

Bg-2019-284: Praetzel et al.

Organic matter and sediment properties determine in-lake variability of sediment CO₂ and CH₄ production....

The study measured transects of sediment characteristics at two depths across a shallow eutrophic lake. Besides chemical and physical variables, the authors measured production rates of CH₄ and total CO₂ and correlated them to various sediment variables, in particular to FTIR spectra resolving polysaccharides, lignin, humic acids, phenols and aliphatics, other aromatics and fats, waxes, lipids; and to the magnitude of electron accepting and donating capacities. They further measured CH₄ and CO₂ fluxes in the centre of the lake and compared these rates to the production rates. The study provided a solid data base and many interesting correlation analyses. Highlights are the negative correlation of sediment gas production rates to recalcitrant organic compounds (fats, humics) and electron accepting capacities. Furthermore there was no obvious correlation between gas production rates and emission fluxes. These were to my opinion the most interesting results that warrant reporting, while observations with respect to the influence of temperature and the thermodynamics of CH₄ production pathways were rather trivial, as they are well known from the literature.

However, I noticed several points that should be addressed by the authors before the ms is accepted.

Major points:

1.L.79-81: The Gibbs free energies given in the ms are either not found in the quoted literature (Whiticar 1999) or are different (Conrad 1999). I assume the reason is that they were calculated using energies of formation for gases in dissolved rather than in gaseous state. This would be consistent with the Nernst equations mentioned later (L.250) also probably using gas concentrations rather than partial pressures. However, the authors should clarify the procedures.

2.L.187-200: There are no isotopic data reported, therefore the description of IRMS methodology is not necessary.

3.Table 2: L.411-412 mentions strong FTIR absorption features of polysaccharides. However, this compound class is not listed in the Table.

4.L.422-425. This is an overview of measured rates. However, the numbers seem to be slightly different from those shown in Fig.2. Although there is probably a reasonable explanation for these differences, I found it confusing. In fact I would be happy just looking at the data in the figure without reading the text. However, one could mention that the rates decreased from the shore to the centre, since this point is later relevant in the Discussion.

5.L.477-487: Here applies the same as in point 4. The data in the text seem to slightly different from those seen in Fig. 7.

6.L.507: Again the data in the text seem to slightly different from those seen in Fig. 8.

7.The discussion is too wordy and should be focused to the really novel results. I also recommend a different structure for the Discussion. I think it is not ideal having individual chapters on spatial variability of OM quality, spatial variability of CO₂ and CH₄ production rates, and influence of OM quality on gas production, since such structure results in too much repetition and also is not very suitable for explaining gas production rates on the basis of OM quality.

9. The discussion on temperature effects can be much shorter, since it is rather well reported in the literature.

10. The discussion of methanogenic pathways (L.648-680) is not really relevant, since the data just show that both methanogenic pathways were exergonic and thus, could well operate. Everything else is speculation and not relevant. The magnitude of the Gibbs free energy does not allow to conclude whether the one pathway is more prevalent than the other. One could however discuss the correlation of the concentrations of H₂ and acetate, and the respective Delta G, with sediment OM quality, since correlations were reported in the Results.

11. The discussion of alternative electron acceptors (L.682-698) is rather short. The authors only discuss correlations. They miss the chance to discuss stoichiometric relations of reduced EAC with the amounts of CO₂ production. Although such mass comparisons apparently have recently been done by other members of the Knorr group (Gao et al. 2019), they would also be interesting for this particular lake. I have the impression that the magnitudes of reducible EACs might explain the CO₂ production in the beginning of the incubations, when rates of CO₂ production were larger than those of CH₄ production, while methanogenic decomposition of OM should result in equal rates. I wonder why this point is not addressed.

12. I noticed that lake sediments were anoxically preincubated for either one week (L:178) or 50 days (L.331). Please clarify! Anyway, the preincubation might have depleted most of the reducible iron and sulfur compounds. This may be the explanation for the low values of EAC_{inorg} (Fig. 7), but is not discussed.

Minor:

1.L.28: what means 'sufficiently' ? rho=0.65 is sufficient? Would rho=0.6 also be sufficient. Is there an objective criterion for sufficiency?

2.L.30-32. I cannot follow the argument of this sentence. I suggest rephrasing.

3.L.67: cellulose is also a polysaccharide. I suggest rephrasing.

4.L.83: The Delta G-zero of hydrogenotrophic methanogenesis is more negative than of acetoclastic methanogenesis. Therefore the acetoclastic pathway is less (not more) energetically favorable.

5.L.91: EAC has not yet been defined. Please check also for other abbreviations.

6.L.107-109: The '4' in CH₄ as superscript

7.L.168: 12 locations; please harmonize with the 13 sampling sites mentioned in the legend of Fig.1.

8.L.207: 'relative abundance' compared to what?

9.L.268: EAC/EDC: I think you mean EAC & EDC rather than the ratio between both. I found similar possible confusions at many places in the text (e.g., L.293, L.369, 370, 383 and in the labels of Fig. 7. Please check carefully.

10.L.299. The reference Tamura et al. (1974) only describes the analysis of Fe(II) (albeit in the presence of Fe(III)). How was Fe(III) analyzed?

11. L.477-479: I cannot follow this sentence. Also compare major point 6 above. Please also note, that Fig. 7 is not mentioned in the text, and that Figure number should be exchanged with that of Fig. 6, since Fig.6 is reported later in the text than Fig. 7.

12. Table 3: Showing the time line as t_0 , t_1 , t_2 etc. is awkward, since one has to consult the explanation in the methods section. I suggest listing the actual time points, i.e. 0, 1, 3 etc. days.

13. Table 4: The numbers in the table show too many decimal positions. Please report only those that are significant. In fact, at numerous places in the text numbers seem to show non-significant decimal positions. Please check and correct.

14. L.535, 538: Should be Table 4 rather Table 5.

15. References. Some of the references use capital letters for the titles.