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Tropospheric CH_4 sink via atomic Cl constrained by observations of carbon monoxide $^{13}C/^{12}C$ isotope ratios

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Next to the hydroxyl radical (OH), atomic chlorine (Cl) is often regarded as a potentially significant sink partner for methane (CH_4) in the troposphere (see, $e.g.$, [1] and refs. therein), as suggested by the analysis [2] of $^{13}C(CH_4)$ isotope observations in the remote marine boundary layer (MBL) in the extra-tropical Southern Hemisphere (ETSH) in 1994-2000. Subsequent theoretical work [3] indicates that methods of [2] are problematic and may yield spuriously large estimates of the $^{13}C(CH_4)$ sink effective fractionation (ε_{CH4}). The latter, inferred to be (7-15)‰, was attributed to a (2-4)% loss of CH_4 via Cl. Nonetheless, neither do [2] and [3] provide means of unambiguously rejecting the MBL CH_4+Cl sink hypothesis, nor do they account for variable and dissimilar (global) trends in CH_4 mixing ratio and $\delta^{13}C$ in the 1990s. On the other hand, a recent detailed study [4] suggest that up to 2.5% of the tropospheric CH_4 sink should occur via Cl, a figure surprisingly close to that of [2]. Therefore is the question: Can we constrain the tropospheric CH_4 Cl sink?

In an alternative approach we analyse the observations of carbon monoxide (CO) isotope ratios, which were performed in the ETSH MBL concomitantly. Produced in the CH_4oxidation cycle, CO allows an independent estimate of the changes to the $^{13}C(CH_4)$ sink effective fractionation, $i.e.$ by looking at the main reaction product (as opposed to residual) of atmospheric CH_4. Using the results of the comprehensive AC-GCM EMAC model [5], we quantify the CH_4-derived fraction of CO in the ETSH and estimate the upper limit of the CH_4+Cl sink variations. These are very unlikely to have caused ε_{CH4} changes larger than ± 2‰ in 1994-2000, even if the tropospheric yield of CO from CH_4 (the largest uncertainty factor of the CO tropospheric budget to date) were as low as 0.7. Furthermore, closing the ETSH and global $^{13}C(CO)$ budgets suggests that the Cl sink plays a very small role in the removal of CH_4 from the troposphere.

References

1. Houweling, S.*, et al.*: Global inverse modeling of CH_4 sources and sinks: an overview of methods, *Atmos. Chem. Phys.*, **17**, 235-256, doi: 10.5194/172352017, 2017.

2. Allan, W., Struthers, H., and Lowe, D. C.: Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: Global model results compared with Southern Hemisphere measurements, *J. Geophys. Res. Atm.*, **112**, D04306, doi: 10.1029/06jd007369, 2007.

3. Lassey, K. R., Allan, W., and Fletcher, S. E. M.: Seasonal interrelationships in atmospheric methane and companion $\delta^{13}C$ values: effects of sinks and sources, *Tellus B*, **63**, 287-301, doi: 10.1111/.16000889.2011.00535.x, 2011.

4. Hossaini, R.*, et al.*: A global model of tropospheric chlorine chemistry: Organic versus inorganic sources and impact on methane oxidation, *J. Geophys. Res. Atm.*, **121**, 14,271-214,297, doi: 10.1002/JD025756, 2016.

5. Jöckel, P.*, et al.*: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geosci. Model Dev.*, **3**, 717-752, doi: 10.5194/37172010, 2010.