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Biogeosciences Discussions

Interactive comment on "Anaerobic oxidation of methane: an underappreciated aspect of methane cycling in peatland ecosystems?" *by* K. A. Smemo and J. B. Yavitt

Anonymous Referee #3

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General Comments

This paper is a very good review about AOM in freshwater systems and in peatlands in particular. The authors provide a good overview of the available literature, maybe one could add some literature as mentioned by Reviewer #1, especially on iron reduction/oxidation and electron shuttling; but in general I find this article contains most of the important findings of the last years. I am not really happy with the structure of the article, so far, as also indicated in more detail below. In its present structure, the authors use a lot of studies to support the importance of AOM in the beginning of the article, of which they state only later that the methodology was somehow not adequate

to provide real evidence. This may be a problem or confusing for readers not being so familiar with e.g. the thermodynamics or other details. When giving the theoretical background first, one may better judge the reliability of the past literature examples.

There are some technical or typing issues in the article that have already been mentioned by the other reviewers, but the general language of the article is very good. Overall, the length, the number of references, and graphs is adequate. Adding a table with to assist the thermodynamic issues may be helpful.

As the topic of the article is a very important current discussion among peatland scientists and will certainly stimulate new research, I recommend rapid publication of the article after addressing the following points.

Detailed comments

When the authors cite existing studies that have found "evidence" for AOM in peatlands or freshwater systems, I would like to read also something about the methodological shortcomings of the respective studies. The authors themselves state at the beginning of the paper "but much of this evidence is anecdotal in nature and strong evidence [. . .] has been limited". There is a lot to discuss here, i.e. the use of inhibitors is controversially discussed, zones of nitrate reduction often contain still small amounts of oxygen, evidence from budget calculations along profiles may be biased due to heterogeneity, and so on. Thus, in the introduction, some statements about "evidence" may need to be weakened a bit. As an example: The early study from Murase & Kimura analyzed the effect of electron acceptors on methane production or consumption. From the data given in the paper I read that the addition of electron acceptors lead to a lower increase of methane in the respective treatments compared to a control. I would attribute this to a decreased production rather than to an anaerobic oxidation, as there is no evidence that the sulfate or iron amendments actually lead to a consumption of methane. You also state these methodological problems, but only on page 7953, after introducing this study to support the occurrence of AOM. Such a discussion could also be helpful to derive further research needs and methods.

Maybe a rearrangement of the paper would help to address these points. If you start with AOM biogeochemistry and thermodynamics you may well explain, why it works in marine systems and why there are problems to support this process in freshwater systems. Then you may describe the existing studies and address their possible shortcomings in methods. The explanations in the "biogeochemistry: electron acceptor" section are very important and from my point of view given too late. Starting with this section would much more emphasize the problems with the AOM studies in freshwater systems so far. On the other hand, you may shorten then the section where you discuss AOM in marine sediments, as in these environments the process has been evaluated in great detail and can be supported by thermodynamics.

So my suggestion about the structure would be: Introduction, Biogeochemistry (maybe including the section about marine sediments, as these systems are well evaluated and may serve as a model system), Microbiology, existing AOM studies in freshwater systems and their limitations, possible mechanisms in freshwater systems and peatlands, future research needs and global implications.

Nevertheless, there remains the thermodynamic problem with AOM: Under in-situ conditions in freshwater wetlands, concentrations of involved species mostly yield a positive (endergonic) or only slightly negative Gibbs free energy for the process that does not suffice to fuel microbial ATP generation (e.g. using thermodynamic data from the studies of Alperin, Schink, Stumm&Morgan or others). In an early study of Martens and Berner 1977 (cited in Murase and Kimura 1994), the authors calculate a sufficient energy gain of approx. -25 kJ/mol for the oxidation of CH4 by reduction of SO4, concentrations are SO4: 10mM, HCO3-: 30mM, HS-: 0.5 mM, CH4: 0.1 mM. When I calculated AOM with sulfate reduction and concentrations I typically observed in a peatland, I end up with -13 kJ/mol, which would be below the threshold of -23 kJ/mol given by Schink and others (inputs: standard Gibbs free energy: -16 kJ/mol, conc. CO2 3 mM, CH4 1 mM, SO4 50 μM, HS- 50 μM, Temp. 10 $^{\circ}$C or 283 K). And: As soon

as you assume Sulfate to be present, bacteria would yield much more energy under most conditions using this Sulfate to oxidize other organic matter. So, I would propose to include a table, where you report typical concentrations of the involved species (if available from studies that reported AOM in freshwater systems) and calculate the energy yield of the process. This would point out the dilemma much better that describing it in the text.

From a thermodynamic point of view, Nitrate would also be most likely an electron acceptor of choice for AOM in peatlands and the work of Ettwig and others looks also very promising to me.

If you state already in the abstract that electron transfer mechanisms and organic matter as an electron acceptor may be important from your point of view, you could extend the section where you discuss this. There are e.g. studies from the group of Andreas Kappler or the group of Don Macalady giving also thermodynamic data on organic matter utilization (e.g. redox potentials and transfer capacities).

Interactive comment on Biogeosciences Discuss., 7, 7945, 2010.