

Interactive comment on “Strong Sensitivity of the Isotopic Composition of Methane to the Plausible Range of Tropospheric Chlorine” by Sarah A. Strode et al.

Tonatiuh Guillermo Nuñez Ramirez

tnunez@bgc-jena.mpg.de

Received and published: 19 December 2019

In the study, OH concentrations were reduced proportionally to the proportion of the sink that the tropospheric Cl represented. However, in reality the relationship between OH and Cl concentrations and the lifetime and thus the CH₄ mole fraction is much more complex and non-linear, and depends also on the geographic and seasonal distribution of the OH, Cl and CH₄ fields. I believe the fact that the SimStd and SimGC simulations underestimate and overestimate, respectively, the observed $\delta^{13}\text{CH}_4$ in 2004, despite the fact that both include only a relatively small CH₄ sink from Cl arise from this issue. This makes the scenarios less comparable. This is a forward simulation and as stated

Printer-friendly version

Discussion paper



by the authors, the isotopic composition is not in steady state, then why should the CH_4 be in steady state? I fear reducing OH may mask some of the impact of Cl on the CH_4 mole fraction. The fact that neither the CH_4 mole fraction nor the $\delta^{13}\text{CH}_4$ are in steady state could be dealt with by subtracting the measured value at SPO.

Furthermore, if one of the objectives of this study was to compare the modeled gradient with observations, why were the OH fields scaled to be higher in the Northern Hemisphere when observational evidence points towards a NH/SH ratio of 0.97 ± 0.12 (Patra et al., 2015)? In the same spirit, if the spatial variations of the $\delta^{13}\text{CH}_4$ signal of emissions has been proven to be important to reproduced the observed signals in the atmosphere (e.g. Schwietzke et al., 2016, Ganesan et al., 2018) why is the SimWet only a sensitivity case and not the standard?

I would like to make you aware of a possible conceptual error. Your VPDB value (0.0112372) is the old Craig (1957) value. This reference material has long been depleted. The actually valid number is 0.0111802 (recognized by IUPAC) from Zhang (1990). Please note that the measured reference in the Zhang (1990) paper was NBS 19, which defines the VPDB scale with $\delta^{13} = +1.95$ per mill (Berglund and Wieser, 2011). Also, you may be treating the CH_4 mole fraction as $^{12}\text{CH}_4$. However, for the CH_4 mixing ratio the mass range covers all masses from 16 ($^{12}\text{CH}_4$) to 21 ($=^{13}\text{CD}_4$). Gas chromatography does not discriminate against higher isotopologues. Laser-based instruments, in contrast, do actually measure $^{12}\text{CH}_4$, but they are calibrated with gases whose composition was determined by gas chromatography. Thus the calibration gases must have a realistic isotopic composition to correct for this issue. To obtain, $^{12}\text{CH}_4$ you have to subtract the contribution of all other isotopologues from the mixing ratio.

I would like to point out some potential improvement for the transmission of information. I would find an analog to figure 5(c and d) for $\delta^{13}\text{CH}_4$ more useful than the maps. I would also recommend to use sine latitude in all the latitudinal profile plots to retain the proportion with respect to the Earth surface. The correlation coefficients of latitudinal

[Printer-friendly version](#)[Discussion paper](#)

gradients of the different scenarios in figure 7 as well a comparison with their latitudinal derivative might also provide additional information. With this respect I believe figures figure S2 and S3 should be in the main text. Finally, a good validation for the different scenarios would be the reproduction of phase ellipses from Allan et al. (2001).

Finally some details in the text:

- In the methods section you describe simStd as
- No description of simWet in methods
- In the description of SimTom "very short lived substances" is repeated twice in the sentence

References

Allan, W., Manning, M. R., Lassey, K. R., Lowe, D. C., Gomez, A. J. (2001). Modeling the variation of $\delta^{13}\text{C}$ in atmospheric methane: Phase ellipses and the kinetic isotope effect. *Global Biogeochemical Cycles*, 15(2), 467. <http://doi.org/10.1029/2000GB001282>

Berglund, M., M. E. Wieser. Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure and Applied Chemistry* 2011, 83, 397.

Craig, H., Isotopic Standards for Carbon and Oxygen and Correction Factors for Mass-Spectrometric Analysis of Carbon Dioxide. *Geochimica Et Cosmochimica Acta* 1957, 12, 133.

Ganesan, A. L., Stell, A. C., Gedney, N., Comyn-Platt, E., Hayman, G., Rigby, M., et al. (2018). Spatially Resolved Isotopic Source Signatures of Wetland Methane Emissions. *Geophysical Research Letters*, 45(8), 3737–3745. <http://doi.org/10.1029/2008GB003299>

[Printer-friendly version](#)[Discussion paper](#)

Patra, P. K., Krol, M. C., Montzka, S. A., Arnold, T., Atlas, E. L., Lintner, B. R., et al. (2015). Observational evidence for interhemispheric hydroxyl-radical parity. *Nature*, 513(7517), 219–223. <http://doi.org/10.1038/nature13721>

Schwietzke, S., Sherwood, O. A., Bruhwiler, L. M. P., Miller, J. B., Etiope, G., Dlugokencky, E. J., et al. (2016). Upward revision of global fossil fuel methane emissions based on isotope database. *Nature*, 538(7623), 88–91. <http://doi.org/10.1038/nature19797>

Q. L. Zhang, T. L. Chang, W. J. Li. A Calibrated Measurement of the Atomic-Weight of Carbon. *Chinese Science Bulletin* 1990, 35, 290.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2019-1047>, 2019.

Printer-friendly version

Discussion paper

