

Reply on RC2

Janne Rinne et al.

Author comment on "Spatial and temporal variation in $\delta^{13}\text{C}$ values of methane emitted from a hemiboreal mire: methanogenesis, methanotrophy, and hysteresis" by Janne Rinne et al., Biogeosciences Discuss., <https://doi.org/10.5194/bg-2022-76-AC2>, 2022

The thank for the positive and constructive comments. We address the comments (in bolded italics) in detail below.

General comments

The study by Rinne et al. investigates CH₄ emission rates and d13C-CH₄ values, and the community structure of methanogenic and methanotrophic communities in a poor fen in southwest Sweden. It is one the most detailed investigation to date pairing high temporal resolution upscaled d13C-CH₄ values with integrated d13C values of CH₄ flux sampled from nocturnal boundary-layer accumulation. The key findings locally are that: (i) the observed spatial and temporal differences in d13C values of CH₄ emissions vary systematically in response to environmental conditions, (ii) the spatial range of values (~15 permil) is larger than temporal variations and appears to be governed by differences in substrate and moisture levels within the peatland that can be identified by vegetation assemblages that can be delineated via remote sensing, and (iii) metagenomic analysis indicates that methanogenic communities within the peatland are diverse and capable of adapting to changes in substrate supply and environmental conditions. I support publication of this work with minor revision.

I recommend that the authors explore further in the Discussion section the implications of their measured d13C values for isotope-weighted global CH₄ budgets. The measured d13C values (~ -81 to -79 permil) of CH₄ emissions from the site are significantly more negative than d13C values typically attributed to global and northern wetlands (e.g., -58‰; Mikaloff-Fletcher et al., 2004a,b; -58‰, Bousquet et al., 2006; -59‰, Monteil et al., 2011;). Similar to Fisher et al. (2017), this study presents further compelling evidence for a need to adjust d13C values attributed to CH₄ emissions from northern peatlands.

We originally did not go into this discussion, as after all our measurements present only one mire ecosystem. Thus, we felt that it may not have wider implications in this context. However, with this encouragement, we will put our mire-scale $\delta^{13}\text{C}$ values into perspective of d13C values observed in other mires in the revised version of the manuscript. The $\delta^{13}\text{C}$ values observed at Mycklemossen mire are indeed in the lower end of those observed in mire ecosystems also in light of some recent reviews (e.g. Menoud et al., 2022).

Specific comments

Manuscript title: '...variation of d13C values of methane...'

This was actually one of the title alternatives we were considering for the initial submission. It is probably slightly more accurate. We will modify the revised version of the manuscript accordingly.

Line 13 – '...offer clues...'?

Thank you for spotting this typo. It will be corrected.

Line 76-77 and elsewhere. Replacing terms such as 'isotopically lighter CH₄' with more specific language would eliminate the need for clarifying statements in parentheses. For example (lines 75-76) could be written as '... hydrogenotrophic methanogenesis typically produced CH₄ that is 13C-depleted relative to CH₄ generated from acetoclastic methanogenesis.'

We will edit the text as suggested here.

Line 108: 'reflect differences in CH₄ production due to differences in substrate availability for methanogenesis.'

In the original sentence we referred to differences in the trophic status that encompasses both quantity and quality of available substrates. The suggested change makes the sentence simpler, and mostly conveys the same content. We will change the sentence accordingly.

Line 110 and elsewhere: 'methanotrophy prefers 12C, leaving more 13C to the emitted CH₄' = 'Enzymatic reactions associated with methanotroph metabolism consume 12CH₄ preferentially, resulting in 13C-enrichment of residual CH₄.'

Yes, the suggested sentence is clearer and we will make a change accordingly.

Line 113 – awkward sentence; 'less 13C depleted CH₄' = '13C-enriched CH₄' or 'CH₄ having more positive d13C values'.

Yes, "less ¹³C depleted" is somewhat like a double negation. However, especially "CH₄ having more positive δ¹³C values" can be also confusing as the δ¹³C values are still negative. "higher δ¹³C values" could be simple and straightforward.

Line 121 – In this context 'substrate supply' rather than 'trophic status' perhaps would more accurately describe the environmental variable impacting CH₄ emission rates.

We used trophic status as used in e.g, Hornibrook and Bowes, 2007, and Hornibrook 2009, although the term in the latter is "trophic level". "Substrate supply" or "substrate availability" can indeed be better in this context.

Furthermore, our sentence, "...the seasonal cycle of the CH₄ emission rate is due to the changes in trophic status, i.e. between acetoclastic-dominated (AM) and hydrogenotrophic-dominated (HM) methanogenesis." implies only changes between acetoclastic and hydrogenotrophic pathways, while also changes in energetics of hydrogenotrophic methanogenesis can work in the same way. Thus, we will change this sentence to reflect this reasoning.

Line 163 – remove capitalization 'polymethyl...'

We will do this.

Lines 203-205 – How was the CRDS calibrated in the field for concentration and stable isotope measurements?

We took parallel samples from chamber closures and run these with IRMS, as explained in the next paragraph. We also occasionally have run standard gas to check the concentration measurement.

Lines 231-233 – Data from chamber 3 are not mentioned?

As there is very little data from chamber 3, and its contribution would be low due to small fluxes. We did not include it to the upscaling calculation. We will mention this explicitly in the revised version of the manuscript.

Line 276 – ‘...seems to be quite similar...’ If this is an important point, perhaps employ a statistical comparison?

This is actually not an important point for this study, just an interesting observation. Thus, we will remove this from the revised version of the manuscript, as it may confuse a reader.

Line 304 – ‘there were hardly any data’

Thank you for spotting this. We will correct it.

References

Menoud, M., van der Veen, C., Lowry, D., Fernandez, J. M., Bakkaloglu, S., France, J. L., Fisher, R. E., Maazallahi, H., Stanisavljević, M., Nećki, J., Vinkovic, K., Łakomiec, P., Rinne, J., Korbeń, P., Schmidt, M., Defratyka, S., Yver-Kwok, C., Andersen, T., Chen, H., and Röckmann, T.: Global inventory of the stable isotopic composition of methane surface emissions, augmented by new measurements in Europe, Earth Syst. Sci. Data Discuss. [preprint], <https://doi.org/10.5194/essd-2022-30>, in review, 2022.

Bousquet, P., Ciais, P., Miller, J.B., Dlugokencky, E.J., Hauglustaine, D.A., Prigent, C., Van der Werf, G.R., Peylin, P., Brunke, E.G., Carouge, C., Langenfelds, R.L., Lathiere, J., Papa, F., Ramonet, M., Schmidt, M., Steele, L.P., Tyler, S.C. and White, J. (2006) Contribution of anthropogenic and natural sources to atmospheric methane variability. Nature 443, 439-443.

Fisher, R. E., France, J. L., Lowry, D., Lanoisellé, M., Brownlow, R., Pyle, J. A., et al. (2017). Measurement of the ¹³C isotopic signature of methane emissions from northern European wetlands. Global Biogeochemical Cycles, 31, 605–623.

Mikaloff Fletcher, S. E., Tans, P. P., Bruhwiler, L. M., Miller, J. B., and Heimann, M. (2004a). CH₄ sources estimated from atmospheric observations of CH₄ and its ¹³C/¹²C isotopic ratios: 1. Inverse modeling of source processes. Global Biogeochem. Cy. 18:GB4004, doi:10.1029/2004GB002223.

Mikaloff Fletcher, S. E., Tans, P. P., Bruhwiler, L. M., Miller, J. B., and Heimann, M. (2004b). CH₄ sources estimated from atmospheric observations of CH₄ and its

13C/12C isotopic ratios: 2. Inverse modeling of CH₄ fluxes from geographical regions. Global Biogeochem. Cy. 18:GB4005, doi:10.1029/2004GB002224.

Monteil, G., Houweling, S., Dlugokenky, E. J., Maenhout, G., Vaughn, B. H., White, J. W. C., and Rockmann, T. (2011). Interpreting methane variations in the past two decades using measurements of CH₄ mixing ratio and isotopic composition, Atmos. Chem. Phys., 11, 9141–9153.