

## ***Interactive comment on “Assessment of the theoretical limit in instrumental detectability of Arctic methane sources using $^{13}\text{C}$ atmospheric signal” by Thibaud Thonat et al.***

### **Anonymous Referee #2**

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GENERAL COMMENT Discriminating between methane sources is critical to determining regional and global emissions budgets and verifying national inventories. Mole fraction information is not enough – to determine sources, isotopic data are needed also. But isotopic measurement is difficult. It is analytically tough to attain both high precision and high sampling rate. Thonat et al. address this problem directly, by using modelling to ask how accurate the measurements need to be. The focus of the paper is the Arctic, but the same type of logic applies to all regions and to global measurement/modelling.

Thus the subject of the paper is important. The analysis that is presented makes a

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valuable contribution towards design of a future measurement network. In detail, the paper is intelligently crafted and well presented. It is clearly laid out and the writing is straightforward and understandable. I have many comments on detail, but overall, the paper makes a valuable and worthwhile contribution to our knowledge and will be influential in planning future measurement systems.

To conclude, I recommend that the paper should be published, after some modifications.

SPECIFIC COMMENTS Title – missing ‘the’ before  $^{13}\text{C}$ . Might be better actually to say ‘the  $\delta^{13}\text{CCH}_4$  atmospheric signal’?

Line 13 First sentence of abstract is waffle. Delete. L 21 Specify that the study is about Carbon isotopes – D/H isn’t mentioned. L 33 20% - could mention the more recent Etminan et al study that implies a larger number. Etminan, M., et al. (2016) Radiative forcing of carbon dioxide, methane and nitrous oxide: a significant revision of the methane radiative forcing. *Geophys. Res. Lett.* 43, 12,614–12,623, L41 Maybe mention Naus et al? Naus, Stijn, et al. (2019) Constraints and biases in a tropospheric two-box model of OH. *Atmospheric Chemistry and Physics* 19, 407-424. L 45 Nisbet et al. 2016 ?wrong year? L 46 and climate risk. L 50 – land thermokarst also? – e.g Yamal blowouts. There is also the wider problem of what is a natural wetland and what is a freshwater system. If the difference is in area of exposed water surface, then it’s a bit like trying to determine who is the world’s smallest giant. L 64 “compared to carbon dioxide’s” – reads more easily if you delete the ‘s. Also maybe cite Kirschke et al here – I know it’s mentioned later and you also cite Saunio, but seems appropriate here? L 81 – This is important – only  $^{13}\text{C}$  is considered. But either here or in the conclusion there should be a discussion of the potential value of restoring D/H measurement, and perhaps also a brief mention of clumped isotopes. L 85 notation - not possible to show in the constraints of acp online but a better notation might be  $\text{d}^{13}\text{C}_{\text{CH}_4}$  L 107 – mention scarcity of D/H measurement. L113 – maybe cite Zazzeri et al here? The coal number is a real problem as Zazzeri found – increasingly open cast mining seems

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to be emitting recently made biological methane coming from present day microbial activity on mine benches and this methane can be very light in C isotopes. L136 – ‘permanently’ increasing??? I used to think this 10 years ago, that optical instruments would soon catch up with mass spectrometry. But not so – if you want high precision (0.05‰ the optical methods need so much sample that the wind has changed by the time you complete the measurement on line, so you have to take grab samples, and then basically the cost and effort is comparable to mass specs. L150 paragraph – good plan! L160-170 Note that methane d13C is also measured in very long time series by NIWA-New Zealand, by the Japanese (e.g. Ny Alesund), and in Europe by RHUL, MPI and Utrecht. From memory, most labs have precision is rather better than 0.1 See Umezawa, T. et al. (2018) Intercomparisons of  $\delta^{13}\text{C}$  and  $\delta\text{D}$  measurements of atmospheric CH<sub>4</sub> for combined use of datasets from different laboratories. *Atmos. Meas. Tech.*, <https://doi.org/10.5194/amt-2017-281> L186 – maybe say a little more about initial conditions? – Important. L197 – wetland/freshwater difference and soil negative source, etc etc. Needs a bit more detail. Maybe also mention Fisher et al (2017) L205 – CH<sub>4</sub> emissions are limited in winter in the Arctic ???????. . .do you just mean wetland emissions? The way this is written implies that Russian gasfield emissions are trivial and can be written off as not important even before you do the study. Yet in the next paragraph you say anthropogenic emissions are >20Tg/yr, and we know much of the gasfield emission is in winter when the gas is being pumped most. L213 – EDGAR – here comes the top-down vs bottom-up problem. Needs to be discussed – you need to justify what EDGAR is the least-worst option. L225 – note Petrenko et al, which strongly challenges the Etiope et al estimates. Petrenko, V.V. et al. (2017) Minimal geological methane emissions during the Younger Dryas–Preboreal abrupt warming event. *Nature* doi:10.1038/nature23316 L231 – ‘prescribed’ – this needs to be justified. Seems rather large. Again, what is a lake? What’s the smallest giant? Why isn’t a 1m<sup>2</sup> puddle a lake? L250 Levin et al – -50 ‰ Russian gas. Note also Meth-MonitEU report in which the St Petersburg team actually measured from a tower in a gasfield. EU Meth-MonitEU Report Section 6 is online. -46‰ seems a bit heavy for Russia as I

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have the sense that the production gas is isotopically lighter in the north. L276 Cattle – depends a lot on C<sub>4</sub> (Maize, Sugar cane tops) or C<sub>3</sub> (temperate hay, other feeds) diet. In the north, the likelihood is that much of the diet is C<sub>3</sub> – the C<sub>4</sub> grasses are mostly tropical or subtropical. C<sub>3</sub> fed ruminants are probably more –ve in CH<sub>4</sub>. L285 -49‰ for geological – I’d query that. Most Arctic geological emission is hydrate and that is simply a storage vehicle for whatever rises into it. More like -50 to 55 per mil. But widely variable. Also see Petrenko et al cited above. L290 – -24 might be too heavy. Biomass burning in the boreal realm is entirely C<sub>3</sub> plants and thus much lighter than tropical C<sub>4</sub> grass fires. I’d take Chanton’s values for northern US. L295 – wetlands – Arctic wetland methane source is entirely C<sub>3</sub> and thus lighter than tropical C<sub>4</sub> swamps – also methanotrophy. Agree with choice of Fisher and France et al values because aircraft sample an integrated signal over a wide area. But they did see a range of values. L322 – freshwater ambiguity again. L342 soil uptake ‘equal to biomass burning’ – no justification given. Can this be discussed? And bulk mass equality doesn’t equal isotopic mass equality. L354 – no mention of the Cl sink. – Use Hossaini numbers? Hossaini, R., et al. (2016) A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation. *Journal of Geophysical Research: Atmospheres* 121.23 (2016). L360 Table 2 and L376 – note that Cold Bay is not Arctic. Average January Max T is near 1 degree C – above freezing. It’s in the warm currents of the N Pacific. 55N – about the same as the chilly icebergs of the island of Sylt, Germany where folk paddle in swimsuits, and south of the deep frozen wastelands of Copenhagen and southernmost Sweden. L374 – the crosses for the data points. The use of crosses implies errors – but these don’t look like the errors. The Time error is essentially zero. The measurement error is perhaps 0.06 per mil plus/minus. The data should be shown as vertical lines plus minus from the dot. L381. Boundary input – for Barrow I suspect the 2007 swing was from air that blew up from the boreal wetlands in mid-summer. L387 a ‘depleted peak’ is an oxymoron. Sounds like someone took a shovel to the top of Mt Everest and scooped off a few hundred metres. Better say ‘spikes’ throughout. Are the peaks ‘observed’ – i.e. real measurements? which data

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show that: what are you classifying as a peak? Am I correct that you are saying that the various drops in the Barrow and Alert records are clearly caused by ESAS? Are you sure they are not just blips in a statistically thin data set? L390 – seasonality capture. Interesting, as Warwick had similar problems with capturing seasonality in her modelling. L400 – maybe a comment on the potential value of D/H also? L433 - -46‰ assumption – is that valid for the Arctic gasfields? What happens if you take a -50 per mil number as supported by Levin et al? The Korotchaev tower measurements (increment  $\sim 100$  ppb) gave around -50 per mil during Sept. 2004 (Meth-MonitEU report Section 6 – Reshetnikov team's results from a gasfield/wetland mix are -49.84 -52.43 -67.16 -65.14 -67.13 -53.49 -55.77 -49.30 depending on proportions of gas and wetland source. Accessible on web). L448 – maybe say 'more negative than' rather than 'less than' L462 – Zeppelin. Is this correct? – See France et al and Fisher et al. Note also that Zeppelin now has 5 samples a week analysed for  $\delta^{13}C$  (MOCA project\_NILU) L469 – varying the isotopic signatures. . . L486 – CL sink is small but has a large isotopic leverage – is this statement valid? Maybe cite Hossaini et al paper (see above). L493 – maybe cite Fisher et al 2006 – 0.05 per mil. Fisher, R., et al. (2006) High precision, automated stable isotopic analysis of atmospheric methane and carbon dioxide using continuous-flow isotope ratio mass spectrometry. *Rapid communications in Mass Spectrometry*, 20, 200-208. Note that the NIWA lines attain 0.03 per mil but with bigger samples. L499 – I'm rather sceptical of optical claims for 0.1 per mil precision in routine operation in remote settings. The cal gas demands would be extreme as the drift is hard to contain. 'Measurements are independent over the day' – but that means you integrate out your signal! Yes, if we mix all the paint in the world in one bucket we will get a very steady high-precision grey, but I rather like looking at colours in paintings. L517 – at ZEP the daily flask measurements are currently to 0.05 per mil. But there have been some contamination problems. L555 – spelling. Schaefer. L569 – basically this is saying that at the moment the high precision of mass spectrometry is needed to get a decent signal? L576-580 - Any thoughts on the usefulness of D/H?

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Table 1- Cold Bay and Churchill are not Arctic, though I accept Churchill is pretty cool in winter. Cold Bay is maritime. Table 2 should give sources perhaps as a ref to Thonat 2017? Table 3 – note Fisher et al have Canadian results ( $-67 \pm 1$  per mil) They have  $-66.8 \pm 1.6\%$  at East Trout Lake in Saskatchewan (Figure S4) and  $-67.2 \pm 1.1$  at Fraserdale, and Kuhlmann et al. 1998 had similar findings in Canada. Kuhlmann, A. J., Worthy, D. E. J., Trivett, N. B. A., & Levin, I. (1998). Methane emissions from a wetland region within the Hudson Bay Lowland: An atmospheric approach. *Journal of Geophysical Research: Atmospheres*, 103(D13), 16009-16016. Table 4 – is this the lowest detectability threshold? Or the highest? – i.e. the system has to be below this to spot the signal? 0.01 per mil for Teriberka ? I'm surprised – intuitively seems rather low? Fig 2 + for observations implies error bars – should be replaced by dots with error lines up and down. . . Time error is minimal. Fig 3 – a bit hard to see colours. Make sure the publication is large for this figure.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1217>, 2018.

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