the Berg et al model at steady state.

This manuscript is difficult to understand manuscript and very technical in its description. What makes this manuscript so hard to read and understand is the multitude of R subscripts that are used in the text and the extensive treatment of the methodology in the appendix. The fractional equations are nowhere introduced. Deserves an explanation. In practice, one has to have a table on the side to look up what reaction a particular R subscript refers to and, in addition, know all the notations from Clayer et al (2018) to follow this work. Still, to follow the conclusions becomes increasingly confusing as one reads along, until one is either lost or exhausted. In the current form, the manuscript cannot be digested.

I recommend that the authors outline the hypothesis, mathematically, in the materials and methods section, of how their methodology allows them to get at the oxidation state of oxidized organic matter. In the current form, the reader has to wade through too much text to get to this most interesting point of the manuscript. This paper requires a much better didactic approach to get methods and goals across and the authors get sidetracked in many details that make it hard to follow their ultimate goal. It is, in its current form, not streamlined enough and requires very significant rewriting and restructuring to make the approach more understandable and possible to evaluate critically. At present, I cannot evaluate the quality of the manuscript, but am left in doubt about its novelty given the similarity to the 2018 GCA paper.

While the fundamental goal, to arrive at the oxidation state of metabolizable organic material, is of some significance, the presentation of the approach is not well developed and can be improved considerably.

Data and basic approach (although I did get lost in the complicated d13C treatment) are, in principle feasible, but overall I am concerned that the instrumental and modelling analytical uncertainty is too great to pin down the COS sufficiently (although an error is given). The authors provide statistical data to support their assertion, but it was not possible for me, based on the complicated description, to relate the outcome of these tests to the goal of the manuscript, i.e., the original oxidation of the degrading organic material. The authors must make sure, in a succinct and understandable and not too wordy fashion, how their methodology allows them to pin this value down sufficiently. Remove as much as possible reiterations of what has already been said and discussed in detail in Clayer et al 2018 GCA and restrict this paper to the novel information.

A lot of the discussion about the CH4 isotopes are not really part of the goal of this paper. This should be separated.

There are a few assumptions whose impact I don't understand or that are difficult to assess, e.g., that there are no anaerobic reoxidation reactions for sulfide; elemental sulfur with FeOOH. The paper does not lost O2 uptake rates for the oxic part of the year, which is an important constraint on the 'background CO2 levels in the buried porewaters. The paper does not constrain oxygen penetration depths or the importance of bioturbation processes for DIC levels, and does not show O2 microelectrode profiles, which would be necessary to constrain the inorganic oxidative processes. Therefore the constraints for the diagenetic system, e.g., by having total O2 uptake rates are far and few. In principle, non-steady state reaction transport modelling with a much more advanced model are necessary to tackle this question, if it is possible at all.

Another curious observation is the omission of NO3 dynamics as part of O2 consumption by nitrification; also here there are no constraints on the system concerning NH4+ to accompany C mineralization dynamics.

The model also ignores O2 consumption due to Fe oxidation, but curiously the authors choose to include instead sulfide oxidation with O2 and FeOOH.

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It seems very hard to see how the boundary conditions can be reasonably constrained to continue with the approach used by the authors.

Line comments: Line 139: There are more products than acetate CO2 and CH4 and H2: Formate, propionate, isopropionate, lactate, butyrate, isobutyrate, pyruvate, succinate, etc.; The sum of the latter can be as high as 30% of the total VFA. Ok, acetate is low, but why should it not, if it is consumed by terminal oxidizers? L.155 Profile underestimates the oxidation rate because it is a fit of a net rate, not a gross rate, e.g., cryptic cycling leads to CO2 production by sulfate reduction in the absence of a curvature in the gradient. Line 191: No good explanation for the low acetate concentrations? Line 281 Equation 9 has not been introduced previously. I don't get those fractions. Line 322: This sentence is confusing, why should hydrogenotrophy produce DIC coupled to fermentation? Only fermentation r1 may produce CO2. L.330: To avoid confusion, a carbon mineralization process leads to the formation of a mineral acid, e.g., carbonic acid. Neither fermentation nor methanogenesis can therefore be called mineralization processes. They are carbon degradation/decomposition processes. Line 332: Please change your terminology Methanogenesis by hydrogenotrophy cannot lead to CO2 formation Line 337-340 This conclusion cannot truly be validated with the approach used here. Line 353-355 Again, the authors make the mistake of modelling net concentration profiles to extract information on gross rates. The H2 production and CO2 production rates by cryptic cycling are not reflected in curvatures of concentration gradients, these only represented the net effect.

A cryptic sulfur cycle is only used to argue for H2 production. Why not CO2 production by sulfate reduction?

The overall problem with the approach is that a balance based on CO2 and CH4 and the OM oxidation state is too poorly constrained. In reality, in addition to a mass balance an independent charge balance should be achieved to constrain the original oxidation state of the OM. The current approach balances the electrons between the mass of methane and total CO2 accounting for diffusive transport. This could likewise

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be achieved by adjusting the alkalinity.

I think that the authors use the model the wrong way. It is perfectly fine for comparing rates in the different zones, but it is not possible to balance the inventories in the respective zones with this model. A more sophisticated reaction transport model that accounts for the cumulative amount of DIC formed during burial needs to be used to explain the amount and isotope composition of DIC. The model Profile only captures a snapshot of a concentration distribution, i.e., the steady state, and it does not allow for calculating cumulative effects during burial, which is important for a diagenetic model and for this case to account for the buried amount of DIC from oxic respiration. In addition, the steady state assumption is invalid for most natural cases except for very small distance, e.g., at the micrometer scale where diffusion is extremely fast. A time-dependent model that includes mass accumulation rates must be used here.