A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane

Sergey Gromov[1,*], Carl A. M. Brenninkmeijer[1] and Patrick Jöckel[2]

[1] Max Planck Institute for Chemistry, Atmospheric Chemistry Department, Mainz, Germany
[2] Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Physik der Atmosphäre, Oberpfaffenhofen, Weßling, Germany
[*] Also at Institute of Global Climate and Ecology Roshydromet & RAS (IGCE), Moscow, Russia

Correspondence to: Sergey Gromov (sergey.gromov@mpic.de)

Abstract

Unexpectedly large seasonal phase differences between CH_4 concentration and its $^{13}C/^{12}C$ isotopic ratio and their inter-annual variations observed in southern hemispheric time series have been attributed to the $Cl+CH_4$ reaction, in which $^{13}CH_4$ is discriminated strongly compared to $OH+CH_4$, and have provided the only and indirect evidence of a hemispheric-scale presence of oxidative cycle-relevant quantities of tropospheric atomic Cl. Our analysis of concurrent New Zealand and Antarctic time series of CH_4 and CO mixing and isotope ratios shows that a corresponding $^{13}C/^{12}C$ variability is absent in CO. Using the AC-GCM EMAC model and isotopic mass balancing for comparing the periods of presumably high and low Cl, it is shown that variations in extra-tropical Southern Hemisphere Cl can not have exceeded 0.9×10^3 atoms cm^{-3}. It is demonstrated that the $^{13}C/^{12}C$ ratio of CO is a sensitive indicator for the isotopic composition of reacted CH_4 and therefore for its sources. Despite ambiguities about the yield of CO from CH_4 oxidation, with this yield being an important factor in the budget of CO, and uncertainties about the isotopic composition of sources of CO, in particular biomass burning, the contribution of Cl to the removal of CH_4 in the troposphere is probably much lower than currently assumed.

1 Introduction

[1] Compared to the troposphere's main oxidant OH (hydroxyl radical), the role of Cl (atomic chlorine) for CH_4 is small. A recently published detailed model-based estimate attributes ~2.6% of methane's photochemical tropospheric loss to Cl (Hossaini *et al.*, 2016). Because this loss constitutes only a small term in the methane budget, it might be deemed not relevant. However, considering that the photochemical sink is the dominant and best-known term in the global methane budget, it makes sense to improve our calculations. The grateful aspect of this endeavour clearly is that one does not need an accurate estimate of Cl as a global tropospheric sink of CH_4 as such. It would already be helpful to have independent estimates of the upper limit for this interesting sink of CH_4, whose rise in the Anthropocene thus far has contributed $^1/_5$ to global warming.

[2] Irrespective of the implications for the CH_4 budget, it stands to reason to fully understand tropospheric Cl and its chemistry in different air masses, from marine boundary layer air to strongly polluted air masses and several studies address these complex processes. It is also clear, that the budget of a species as fickle as atomic chlorine is hard to determine in general terms (which forms a less grateful aspect of "assessing chlorine"). Nevertheless, a new effort – in assessing chlorine's role on a larger than regional scale, on the basis of trace gas measurements, may be useful.

[3] Even more so than for OH, estimates of the abundance of Cl atoms are chiefly based on indirect evidence. Direct measurements of OH concentrations ([OH]) being difficult and rare, for [Cl] this is even much more so. Therefore the method (by

Atmospheric
Chemistry
and Physics
Discussions

choice or opportunity) is indirect. It is easier and gives time and space averaged estimates for the abundance of these radicals to use measurements of trace gases that react with OH and Cl. In this case, one can select for instance 2 hydrocarbons one of which has a comparatively high reactivity to Cl. The change in ratio between the two hydrocarbon concentrations gives information on [Cl] relative to [OH].

30 [4] Using stable isotope ratio information offers another such indirect method. The intrinsic advantage here is that one can use a single trace gas, a single hydrocarbon, or even the much studied greenhouse gas CH_4 itself. Although the rate coefficient for the reaction of OH with $^{12}CH_4$ is only ~4‰ faster than that with $^{13}CH_4$ (Saueressig *et al.*, 2001), for $Cl+CH_4$ the difference is much larger (Saueressig *et al.*, 1995; Crowley *et al.*, 1999), *viz.* (63–75)‰ (at the range of tropospheric temperatures). Broadly speaking, the presence of ^{13}C enriched CH_4 points to reaction with Cl. If this were not enough, one could measure the D/H

35 ratio of CH_4 and obtain additional valuable information because of the large isotope fractionation (KIE, Kinetic Isotope Effect, formerly and still expressed using the kinetic fractionation constant $\varepsilon = \alpha - 1$) and the differences between the KIEs for ^{13}C and D. A recent paper (Whitehill *et al.*, 2017) reports changes in the clumped isotopic composition of CH_4 in reaction with Cl based on laboratory experiments, raising hope that clumped isotope measurements (which are very difficult) may in an additional way assist to further assess the role of Cl in the oxidation of CH_4 in the atmosphere.

40 [5] An advantage is that the "stable isotope method" in principle removes the uncertainty about variability induced by having to use two different trace gas species, each of which may have an independent, variable source. Routinely overlooked is another (principle) advantage of stable isotope analysis offered in the case of atmospheric $CH_4 \rightarrow CO$ conversion, namely measurement of the isotopic composition of the reaction product CO. Even though variations in [CO] may not be resolvable due to the large spatio-temporal variability of its sources and sink, its $^{13}C/^{12}C$ ratio may well tell a clearer story. This is the added ad-

45 vantage of the stable isotope method (we note that the lifetime of ^{14}C is sufficiently long to render much of what is stated to also apply to this well-known radioisotope, but there are complications on which we cannot dwell here).

[6] In this way the presence of Cl during Antarctic ozone hole conditions could be inferred in an independent fashion (Brenninkmeijer *et al.*, 1996). Not only became the CH_4 inventory slightly enriched in ^{13}C due to the large KIE in $Cl+CH_4$, the CO ensuing from CH_4 resulted in strong depletions in ^{13}C of background CO. There are at least three reasons for the strong isotope

50 depletion. Firstly, CO concentrations are low in the stratosphere and the in situ produced CO had a large impact. Secondly, the ^{13}C content of CH_4 is characteristically low due to its chiefly bacterial origin. Thirdly, and this is an important point mentioned above, the ^{13}C KIE for $Cl+CH_4$ happens to be very large. The combination of these effects renders the stable isotope analysis of CO a sensitive indicator. Dealing with tropospheric Cl, the same principle has been applied during springtime tropospheric ozone depletion events in the Arctic. Short-term bursts of free Cl could be inferred from concomitant decreases in $\delta^{13}C(CO)$

55 within a per mil[1] range (Röckmann *et al.*, 1999).

[7] In this brief account we cannot do justice to all tropospheric Cl related papers in the literature and we refer to the recent model based paper by Hossaini *et al.* (2016) and references therein. In comparison with OH, which is recycled in about two of three reactions in the troposphere (Lelieveld *et al.*, 2016), the role of recycling of Cl is lower and not known well. The presence of Cl in the marine boundary layer has been inferred using hydrocarbon measurements (early reference Parrish *et al.*, 1993)

---

[1] Hereinafter we report the $^{13}C/^{12}C$ ratio as per mil delta values. The $\delta^{13}C$ is defined as $\delta^{13}C = (R/R_{st} - 1)$, where R and R_{st} denote the sample and standard $^{13}C/^{12}C$ ratios. We use the V-PDB scale with $R_{st} = 11237.2\times10^{-6}$ (Craig, 1957) throughout this paper (for details on choosing this value see Gromov *et al.*, 2017, Appendix A).

60 and likewise during polar sunrise (Jobson *et al.*, 1994), Cl_2 has been measured in situ in coastal air (Spicer *et al.*, 1998) and in the Arctic (Liao *et al.*, 2014). $ClNO_2$, which is an important precursor, has been measured (Osthoff *et al.*, 2008 and Thornton *et al.*, 2010), also by Young *et al.* (2012), who however found no Cl fingerprint in hydrocarbon ratios.

[8] Recently, Baker *et al.* (2016) inferred the presence of Cl in pollution outflow from continental Asia using hydrocarbon measurements on air samples collected at cruise altitude by the CARIBIC Lufthansa Airbus aircraft observatory. Before that,
65 Baker *et al.* (2011) had likewise inferred Cl being formed in an emission plume of the Eyjafjallajökull volcano probed by the same CARIBIC A340 aircraft. All these and other publications discuss the presence of Cl in a variety of tropospheric environments wrestling with the complexity of its chemistry and paucity of experimental data.

[9] Additional importance of revisiting the role of Cl radicals in the present atmosphere actually surfaces in the reconstruction and understanding of the budget of CH_4 in the past. Changes in the tropospheric burden of CH_4 that occurred in the past (last
70 glacial maximum – present) are due to changes in CH_4 sources and to a minor degree to changes in OH chemistry (Levine *et al.*, 2011b). One would *a priori* expect $\delta^{13}C(CH_4)$ to provide additional information on source changes, as it did for immediate past changes (Schaefer *et al.*, 2016), were it not that large changes in Cl abundance may well have affected the $\delta^{13}C(CH_4)$ record (Levine *et al.*, 2011a). If this is the case indeed, changes in Cl abundance in the past may have not affected the CH_4 budget itself significantly, but may have invalidated to a certain degree the $\delta^{13}C(CH_4)$ isotope method for determining changes
75 in sources (biogenic *vs.* biomass burning).

[10] We turn our attention to a paradox concerning today's tropospheric Cl, namely: If the presence of tropospheric Cl has been inferred from ^{13}C isotope enrichment in CH_4, why is this effect not visible as concurrent isotope depletion in CO? Or, more explicitly stated, if the $\delta^{13}C(CO)$ isotope method for Cl detection works well for the austral polar stratosphere in spring (Brenninkmeijer *et al.*, 1996) and for the polar sunrise in the Arctic (Röckmann *et al.*, 1999), why not so for the troposphere, or does
80 it? Is a clear negative signal in $\delta^{13}C(CO)$ absent indeed, and if so, does this absence allow us to cap estimates of tropospheric Cl levels?

2 Data analysis

2.1 Chlorine in the Southern Hemisphere

[11] Because the budgets of CH_4 and CO in the Southern Hemisphere (SH) are less complicated as is witnessed by their compact regular seasonal cycles at remote observatories[2], and because long records of CO and CH_4 including isotopic data are available, we focus on the Southern Hemisphere. In the SH evidently the emphasis is on Cl generated in the marine boundary layer
85 (MBL).

[12] We first revisit the information on Cl based on $\delta^{13}C$ measurements of CH_4. Initially, mixing ratio and $\delta^{13}C(CH_4)$ values for shipboard collected air samples in the Pacific pointed to a large apparent sink isotope fractionation ("apparent" KIE) of $(12-15)‰$ – well in excess of the aforementioned 4‰ from $OH+CH_4$ – which led to the conjecture that a fraction of CH_4 is removed in the MBL by Cl atoms which discriminate strongly against $^{13}CH_4$ (Lowe *et al.*, 1999). Following several publica-
90 tions exploring this effect, Allan *et al.* (2007) (hereinafter referred to as A07) using global modelling and observational data

---

2   See, *e.g.*, the synthesis of the CO and CH_4 observational data at https://www.esrl.noaa.gov/gmd/ccgg/gallery/figures/ and refs. provided therein (last access: December 2017).

Atmospheric
Chemistry
and Physics
Discussions

from the extratropical Southern Hemisphere (ETSH), confirmed a large apparent KIE and could estimate a global marine boundary layer based Cl sink for CH_4 averaging at 25 Tg(CH_4) yr^{-1}.

[13] Given this number, a first order estimate of the accompanying response of $\delta^{13}C$ of CO to the production of CO from Cl+CH_4 can be made. Assuming a 100% yield of CO from OH+CH_4 (and likewise Cl+CH_4), the 25 Tg yr^{-1} CH_4 sink corresponds to a Cl based annual CO production of 44 Tg yr^{-1}, which is ~1.8% of the total CO budget. By using a $\delta^{13}C$ value of CO of −28‰ (annual tropospheric average), that of CH_4 of −48‰ and a KIE of 70‰, (Cl+CH_4) causes a shift in $\delta^{13}C(CO)$ of about −1.6‰. Considering that the lifetime of CO is much shorter than that of CH_4 and that Cl is concentrated in the MBL, the local/seasonal effect on $\delta^{13}C(CO)$ would be even larger.

[14] Unfortunately, a negative shift in $\delta^{13}C(CO)$ is upfront unwelcome in attempts to close the SH CO budget using $\delta^{13}C$. The latter, as Manning *et al.* (1997) showed, is only possible when the yield of CO from CH_4+OH (denoted hereinafter λ) is assumed to be merely about 0.7. In other words, even without incorporating the formation of CO from Cl+CH_4, the CH_4-derived ^{13}C-depleted fraction of CO (which is high in the ETSH at above 40%) seems to be too dominant and had to be reduced by assuming lower yields of CO from CH_4. Soon thereafter also Bergamaschi *et al.* (2000) encountered this problem in a 3D inverse modelling study using the isotopic composition of CO and could best reconcile data and model by reducing λ to about 0.86. They do mention that incorporating CO from Cl+CH_4 would require λ values as low as 0.71. Also Platt *et al.* (2004) who discuss mechanisms for the production of Cl in the marine boundary layer allude to the necessity to have to reduce the assumed CO yield of OH+CH_4.

[15] One difficult feature of the $\delta^{13}C(CH_4)$-based Cl estimate was a large inter-annual variability that could not be explained. A07 identified two periods of different Cl abundance in the ETSH, namely 1994–1996 with MBL values of 28×10^3 atoms cm^{-3} (high-Cl period, "HC") and 1998–2000 with much lower values, *viz.* 9×10^3 atoms cm^{-3} (low-Cl period, "LC"). The nearly threefold drop in the resulting Cl+CH_4 sink rate (37 to 13 Tg(CH_4) yr^{-1}, or 6.4% to 2.2% of the total, respectively) inferred from $\delta^{13}C(CH_4)$ for the two periods is not discernible in the simultaneous $\delta^{13}C(CO)$ record (see Sect.2.2).

[16] Later, Lassey *et al.* (2011) investigated the apparent KIE in detail and found that it can differ markedly from both the seasonal and mass-balanced KIEs. In other words, the apparent KIE derived from the seasonal changes in [CH_4] and $\delta^{13}C(CH_4)$ value appeared not to properly represent the respective effects of the two KIEs. The implication is that the inferred very large range of [Cl] may be in error, and absence of a corresponding signal in $\delta^{13}C(CO)$ is in that respect an experimental confirmation. Below we will go into detail.

2.2 Observations in the ETSH

[17] We scrutinise the mixing and $^{13}C/^{12}C$ ratios of CH_4 and CO in the MBL air at Baring Head, New Zealand (41.41°S, 174.87°E, 85 m a.s.l., denoted hereinafter "BHD") and at Scott Base (Arrival Heights), Antarctica (77.80°S, 166.67°E, 184 m a.s.l., denoted "SCB") provided by the National Institute of Water and Atmospheric Research (NIWA, 2010). Examined in the A07 study on CH_4, these data are the result of laboratory analyses of large air samples collected on a monthly to weekly basis. The collection strategy (using wind direction, CO_2 mixing ratio temporal stability and back-trajectory analysis) allows selecting air masses that represent background ETSH air. Established over two decades, these time series confer the longest continuous records of $^{13}CH_4$ and ^{13}CO observations to date. The reported overall uncertainties of the CH_4 mixing ratio and $\delta^{13}C$ do not exceed ±0.3% (about ±5 nmol/mol) and ±0.05‰ (Lowe *et al.*, 1991). For CO, the respective uncertainties are

Atmospheric
Chemistry
and Physics
Discussions

±4‰/±0.2‰ (prior to 1994, Brenninkmeijer, 1993) and ±7‰/±0.8‰ (since 1994, NIWA, 2010). The CO records from BHD/SCB exhibit small variations in annual (minimum-to-maximum) span and no long-term trend in both mixing and isotope ratios throughout 1990−2005 (see Gromov, 2013, Sect. 4.4.1). In contrast to this, the concomitant [CH₄] values have increased on average by about 5% within the same period, which is consistent with other observational records (Lassey *et al.*, 2010). It

130 can be concluded, that such augmentation of atmospheric burden of the major (and largely depleted in ^{13}C) in-situ sources of CO remains statistically indiscernible in the ETSH δ^{13}C(CO) record, because of more perceptible variations caused by changes in sink and/or the other (foremost biomass burning) sources of CO.

[18] We subsequently regard the statistics of the two subsets of observational data falling into the HC and LC periods, as shown in Fig. 1. For testing the robustness of our comparison against the timing of the air sampling, we "bootstrap" the data by

135 selecting only the pairs of CH₄/CO samples collected within one-week windows (shown with solid boxes in Fig. 1). This operation has virtually no effect on CO distributions, as its statistic is smaller (total of 116 and 88 samples at BHD and SCB, respectively) and controls the sub-sampling of the datasets. For CH₄, also no effect is noted, with an exception of significant (*i.e.* exceeding measurement uncertainty) changes to the "bootstrapped" median CH₄ mixing ratio at BHD, which is some 6 nmol/mol lower during the HC. Such is an indication that the CO sampling times are likely more representative for back-

140 ground air. Overall, we conclude that the CH₄ and CO datasets reflect variations in the composition of the same background air. Contrary to CH₄, there is no perceptible reduction in seasonal variations of mixing and isotope ratios of CO at SCB throughout the HC period.

[19] To determine the significance of observed changes in CO using sufficient statistics, we derive quasi-annual averages (QAA) of CO mixing/isotope ratio averages representing the HC, LC and long-term periods (all data and from 1994 onwards). For the

145 correct temporal weighting of the samples, we first calculated quasi-monthly averages and their variances, which then equally contributed to the QAA. Table 1 lists the results along with the number of samples used in the calculation. Note that there are about twice as many outliers[3] in the entire BHD record (3.8%) compared to that for SCB (2.2%), which suggests that the estimated difference between the HC and LC averages (HC−LC, denoted Δ) is probably more influenced by regional sources at BHD. Except for δ^{13}C(CO) at SCB (with considerable significance of Δ being negative, *p*-value of 0.79), we conclude that

150 all CO QAAs emerge as statistically indistinguishable, also when compared to the long-term averages. For CO mixing ratios, the Cl-driven difference should amount to ~0.6 nmol/mol (using 24–25 nmol/mol derived from CH₄, see Sect. 2.3), which is times smaller than the errors in Δ. Significant or not, the Δ values indicate changes to the atmospheric reservoir involving ^{13}C-depleted CO, however in opposite directions (*i.e.* a removal at BHD – which contradicts A07 – and an addition at SCB). It is important to note that the CO+OH sink alters atmospheric CO in a similar fashion (*i.e.*, the remaining CO burden becomes

155 enriched in ^{13}C).

---

3 We follow the conventions from Natrella (2003) for identifying statistically significant outliers in the datasets. Samples with mixing ratios falling outside inner and outer statistical fences of ±1.5 and ±3 interquartile ranges (IQR) about the median are considered mild and extreme outliers, respectively.

Atmospheric
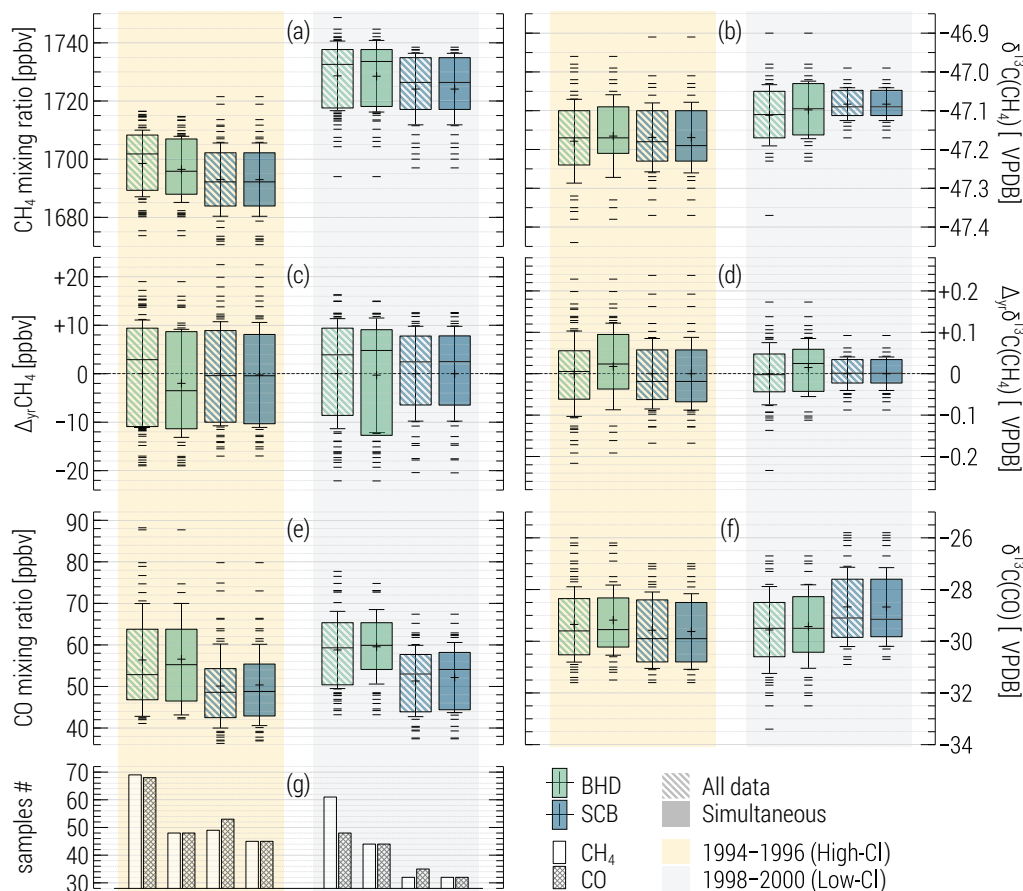Chemistry
and Physics
Discussions

Fig. 1 Statistics on the CH₄ and CO mixing and ¹³C/¹²C ratios observed at Baring Head (BHD) and Scott Base (SCB) throughout the high-Cl (HC, orange shaded) and low-Cl (LC, grey shaded) periods hypothesised by Allan *et al.* (2007) (see text for details). Panels (**c, d**) show statistics on the anomalies with respect to the annual averages (denoted with "Δ_{yr}"). Panel (**g**) displays the number of samples in each subset, respectively. The full time series of the data are shown in the Supplement (Fig. S2). Boxes and whiskers present the median/interquartile range and $\pm 1\sigma$ (of the population) of the data. Plus and minus symbols denote the averages and samples falling outside $\pm 1\sigma$. Solid boxes denote the subset of data when CH₄ and CO samples were taken simultaneously (up to 7 days apart); hatched boxes refer to all data.

Table 1   Statistics on quasi-annual average (QAA) mixing/isotope ratios of CO observed/simulated at BHD and SCB.

Data	Period	BHD			SCB		
		n	CO [nmol/mol]	$\delta^{13}C(CO)$ [‰]	n	CO [nmol/mol]	$\delta^{13}C(CO)$ [‰]
HC	1994–1996	65	56.1 ±2.0	−28.97 ±0.25	51	50.5 ±2.6	−29.31 ±0.64
LC[a]	1998–2000	48	58.4 ±2.1	−29.48 ±0.36	35	49.7 ±2.5	−28.57 ±0.64
Δ	HC−LC		−2.2 ±2.9	+0.51 ±0.43		+0.8 ±3.6	−0.74 ±0.90
	Significance (*p*-value)[b]			0.12 / 0.002			0.79 / 0.28
All data	1989–2005	379(15/4)	59.2 ±1.8	−29.52 ±0.29	227(5/0)	51.7 ±2.1	−29.21 ±0.50
	1994–2005	192(5/1)	57.8 ±2.1	−29.38 ±0.36	155(0/0)	50.8 ±2.3	−29.13 ±0.58
EMAC	1996–2005[c]		57.0 ±3.5			51.3 ±1.7	
	(incl. from CH₄ oxidation)		24.8 ±0.6			23.7 ±0.3	

Notes: Values in parentheses are the number of mild/extreme outliers (see the note[3]); the latter were excluded from the calculation of the long-term (up to 2005) averages. Quoted are standard errors of quasi-annual averages ($\pm 1\sigma$).
[a]   Time-interpolated value is used for February (no samples are available at SCB during the LC).
[b]   *p*-value is estimated for the null hypothesis that Δ of $\delta^{13}C(CO)$ QAA is below 0 / -2σ (left-tail test).
[c]   The aggregate of the emission inventories used in the simulation correspond closest to 2000 (see details in Gromov *et al.*, 2017).

2.3 EMAC model

[20] For extending the interpretation of observed ETSH CO, we resort to the results of simulations performed with the ECHAM5/MESSy Atmospheric Chemistry (EMAC) general circulation model (Jöckel *et al.*, 2010). EMAC includes all relevant processes (atmospheric transport, calculation of chemistry kinetics, photolysis rates, trace gas emissions, *etc.*) for simulating the current global atmospheric state. The setup we use resembles that of the EMAC evaluation study (MESSy Development Cycle 2, Jöckel *et al.*, 2010) and is augmented with kinetic tagging tools (Gromov *et al.*, 2010). These allow direct quantification of the CO component stemming from CH_4 oxidation (and as corollary provide λ) by following the carbon (C) exchanges through all intermediates (shown in Fig. S1) within a comprehensive chemistry mechanism simulated by the MECCA submodel (Module Efficiently Calculating the Chemistry of the Atmosphere, Sander *et al.*, 2011). The emission setup contains only the standard emissions/precursors of Cl (similar to, *e.g.*, the ORG2 setup used by Hossaini *et al.*, 2016) and yields average MBL Cl concentrations in the order of 10^1–10^2 atoms cm^{-3} (see the detailed simulated budgets in the Supplement, Table S1).

[21] The QAAs of [CO] simulated in EMAC for the period 1996–2005 in the gridboxes enclosing the locations of BHD and SCB are also given in Table 1. Despite the spatial and temporal averaging used (~2.8° horizontal gridcell size at the T42L31-ECMWF resolution, weekly averages), model QAAs match observations well and have similar uncertainties (resulting from monthly means variation; the observed/simulated seasonalities are shown in the Supplement, Fig. S3). More importantly, due to longer lifetimes of CO and CH_4 in the well-mixed ETSH, we expect much lower (factor $\sim 1/5$) variation in the CH_4-derived [CO] component. The average fraction of the latter (denoted γ, see Table 2) is proportional to the average tropospheric λ of 93% (diagnosed simulated value). Depending on the zonal domain, Cl atoms in EMAC initiate (0.15–0.25)% of CH_4 sink in the troposphere. The fraction of CH_4 removed in the ETSH (43 Tg(C) yr^{-1}) is minor compared to that in the tropics (271 Tg(C) yr^{-1}). About 13% of tropospheric sink occurs in the boundary layer.

[22] Additionally, we simulate the effective ^{13}C enrichment in CO (denoted η_c) resulting from the ^{12}C-preferential CO+OH sink and removal of the $CH_4 \rightarrow CO$ chain intermediates (dry/wet deposition, when $\gamma < 1$), convoluted with atmospheric mixing and transport (see details in Gromov (2013), Sects. 6.2.4–5). The corresponding η_c value equals the difference between the $\delta^{13}C$ of the airborne CO and that of the mix of its sources at a given point in space-time. Altogether, values of γ and η_c at the stations and domain-wise integrals of CH_4 sink (*S*) and λ (listed in Table 2) are used in the calculations that follow now.

2.4 Sensitivity of δ¹³C(CO) to the CH₄+Cl sink

[23] Using the observational and model data, we attempt to estimate the sensitivity of $\delta^{13}C(CO)$ at a given station to supposed inter-annual changes in the Cl-initiated CH_4 sink. The QAA of $\delta^{13}C(CO)$ (denoted δ_c) can be approximated as due to a two-component mixture of CH_4- and non-CH_4-derived CO sources augmented by the effective sink enrichment:

$$\delta_c \cong (1 - \gamma)\delta_n + \gamma(\delta_m - \varepsilon_m) + \eta_c . \tag{1}$$

We refer the reader to Table 2 for the explanation of the parameters and their values. In essence, we account for the fractionations induced in atmospheric sinks (η_c in CO and ε_m in CH_4) and mix the sources in the proportion defined by γ. Exemplifying the estimate from A07, SH Cl changes should cause ε_m to drop from 15‰ to 7‰ between the HC and LC, rendering $\delta^{13}C$ of the carbon from CH_4 arriving to CO of −62.2‰ and −54.2‰, respectively. By rearranging Eq. (1) we derive the non-CH_4 CO source $\delta^{13}C$ signature δ_n (see Table 2). Since there are virtually no surface sources of CO south of 40°S in the ETSH (see, *e.g.*,

Atmospheric
Chemistry
and Physics
Discussions

Gromov *et al.*, 2017, Sect. 3.4), the difference in δ_n at BHD and SCB could be driven only by poleward ^{13}C-enrichment of the

190 non-CH$_4$ in-situ sources (*e.g.* oxidation of higher hydrocarbons) and/or a stronger (than simulated in EMAC) zonal gradient in

η_c. Note that the station-wise δ_n discrepancy scales with the ε_m value, however not strongly: at ε_m of OH sink KIE (3.9‰) it

reduces from (2.2±2.1)‰ to (1.5±2.2)‰. In a statistical sense, the derived δ_n values reflect the same underlying source signa-

ture (*p*-value is 0.31).

Table 2 Parameters used in calculus

Species / Parameter [unit]			Value	
CO		Station:	BHD	SCB
$\gamma^{\dagger}$	CH$_4$-derived component [%]		43±3	46±2
$\eta_c{}^{\dagger}$	Eff. ^{13}C fractionation [‰]		+4.2±0.2	+4.6±0.1
$\delta_n{}^{*}$	δ^{13}C of non-CH$_4$ sources [‰]		−15.0±1.7	−12.8±1.3
δ_c	Observed δ^{13}C(CO) [‰]		−29.5±0.3	−29.2±0.5
CH$_4$		Domain:	SH	ETSH
$S^{\dagger,\S}$	Total sink [Tg(C) yr^{-1}]		187.8	52.5
δ_m	Observed δ^{13}C(CH$_4$) [‰]		−47.2	
$\lambda^{\dagger}$	Yield of CO from CH$_4$		93%	
		Period:	HC	LC
$\Delta S^{\ddagger}$	Changes to S due to Cl variations [Tg(C) yr^{-1}]		+18	0
$\varepsilon_m{}^{\ddagger}$	Total CH$_4$ sink KIE [‰]		15	7

Notes: Quoted QAAs and standard errors (±1σ); the latter are omitted for the components contributing to δ_c and δ_n errors insignificantly.
$^{\dagger/\ddagger}$An assumption or model estimate (from EMAC/A07).
$^{*)}$ Derived at ε_m = 11‰ (average of the LC and HC).
$^{\S)}$ Includes the LC Cl sink term from A07 (9.7 Tg(C) yr^{-1}). For the SH, the sum of the ETSH and halved intra-tropical integrals is taken.

[24] By subtracting Eq. (1) for the HC and LC periods, one obtains the sensitivity of δ_c to changes in the CH$_4$+Cl sink (ΔS) and

195 in the total sink KIE ($\Delta\varepsilon_m$):

$$\Delta\delta_c = (\lambda_a/\lambda)^{\mathrm{LC}}\gamma\left((\delta_m - {}^{\mathrm{HC}}\varepsilon_m - \delta_n)\mu - \Delta\varepsilon_m\right). \qquad (2)$$

Here superscripts indicate the period the values are taken for, Δ denotes the HC−LC difference (same as in Sect. 2.2 above)

and $\mu = \Delta S/^{\mathrm{LC}}S$. The total CH$_4$ sink S is chosen for the tropospheric column of a given domain, *i.e.* we assume that ΔS is

distributed homogeneously over the SH or ETSH. Formulated using γ, Eq. (2) allows projecting the results for the alternative

CO yield value λ_a (different from that obtained in EMAC), as our simulations confirm that λ directly proportionates γ and S in

200 the tropospheric column (but not in the MBL). Furthermore, $\Delta\delta_c$ is derived under the assumption of constancy of η_c and δ_n

values. Whilst for η_c such is likely the case (judging by the very similar observed CO mixing ratios, hence lifetimes, during

HC and LC), for the latter an upper limit of ±1‰ can be put from the typical variation in the δ^{13}C of the underlying sources

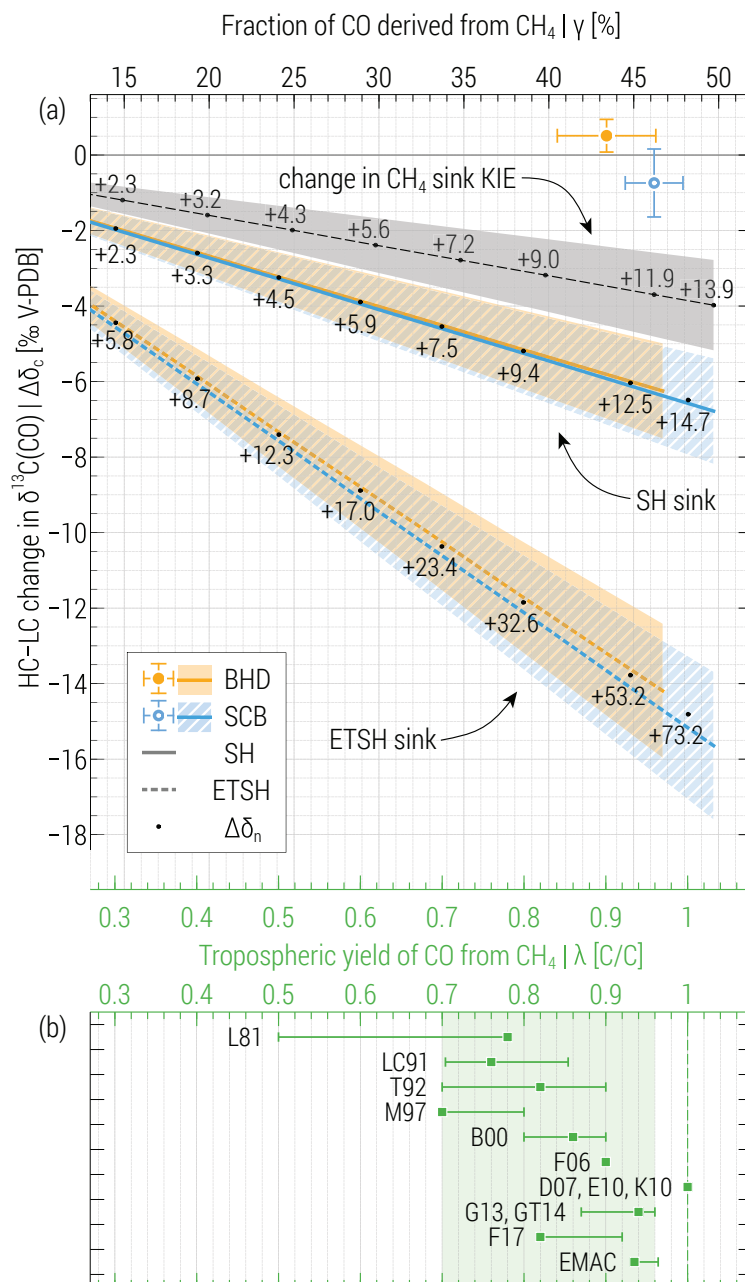(see Gromov *et al.*, 2017, Table 5). We discuss the implications of δ_n constancy below.

Atmospheric
Chemistry
and Physics
Discussions

Fig. 2 (**a**) Expected CH_4+Cl sink-driven changes to $\delta^{13}C(CO)$ between HC−LC at the ETSH stations ($\Delta\delta_c$) as a function of CH_4-derived CO fraction (γ, top axis) and yield (λ, bottom axis, approximate). Large symbols denote the observed (ordinate) and simulated (abscissa, EMAC) values. Thick lines present $\Delta\delta_c$ values calculated using Eq. (2) assuming that changes to CH_4+Cl sink occur within the SH (solid) and ETSH (dashed). Thin dashed line exemplifies the effect due to changes in CH_4 sink KIE ($\Delta\varepsilon_m$) only. Labels indicate the average augmentation to the non-CH_4 sources signature ($\Delta\delta_n$) required to compensate $\Delta\delta_c$ at the respective values/domains. Errors bars/shaded areas denote $\pm 1\sigma$ of the annual means/derived estimates. See Sect. 2.4 for details. (**b**) Tropospheric yield of CO from CH_4 oxidation reckoned in the current and previous studies. Symbols (error bars) denote the best (range of) estimates or the global (domain) averages. Abbreviations refer to: L81 − Logan *et al.* (1981), LC91 − Lelieveld and Crutzen (1991), T92 − Tie *et al.* (1992), M97 − Manning *et al.* (1997), B00 − Bergamaschi *et al.* (2000), F06 − Folberth *et al.* (2006), D07 − Duncan *et al.* (2007), E10 − Emmons *et al.* (2010), K10 − M. Kroll, IMAU (pers. comm., 2010), G13 − Gromov (2013), GT14 − Gromov and Taraborrelli, MPI-C (unpublished results using EMAC, 2014), F17 − Franco *et al.* (2017), EMAC − current study.

[25] Fig. 2 **(a)** shows the values of $\Delta\delta_c$, calculated for different stations/domains, as a function of γ (scaling with λ). Very large changes are expected for the ETSH, where $\Delta S/{}^{LC}S$ is about four times that in the SH. Importantly, the ${}^{LC}S$ value includes the Cl sink term from A07 (replacing that of EMAC), hence we receive the "lowest sensitivity" for the case when the Cl sink is added up to (instead of competing with) the other CH_4 sinks, *e.g.* that via OH. Alternatively, $\Delta\delta_c$ will additionally increase by $-0.2‰$ and $-(1.8–2.1)‰$ in the SH and ETSH, respectively. By setting $\Delta S/{}^{LC}S = 0$ in Eq. (2), we quantify the contribution of the CH_4 sink KIE (which increases by $\Delta\varepsilon_m$). Independent from the assumptions on the Cl sink domain and magnitude, it demonstrates the effect of mere lowering of $\delta^{13}C$ of C arriving to CO from CH_4 and accounts for $^1/_3$–$^2/_3$ of the total $\Delta\delta_c$ value (*cf. ibid.*, thin dashed line).

[26] At last, we estimate the equivalent increase in the $\delta^{13}C$ value of the non-CH_4 sources ($\Delta\delta_n$) that would be required to mask the depleting effect of a hypothetical CH_4+Cl sink increase. We subtract Eq. (1) written for the HC and LC and solve it assuming $\Delta\delta_c = 0$ (notation from Eq. (2) is kept):

$$\Delta\delta_n = \frac{(\delta_n - (\delta_m - \varepsilon_m))\mu + (1 + \mu)\Delta\varepsilon_m}{((\lambda_a/\lambda)^{LC}\gamma)^{-1} - (1 + \mu)}. \tag{3}$$

Averages of $\Delta\delta_n$ at BHD/SCB are depicted in Fig. 2 **(a)** next to the black dots denoting the corresponding $\Delta\delta_c$ values. Similar to $\Delta\delta_c$, $\Delta\delta_n$ scales with the assumed domain and CH_4 input to CO, however stronger, because δ_n is closer to the $\delta^{13}C$ of the total CO source ($\delta_c-\eta_c$) as compared to that for CH_4 ($\delta_m-\varepsilon_m$). Thus, if we accept the EMAC-suggested tropospheric CO yield in the SH of $\lambda = 93\%$, Cl-driven changes to the $\delta^{13}C(CO)$ at BHD/SCB are expected to be of at least $-(5.8–6.3)‰$ between the LC and HC, unless these are masked by unrealistic concurrent increases in $\delta^{13}C$ of the non-CH_4 sources of about $+(11.6–13.5)‰$. If one assumes the CH_4+Cl sink changes only within the ETSH, these estimates scale to $-(13.1–14.5)‰$ and $+(46–61)‰$, respectively. It is important to note, that we gauge the expected changes to the annual averages of $\delta^{13}C(CO)$, which do integrate seasonal variations. The latter are observed at merely $\pm1.5‰$ (*cf.* Figs. 1 and S2) and should also increase strongly, if the Cl sink has a similar seasonal variation to that of OH, as proposed by A07.

3 Discussion

[27] The photochemical yield of CO from CH_4 still happens to be a major factor of uncertainty in the CO budget. Modelling studies to date agreed on values of $\lambda \geq 0.7$ (see the overview in Fig. 2 **(b)**). Several recent studies (refs. D07 and E10) suggest however λ being close to unity and by doing so contradict findings of ^{13}CO-inclusive studies (*ibid.*, refs. M97, B00 and G13). The cases of $\lambda < 0.7$ or $\lambda \sim 1$, if true, would imply that we are ignorant about the basic principles implemented in the global atmospheric models, *i.e.* photochemical kinetics and/or dry and wet removal processes affecting the intermediates of the $CH_4 \rightarrow CO$ chain.

[28] Our estimates of $\Delta\delta_c$ bear the uncertainty of the assumed λ value; nonetheless, they affirm that even if only 70% of reacted CH_4 molecules yield CO, at least one-third of the changes to the $\delta^{13}C$ signature of this source (that is, $\delta_m+\varepsilon_m$) should be expressed in the ETSH $\delta^{13}C(CO)$. Since δ_m changed by about $+0.1‰$ between the HC and LC (*cf.* Fig. 1 **(b)**), we conclude that ε_m could not change by more than $+2‰$ in the SH as well (with this estimate being lower for λ above 0.7). Furthermore, statistically significant non-zero $\Delta\delta_c$ values (*p*-value of 0.01) should appear at very low λ, *viz.* above 0.05 (ETSH sink) and 0.12 (SH sink, respectively). We regard these two atmospheric domains because observations in the well-mixed ETSH may not single out the actual location of the $Cl+CH_4$ sink: The large part of sink-driven variations in mixing ratio and $\delta^{13}C$ of CH_4

and CO is merely transported into the ETSH from the tropics, where almost $^3/_4$ of the total CH_4 sink and accompanying CO

production is expected (see Table S1 for EMAC results, also Gromov (2013), Sect. 6.2.3). Accordingly, Hossaini *et al.* (2016)

also assign a major fraction of the CH_4+Cl sink to the lower latitudes. If such were not the case (*i.e.* varying Cl+CH_4 sink were

240 confined to the ETSH), the estimated effect on $δ^{13}C(CO)$ would roughly be twice that reckoned for the SH, *i.e.* extreme values.

[29] There are a few remarks on the usability of the method used by A07, in addition to the thorough theoretical enquiry by

Lassey *et al.* (2011). Evidence, or at least indications, for Cl in the ETSH is based on the $[CH_4]$ *vs.* $δ^{13}C(CH_4)$ Lissajous (a.k.a.

phase-) diagrams being ellipses in the case of seasonal cycles. The slope of their major axis gives the "apparent" KIE, from

which the ratio Cl/OH can be inferred knowing the individual KIEs. Clearly, Cl was not assessed on the basis of the annual

245 average value of $δ^{13}C(CH_4)$ but on the basis of its seasonal cycle, which is small. Using annual averages, however, is yet

impeded by perceptible long-term trends in $[CH_4]$ and $δ^{13}C(CH_4)$, which neither A07 (who consider the final 8 equilibrated

years of the 40-year spin-up simulations) nor Lassey *et al.* (2011) (who use a rather idealised model) have accounted for.

Through not de-trended seasonal variations (regardless whether absolute or related to the annual averages) these trends are

intrinsically present in the phase diagrams; whereas $[CH_4]$ growth is similar throughout both HC and LC, such is not the case

250 for $δ^{13}C(CH_4)$ which does not increase in the LC (*cf.* Fig. S2 (**a**, **c**) and, in particular, the seasonal time series fits for CH_4 at

the NIWA website[4]). Furthermore, the latter is likely a global signal of the 2000–2007 hiatus in tropospheric CH_4 evolution,

which manifested itself in $δ^{13}C$ earlier than in mixing ratios and terminated with the reversed $^{13}C/^{12}C$ trend (see, *e.g.*,

Nisbet *et al.*, 2016). Currently available observational data do not allow unambiguous attribution of this global phenomenon

to one or several causes proposed (Turner *et al.*, 2017), none of which include the role of Cl, however.

255 [30] Our incomplete information about the ^{13}C isotopic composition of CH_4 sources presently prevents to single out a Cl-induced

input into the annual average value of $δ^{13}C(CH_4)$, even though it should be perceptible (about +1.5‰, assuming for the sake

of matter a 2.5% Cl sink). The corresponding shift in $δ^{13}C(CO)$ is about −1.6‰ (estimated in Sect. 2.1). In this respect,

$δ^{13}C(CH_4)$ and $δ^{13}C(CO)$ are equally sensitive to Cl. Because the oxidation of CH_4 is a main source of CO in the ETSH, and

its isotopic composition is better known, it may well be that the annual average value of $δ^{13}C(CO)$ is useful, in contrast to that

260 of $δ^{13}C(CH_4)$. Furthermore, the relatively long lifetime and small seasonality in sources result in weak seasonal cycles of

mixing ratio and $δ^{13}C$ in CH_4. In contrast, the seasonal cycle of $δ^{13}C(CO)$ is dominated by the large difference in isotopic

composition of its sources, with the main driver being the switch between CO from CH_4 oxidation and that of the other sources.

Since the presence of Cl makes CH_4 oxidation an even more ^{13}C-depleted source, the impact of CH_4 oxidation on CO in the

ETSH peaks and may render the seasonal amplitude/summer minima of $δ^{13}C(CO)$ a sensitive indicator for Cl.

265 [31] A fundamental problem remains that the ETSH $δ^{13}C(CO)$ budget cannot be closed even when a Cl sink is excluded, unless

a CO yield from CH_4 of 0.7–0.86 is assumed (Manning *et al.*, 1997, Bergamaschi *et al.*, 2000). Yields below unity leave

however the possibility that a positive fractionation in the removal of the $CH_4 \rightarrow CO$ intermediates may be at play. Using $λ =$

(0.7–0.86) and $γ = 0.3$ for the troposphere, one calculates that an average KIE of (11–33)‰ should escort the removal of

intermediates in order to offset the Cl input to $δ^{13}C(CO)$. This estimate is 3–8 times higher than current parameterisations

270 suggest (about 4‰, see Gromov, 2013, Sect. 6.2.4) and is even higher in the SH, where $γ$ is above 0.4. Another complication

is potentially present because one cannot exclude, that the room temperature laboratory data for the ^{13}C KIE for CO+OH

---

4   https://www.niwa.co.nz/atmosphere/our-data/trace-gas-plots/methane (last access: December 2017).

Atmospheric
Chemistry
and Physics
Discussions

reaction are not applicable to the bulk of the troposphere, even though the reaction itself is not temperature but pressure dependent (see Gromov, 2013, Sect. 6.1.4). The unbalanced ^{13}C(CO) budget may then be the consequence of underestimating the CO sink KIE in the models, despite adequate estimates of the sources' ^{13}C/^{12}C ratios.

4 Conclusions

275 [32] Although invoking isotopic information often is like opening a can of worms (scientists' favourite diet), relevant conclusions emerge. Lassey *et al.* (2011) exposed shortcomings of the phase diagram method; we show here, using a low- and high-Cl scenario, that unrealistic yield values of CO from CH$_4$ oxidation (λ below 0.12 in the SH) and/or implausible increases in the δ^{13}C of non-CH$_4$ sources of CO (exceeding +7‰ at realistic $\lambda \geq 0.7$) would have to be assumed to explain the absence of concurrent inter-annual variations in δ^{13}C(CO) in the ETSH. This constitutes an independent, observation-based evaluation of

280 [Cl] variations envisaged by Allan *et al.* (2007), from which we conclude that such variations are extremely unlikely. Concerning estimates of background levels of Cl, even attributing 1% of the total tropospheric sink of CH$_4$ to Cl aggravates the non-trivial problem of balancing the global ^{13}C(CO) budget. It follows that the role of tropospheric Cl as a sink of CH$_4$ oxidation (see, *e.g.*, Saunois *et al.*, 2016, and refs. therein) is seriously overestimated.

[33] We emphasise the value of long-term observations of CO isotopic composition, especially at locations like Scott Base

285 (Antarctica), where influence of local sources is least and the fraction of photochemically produced CO is largest. In combination with modelling (*e.g.* EMAC), δ^{13}C(CO) allows monitoring for intra-annual changes in the carbon isotopic composition of CH$_4$-derived CO, namely the δ^{13}C value of reacted CH$_4$ modified by the total sink KIE (ε_m). Within the range of probable λ values (0.7−0.93), we are able to cap the potential changes in ε_m by +(2.0–1.5)‰ between 1994−1996 and 1998−2000 in the ETSH, which contrasts the +8‰ derived by Allan *et al.* (2007). Conversely, δ^{13}C(CO) may also be employed for "top-down"

290 estimates of δ^{13}C values of CH$_4$ sources, provided the ε_m is equilibrated on a scale of tropospheric CH$_4$ lifetime.

[34] We conclude that δ^{13}C(CO) is particularly sensitive to the CH$_4$+Cl sink. Nevertheless, its temporal variations, if they exist, may allow to calibrate an independent "bottom-up" [Cl] proxy, *e.g.* emissions of Cl simulated in process-based models. For example, changes in observed δ^{13}C(CO) at SCB (see Table 1) allow variations of the Cl-driven sink of CH$_4$ not larger than $(1.5\,\lambda_a^{-1})$% of its total (assuming the yield λ_a of CO from CH$_4$). Projecting this figure onto EMAC results (Table S1, tropo-

295 spheric integrals) implies that variations in mean ETSH chlorine abundance should have not exceeded Δ[Cl] $= (0.9\,\lambda_a^{-1}) \times 10^3$ atoms cm^{-3} between 1994–1996 and 1998–2000. That is still a perceptible variation (about ±30%) compared to the average [Cl] estimated by Hossaini *et al.* (2016). Regarding the fact that Manning *et al.* (1997) and Bergamaschi *et al.* (2000) could only close the SH ^{13}C(CO) budget assuming λ values of 0.7 and 0.86, which are within the generally accepted range, there is no scope for SH Cl at all.

Code availability

300 [35] The Modular Earth Submodel System (MESSy) is continuously further developed and applied by a consortium of institutions. The usage of MESSy (including the EMAC model) and access to the source code is licenced to all affiliates of institutions which are members of the MESSy Consortium. Institutions can become a member of the MESSy Consortium by signing the MESSy Memorandum of Understanding. More information can be found on the MESSy Consortium Website (http://www.messy-interface.org).

Atmospheric
Chemistry
and Physics
Discussions

Acknowledgements

References

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: 10.1029/2006jd007369, http://dx.doi.org/10.1029/2006JD007369, 2007.

Baker, A. K., Rauthe-Schöch, A., Schuck, T. J., Brenninkmeijer, C. A. M., van Velthoven, P. F. J., Wisher, A., and Oram, D. E.: Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using observed depletions in non-methane hydrocarbons, *Geophys. Res. Lett.*, **38**, L13801, doi: 10.1029/2011GL047571, http://dx.doi.org/10.1029/2011GL047571, 2011.

Baker, A. K., Sauvage, C., Thorenz, U. R., van Velthoven, P., Oram, D. E., Zahn, A., Brenninkmeijer, C. A. M., and Williams, J.: Evidence for strong, widespread chlorine radical chemistry associated with pollution outflow from continental Asia, *Sci. Rep.*, **6**, 36821, doi: 10.1038/srep36821, http://dx.doi.org/10.1038/srep36821, 2016.

Bergamaschi, P., Hein, R., Brenninkmeijer, C. A. M., and Crutzen, P. J.: Inverse modeling of the global CO cycle 2. Inversion of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotope ratios, *J. Geophys. Res. Atm.*, **105**, 1929−1945, doi: 10.1029/1999jd900819, http://dx.doi.org/10.1029/1999jd900819, 2000.

Brenninkmeijer, C. A. M.: Measurement of the abundance of ^{14}CO in the atmosphere and the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratio of atmospheric CO with applications in New Zealand and Antarctica, *J. Geophys. Res. Atm.*, **98**, 10595−10614, doi: 10.1029/93JD00587, http://dx.doi.org/10.1029/93JD00587, 1993.

Brenninkmeijer, C. A. M., Müller, R., Crutzen, P. J., Lowe, D. C., Manning, M. R., Sparks, R. J., and van Velthoven, P. F. J.: A large ^{13}CO deficit in the lower Antarctic stratosphere due to "Ozone Hole" Chemistry: Part I, Observations, *Geophys. Res. Lett.*, **23**, 2125−2128, doi: 10.1029/96gl01471, http://dx.doi.org/10.1029/96GL01471, 1996.

Craig, H.: Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide, *Geochim. Cosmochim. Acta*, **12**, 133−149, doi: 10.1016/0016-7037(57)90024-8, http://dx.doi.org/10.1016/0016-7037(57)90024-8, 1957.

Crowley, J. N., Saueressig, G., Bergamaschi, P., Fischer, H., and Harris, G. W.: Carbon kinetic isotope effect in the reaction CH₄+Cl: a relative rate study using FTIR spectroscopy, *Chem. Phys. Lett.*, **303**, 268−274, doi: 10.1016/S0009-2614(99)00243-2, http://dx.doi.org/10.1016/S0009-2614(99)00243-2, 1999.

Duncan, B. N., Logan, J. A., Bey, I., Megretskaia, I. A., Yantosca, R. M., Novelli, P. C., Jones, N. B., and Rinsland, C. P.: Global budget of CO, 1988-1997: Source estimates and validation with a global model, *J. Geophys. Res. Atm.*, **112**, D22301, doi: 10.1029/2007jd008459, http://dx.doi.org/10.1029/2007jd008459, 2007.

Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J. F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, **3**, 43−67, doi: 10.5194/gmd-3-43-2010, http://www.geosci-model-dev.net/3/43/2010/, 2010.

Folberth, G. A., Hauglustaine, D. A., Lathière, J., and Brocheton, F.: Interactive chemistry in the Laboratoire de Météorologie Dynamique general circulation model: model description and impact analysis of biogenic hydrocarbons on tropospheric chemistry, *Atmos. Chem. Phys.*, **6**, 2273−2319, doi: 10.5194/acp-6-2273-2006, http://www.atmos-chem-phys.net/6/2273/2006/, 2006.

Franco, B., Taraborrelli, D., Gromov, S., and *al.*: Manuscript under review, 2017.

Gromov, S., Jöckel, P., Sander, R., and Brenninkmeijer, C. A. M.: A kinetic chemistry tagging technique and its application to modelling the stable isotopic composition of atmospheric trace gases, *Geosci. Model Dev.*, **3**, 337−364, doi: 10.5194/gmd-3-337-2010, http://www.geosci-model-dev.net/3/337/2010/, 2010.

Gromov, S., Brenninkmeijer, C. A. M., and Jöckel, P.: Uncertainties of fluxes and $^{13}C/^{12}C$ ratios of atmospheric reactive-gas emissions, *Atmos. Chem. Phys.*, **17**, 8525−8552, doi: 10.5194/acp-17-8525-2017, https://www.atmos-chem-phys.net/17/8525/2017/, 2017.

Gromov, S. S.: Stable isotope composition of atmospheric carbon monoxide: A modelling study, Johannes Gutenberg-Universität, Mainz, urn: urn:nbn:de:hebis:77-37475, http://nbn-resolving.de/urn:nbn:de:hebis:77-37475, 2013.

Atmospheric
Chemistry
and Physics
Discussions

Hossaini, R., Chipperfield, M. P., Saiz-Lopez, A., Fernandez, R., Monks, S., Feng, W., Brauer, P., and von Glasow, R.: 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: 10.1002/2016JD025756, http://dx.doi.org/10.1002/2016JD025756, 2016.

Jobson, B. T., Niki, H., Yokouchi, Y., Bottenheim, J., Hopper, F., and Leaitch, R.: Measurements of C_2–C_6 hydrocarbons during the Polar Sunrise1992 Experiment: Evidence for Cl atom and Br atom chemistry, *J. Geophys. Res. Atm.*, **99**, 25355−25368, doi: 10.1029/94JD01243, http://dx.doi.org/10.1029/94JD01243, 1994.

Jöckel, P., Kerkweg, A., Pozzer, A., Sander, R., Tost, H., Riede, H., Baumgaertner, A., Gromov, S., and Kern, B.: Development cycle 2 of the Modular Earth Submodel System (MESSy2), *Geosci. Model Dev.*, **3**, 717−752, doi: 10.5194/gmd-3-717-2010, http://www.geosci-model-dev.net/3/717/2010/, 2010.

Lassey, K. R., Brailsford, G. W., Bromley, A. M., Martin, R. J., Moss, R. C., Gomez, A. J., Sherlock, V., Allan, W., Nichol, S. E., Schaefer, H., Connor, B. J., Robinson, J., and Smale, D.: Recent changes in methane mixing ratio and its ^{13}C content observed in the southwest Pacific region, *J. Integr. Env. Sci.*, **7**, 109−117, doi: 10.1080/19438151003621441, http://dx.doi.org/10.1080/19438151003621441, 2010.

Lassey, K. R., Allan, W., and Fletcher, S. E. M.: Seasonal inter-relationships in atmospheric methane and companion δ^{13}C values: effects of sinks and sources, *Tellus B*, **63**, 287−301, doi: 10.1111/j.1600-0889.2011.00535.x, http://dx.doi.org/10.1111/j.1600-0889.2011.00535.x, 2011.

Lelieveld, J. and Crutzen, P. J.: The Role of Clouds in Tropospheric Photochemistry, *J. Atmos. Chem.*, **12**, 229−267, doi: 10.1007/BF00048075, http://doi.org/10.1007/BF00048075, 1991.

Lelieveld, J., Gromov, S., Pozzer, A., and Taraborrelli, D.: Global tropospheric hydroxyl distribution, budget and reactivity, *Atmos. Chem. Phys.*, **16**, 12477−12493, doi: 10.5194/acp-16-12477-2016, http://www.atmos-chem-phys.net/16/12477/2016/, 2016.

Levine, J. G., Wolff, E. W., Jones, A. E., and Sime, L. C.: The role of atomic chlorine in glacial-interglacial changes in the carbon-13 content of atmospheric methane, *Geophys. Res. Lett.*, **38**, L04801, doi: 10.1029/2010GL046122, http://dx.doi.org/10.1029/2010GL046122, 2011a.

Levine, J. G., Wolff, E. W., Jones, A. E., Sime, L. C., Valdes, P. J., Archibald, A. T., Carver, G. D., Warwick, N. J., and Pyle, J. A.: Reconciling the changes in atmospheric methane sources and sinks between the Last Glacial Maximum and the pre-industrial era, *Geophys. Res. Lett.*, **38**, L23804, doi: 10.1029/2011GL049545, http://dx.doi.org/10.1029/2011GL049545, 2011b.

Liao, J., Huey, L. G., Liu, Z., Tanner, D. J., Cantrell, C. A., Orlando, J. J., Flocke, F. M., Shepson, P. B., Weinheimer, A. J., Hall, S. R., Ullmann, K., Beine, H. J., Wang, Y., Ingall, E. D., Stephens, C. R., Hornbrook, R. S., Apel, E. C., Riemer, D., Fried, A., Mauldin Iii, R. L., Smith, J. N., Staebler, R. M., Neuman, J. A., and Nowak, J. B.: High levels of molecular chlorine in the Arctic atmosphere, *Nat. Geosci.*, **7**, 91, doi: 10.1038/ngeo2046, http://dx.doi.org/10.1038/ngeo2046, 2014.

Logan, J. A., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Tropospheric chemistry: A global perspective, *J. Geopys. Res. Oceans*, **86**, 7210−7254, doi: 10.1029/JC086iC08p07210, http://dx.doi.org/10.1029/JC086iC08p07210, 1981.

Lowe, D. C., Brenninkmeijer, C. A. M., Tyler, S. C., and Dlugkencky, E. J.: Determination of the isotopic composition of atmospheric methane and its application in the Antarctic, *J. Geophys. Res. Atm.*, **96**, 15455−15467, doi: 10.1029/91JD01119, http://dx.doi.org/10.1029/91JD01119, 1991.

Lowe, D. C., Allan, W., Manning, M. R., Bromley, T., Brailsford, G., Ferretti, D., Gomez, A., Knobben, R., Martin, R., Mei, Z., Moss, R., Koshy, K., and Maata, M.: Shipboard determinations of the distribution of ^{13}C in atmospheric methane in the Pacific, *J. Geophys. Res. Atm.*, **104**, 26125−26135, doi: 10.1029/1999jd900452, http://dx.doi.org/10.1029/1999JD900452, 1999.

Manning, M. R., Brenninkmeijer, C. A. M., and Allan, W.: Atmospheric carbon monoxide budget of the southern hemisphere: Implications of ^{13}C/^{12}C measurements, *J. Geophys. Res. Atm.*, **102**, 10673−10682, doi: 10.1029/96JD02743, http://dx.doi.org/10.1029/96JD02743, 1997.

Natrella, M.: NIST/SEMATECH e-Handbook of Statistical Methods, edited by: Croarkin, C. and Tobias, P., NIST/SEMATECH, http://www.itl.nist.gov/div898/handbook/ (last access: 20 August 2015), 2003.

Nisbet, E. G., Dlugokencky, E. J., Manning, M. R., Lowry, D., Fisher, R. E., France, J. L., Michel, S. E., Miller, J. B., White, J. W. C., Vaughn, B., Bousquet, P., Pyle, J. A., Warwick, N. J., Cain, M., Brownlow, R., Zazzeri, G., Lanoisellé, M., Manning, A. C., Gloor, E., Worthy, D. E. J., Brunke, E. G., Labuschagne, C., Wolff, E. W., and Ganesan, A. L.: Rising atmospheric methane: 2007–2014 growth and isotopic shift, *Glob. Biogeochem. Cyc.*, **30**, 1356−1370, doi: 10.1002/2016GB005406, http://dx.doi.org/10.1002/2016GB005406, 2016.

NIWA: Publicly available data on from several greenhouse gas measurement projects (TROPAC), National Institute of Water and Atmospheric Research, New Zealand, ftp://ftp.niwa.co.nz/tropac/ (last access: June 2016), 2010.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, **1**, 324, doi: 10.1038/ngeo177, http://dx.doi.org/10.1038/ngeo177, 2008.

Atmospheric
Chemistry
and Physics
Discussions

Parrish, D. D., Hahn, C. J., Williams, E. J., Norton, R. B., Fehsenfeld, F. C., Singh, H. B., Shetter, J. D., Gandrud, B. W., and Ridley, B. A.: Reply [to "Comment on 'Indications of photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California' by D. D. Parrish et al."], *J. Geophys. Res. Atm.*, **98**, 14995−14997, doi: 10.1029/93JD01416, http://dx.doi.org/10.1029/93JD01416, 1993.

Platt, U., Allan, W., and Lowe, D.: Hemispheric average Cl atom concentration from $^{13}C/^{12}C$ ratios in atmospheric methane, *Atmos. Chem. Phys.*, **4**, 2393−2399, doi: 10.5194/acp-4-2393-2004, http://www.atmos-chem-phys.net/4/2393/2004/, 2004.

Röckmann, T., Brenninkmeijer, C. A. M., Crutzen, P. J., and Platt, U.: Short-term variations in the $^{13}C/^{12}C$ ratio of CO as a measure of Cl activation during tropospheric ozone depletion events in the Arctic, *J. Geophys. Res. Atm.*, **104**, 1691−1697, doi: 10.1029/1998JD100020, http://dx.doi.org/10.1029/1998JD100020, 1999.

Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., Kubistin, D., Regelin, E., Riede, H., Sandu, A., Taraborrelli, D., Tost, H., and Xie, Z. Q.: The atmospheric chemistry box model CAABA/MECCA-3.0, *Geosci. Model Dev.*, **4**, 373−380, doi: 10.5194/gmd-4-373-2011, http://www.geosci-model-dev.net/4/373/2011/, 2011.

Saueressig, G., Bergamaschi, P., Crowley, J. N., Fischer, H., and Harris, G. W.: Carbon kinetic isotope effect in the reaction of CH_4 with Cl atoms, *Geophys. Res. Lett.*, **22**, 1225−1228, doi: 10.1029/95GL00881, http://dx.doi.org/10.1029/95GL00881, 1995.

Saueressig, G., Crowley, J. N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C. A. M., and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH_4 with $O(^1D)$ and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, *J. Geophys. Res. Atm.*, **106**, 23127−23138, doi: 10.1029/2000jd000120, http://dx.doi.org/10.1029/2000JD000120, 2001.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J. G., Dlugokencky, E. J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F. N., Castaldi, S., Jackson, R. B., Alexe, M., Arora, V. K., Beerling, D. J., Bergamaschi, P., Blake, D. R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Covey, K., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H. S., Kleinen, T., Krummel, P., Lamarque, J. F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K. C., Marshall, J., Melton, J. R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F. J. W., Patra, P. K., Peng, C., Peng, S., Peters, G. P., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W. J., Saito, M., Santini, M., Schroeder, R., Simpson, I. J., Spahni, R., Steele, P., Takizawa, A., Thornton, B. F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G. R., Weiss, R., Wiedinmyer, C., Wilton, D. J., Wiltshire, A., Worthy, D., Wunch, D., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z., and Zhu, Q.: The global methane budget 2000– 2012, *Earth Syst. Sci. Data*, **8**, 697−751, doi: 10.5194/essd-8-697-2016, https://www.earth-syst-sci-data.net/8/697/2016/, 2016.

Schaefer, H., Fletcher, S. E. M., Veidt, C., Lassey, K. R., Brailsford, G. W., Bromley, T. M., Dlugokencky, E. J., Michel, S. E., Miller, J. B., Levin, I., Lowe, D. C., Martin, R. J., Vaughn, B. H., and White, J. W. C.: A 21st century shift from fossil-fuel to biogenic methane emissions indicated by $^{13}CH_4$, *Science*, 80−83, doi: 10.1126/science.aad2705, http://dx.doi.org/10.1126/science.aad270, 2016.

Spicer, C. W., Chapman, E. G., Finlayson-Pitts, B. J., Plastridge, R. A., Hubbe, J. M., Fast, J. D., and Berkowitz, C. M.: Unexpectedly high concentrations of molecular chlorine in coastal air, *Nature*, **394**, 353−356, http://dx.doi.org/10.1038/28584, 1998.

Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dubé, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry, *Nature*, **464**, 271-274, doi: 10.1038/nature08905, http://dx.doi.org/10.1038/nature08905, 2010.

Tie, X., Jim Kao, C. Y., and Mroz, E. J.: Net yield of OH, CO, and O_3 from the oxidation of atmospheric methane, *Atmos. Environ. A Gen.*, **26**, 125−136, doi: 10.1016/0960-1686(92)90265-M, http://dx.doi.org/10.1016/0960-1686(92)90265-M, 1992.

Turner, A. J., Frankenberg, C., Wennberg, P. O., and Jacob, D. J.: Ambiguity in the causes for decadal trends in atmospheric methane and hydroxyl, *Proc. Natl. Acad. Sci. USA*, **114**, 5367−5372, doi: 10.1073/pnas.1616020114, http://www.pnas.org/content/114/21/5367.abstract, 2017.

Whitehill, A. R., Joelsson, L. M. T., Schmidt, J. A., Wang, D. T., Johnson, M. S., and Ono, S.: Clumped isotope effects during OH and Cl oxidation of methane, *Geochim. Cosmochim. Acta*, **196**, 307−325, doi: 10.1016/j.gca.2016.09.012, http://dx.doi.org/10.1016/j.gca.2016.09.012, 2017.

Young, C. J., Washenfelder, R. A., Roberts, J. M., Mielke, L. H., Osthoff, H. D., Tsai, C., Pikelnaya, O., Stutz, J., Veres, P. R., Cochran, A. K., VandenBoer, T. C., Flynn, J., Grossberg, N., Haman, C. L., Lefer, B., Stark, H., Graus, M., de Gouw, J., Gilman, J. B., Kuster, W. C., and Brown, S. S.: Vertically Resolved Measurements of Nighttime Radical Reservoirs in Los Angeles and Their Contribution to the Urban Radical Budget, *Environ. Sci. Technol.*, **46**, 10965−10973, doi: 10.1021/es302206a, http://dx.doi.org/10.1021/es302206a, 2012.