ENVIRONMENTAL RESEARCH LETTERS

CrossMark

LETTER

OPEN ACCESS

RECEIVED 31 October 2023

REVISED 2 March 2024

ACCEPTED FOR PUBLICATION 25 April 2024

PUBLISHED 7 June 2024

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence.

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



The use of δ^{13} C in CO to determine removal of CH₄ by CI radicals in the atmosphere^{*}

Thomas Röckmann^{1,**}, Maarten van Herpen², Chloe Brashear¹, Carina van der Veen¹, Sergey Gromov³, Qinyi Li⁴, Alfonso Saiz-Lopez⁵, Daphne Meidan⁵, Africa Barreto⁶, Natalia Prats⁶, Ignacio Mármol⁶, Ramón Ramos⁶, Isabel Baños⁷, Jesús M Arrieta⁷, Sönke Zaehnle⁸, Armin Jordan⁸, Heiko Moossen⁸, Helder Timas⁹, Dickon Young¹⁰, Peter Sperlich¹¹, Rowena Moss¹¹ and Matthew S Johnson¹²

- Institute for Marine and Atmospheric Research Utrecht, Department of Physics, Faculty of Science, Utrecht University, 3584 CS Utrecht, The Netherlands
- ² Acacia Impact Innovation, 5384 BB Heesch, The Netherlands
- ³ Atmospheric Chemistry Department, Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
- ⁴ Environment Research Institute, Shandong University, Qingdao, Shandong 266237, People's Republic of China
- ⁵ Department of Atmospheric Chemistry and Climate, Institute of Physical Chemistry Blas Cabrera, Spanish National Research Council (CSIC), 28006 Madrid, Spain
- ⁶ Izaña Atmospheric Research Centre (IARC), State Meteorological Agency of Spain (AEMet), Santa Cruz de Tenerife, Spain
- ⁷ Canary Islands Oceanographic Center, Spanish Institute of Oceanography (IEO-CSIC), Santa Cruz de Tenerife, Spain
- ⁸ Max Planck Institute for Biogeochemistry, Hans-Knöll-Str.10, 07745 Jena, Germany ⁹ Institute National De Mateoralezia e Configure Mindele São Visente Cone Varda
- ⁹ Instituto Nacional De Meteorologia e Geofísica, Mindelo, São Vicente, Cape Verde ¹⁰ School of Chamistry, University of Briefel, Briefel, Briefel, BS, 175, United Kingdom
- ¹⁰ School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom
 - National Institute of Water & Atmospheric Research Ltd (NIWA), Hataitai, Wellington 6021, New Zealand
- ¹² Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark
- * This paper is dedicated to Carl A M Brenninkmeijer
- * Author to whom any correspondence should be addressed.

E-mail: t.roeckmann@uu.nl

Keywords: δ^{13} C, CO, CH₄, Cl

Supplementary material for this article is available online

Abstract

The reaction of CH_4 with chlorine (Cl) radicals in the atmosphere is associated with an extraordinarily strong isotopic fractionation, where ¹²CH₄ reacts about 70 ‰ faster with Cl than ¹³CH₄. Therefore, although the Cl-based sink of CH_4 constitutes only a small contribution to its total removal rate, the uncertainty in this small sink has been identified as one of the two largest uncertainties of isotope-based CH_4 source apportionment at the global scale. The uncertainty arises from the fact that Cl levels in the atmosphere are so low that they cannot be detected directly. One very sensitive indirect method to identify and quantify the $CH_4 + Cl$ reaction in the atmosphere is the detection of the extremely ¹³C-depleted reaction product carbon monoxide (CO) from this reaction. This article reviews the concept of this approach, its successful application in the atmosphere, its challenges and opportunities for identifying and quantifying Cl-based removal of CH_4 at the regional and global scale and its potential to detect and evaluate possible attempts to enhance CH_4 removal from the atmosphere.

1. Introduction

Methane (CH_4) is the second most important anthropogenic greenhouse gas, and its enhanced emissions are responsible for about half a degree of warming since pre-industrial times (IPCC AR6, 2022). Due to its relatively short lifetime in the atmosphere of about 10 years, CH_4 is considered an

attractive emission mitigation target, and reduction in CH_4 levels could slow down global warming on a relative short term (Ocko *et al* 2021, Cael and Goodwin 2023). Therefore, more than 150 nations have joined the Global Methane Pledge to reduce anthropogenic CH_4 emissions by 30% by the year 2030, compared to 2020 levels. This is an ambitious goal given the wide range of sources from anthropogenic activities, which include exploration, transport, storage and use of fossil fuels, waste management, ruminant and rice agriculture and industrial combustion and non-combustion processes (Saunois *et al* 2020). Numerous activities in the past decades have addressed quantifying and reducing CH₄ emissions across all these sectors, e.g. (Brandt *et al* 2014, Alvarez *et al* 2018, Shindell *et al* 2021, Smith *et al* 2021, Stavropoulou *et al* 2023, Wang *et al* 2023). Nevertheless, CH₄ levels in the atmosphere are still increasing, and the growth rate has been particularly high in the post-2020 years (Lan *et al* 2023).

The causes of the multi-year variations in CH₄ over the last decades are still being debated, and different studies have attributed them to either increasing emissions from anthropogenic sources (Chandra et al 2021, Zhang et al 2021) biogenic sources (Nisbet et al 2016, Schaefer et al 2016, Lan et al 2021, Basu et al 2022, Oh et al 2022), both categories (Worden et al 2017, Thanwerdas et al 2023) or changes in the removal by the main sink, reaction with OH (Rigby et al 2017, Turner et al 2017, Stevenson et al 2022). Key information comes from the temporal evolution of the carbon isotopic composition of CH₄. The reversal of the temporal δ^{13} C trend (Nisbet *et al* 2016, Schaefer et al 2016, Lan et al 2021) suggests that the recent rise of CH₄ is different from the rise before the year 2000, and that fossil sources may no longer be responsible for the increase. In this case, the ongoing rise of CH₄ likely originates from biogenic sources, including the possibility that we already see a feedback of the global climate system to ongoing global warming, which is likely more difficult to mitigate than anthropogenic sources (Nisbet et al 2023). Note, however, that Thanwerdas et al (2023) suggest that the δ^{13} C trend reversal could be explained by a shift in the source signatures without a large reduction in the relative share of the fossil sources. Notwithstanding, Kleinen et al (2021) showed that increased emissions from natural sources may cause future CH4 concentrations to rise higher than expected in current global projections. In this case, emission reductions from anthropogenic sources may not be adequate to reduce CH₄ sufficiently.

An additional possible way to reduce atmospheric CH_4 levels is the acceleration of its removal. Most of the CH_4 is removed by reaction with the hydroxyl radical (OH), with small contributions from soil uptake and removal by atomic oxygen and chlorine (Cl) radicals. The Cl-based sink in the troposphere is very difficult to quantify because Cl levels are so low that they cannot be measured directly. Thus they have to be quantified by indirect measurements of Cl precursors, either in combination with models of atmospheric photochemistry (Hossaini *et al* 2016) or by measurable effects that reactions with Cl imprint on more stable species. This paper discusses the potential, challenges and opportunities of using the carbon isotopic composition of CO, the product of atmospheric oxidation reactions of CH_4 , as a tool to quantify the contribution of Cl to the removal of CH_4 and to identify regions and processes where CH_4 is removed by Cl in the atmosphere.

1.1. Isotope-based detection and quantification of Cl

The basis of this method is the extraordinarily strong ${}^{13}C/{}^{12}C$ kinetic isotope effect in the reaction CH₄ + Cl. Saueressig *et al* (1995) discovered that in the range of tropospheric temperatures Cl reacts about 70‰ faster with ${}^{12}CH_4$ than with ${}^{13}CH_4$, an astonishingly strong kinetic stable carbon isotope effect. Thus, wherever this reaction is significant, it leads to a ${}^{13}C$ enrichment in the remaining CH₄, and a depletion in the CO produced.

The carbon isotopic composition of CO is quantified in the common delta (δ) notation as

$$\delta^{13} C_{\rm CO} = \frac{{}^{13} R_{\rm CO}}{{}^{13} R_{\rm VPDB}} - 1 \tag{1}$$

where ¹³*R* is the ¹³C/¹²C ratio and VPDB is the international reference material Vienna PeeDeeBelemnite with ¹³*R*_{VPDB} = 0.011180 (28) (Zhang *et al* 1990). For CH₄, δ^{13} C_{CH4} is defined analogously. The kinetic fractionation factor α of a certain reaction is the ratio between the rate coefficients of the reactions of the different isotopologues. α also is equal to the isotope ratio of the instantaneously produced reaction product (here CO, assuming complete conversion to CO) relative to the one of the substrates (here CH₄), thus

$$\alpha_{\rm Cl+CH4} = \frac{{}^{13}k_{\rm Cl+CH4}}{{}^{12}k_{\rm Cl+CH4}} = \frac{{}^{13}R_{\rm CO}}{{}^{13}R_{\rm CH4}} = \frac{\delta^{13}C_{\rm CO_{Cl+CH4}} + 1}{\delta^{13}C_{\rm CH4} + 1}.$$
(2)

For the reaction under consideration, when CH₄ $(\delta^{13}C_{CH4} = -48\%)$ is removed via the Cl + CH₄ reaction $(\alpha_{Cl+CH4} = 0.935)$, the $\delta^{13}C$ of the produced CO is

$$\delta^{13}C_{CO_{Cl+CH4}} = \alpha_{Cl+CH4} \left(\delta^{13}C_{CH4} + 1 \right) - 1$$

= 0.935 * 0.952 - 1 = -110‰. (3)

Thus, if only 1 ppb of CO with this depleted signature is added to an ambient reservoir of 100 ppb of CO with $\delta^{13}C_{CO_{amb}} = -25\%$, the mixture will have a significantly different isotopic composition

$$\delta^{13}C_{CO_{mix}} = \frac{100 * \delta^{13}C_{CO_{amb}} + 1 * \delta^{13}C_{CO_{Cl+CH4}}}{101} - 1 = -25.8\%.$$
 (4)

2. Methods

For the new samples presented below, ambient air samples were collected in 1 l glass flasks at five fixed sampling stations (Izaña Atmospheric

Observatory and Oceanographical Institute (both Tenerife), Cape Verde Atmospheric Observatory, Ragged Point (Barbados), Atto tower (Brazil), and on board of ships (Visby and Cap San Augustine) operated by Maersk, crossing the North Atlantic region affected by mineral dust. High precision measurements of the isotopic composition of atmospheric CO were performed using isotope ratio mass spectrometry (IRMS). CO is converted to CO₂ using Schütze reagent (Smiley 1965), an oxidant that adds one O atom to the original CO atom. The earlier applications of the technique, e.g. (Stevens and Krout 1972, Brenninkmeijer 1993) required large air samples (hundreds of liters), because purified gases had to be inserted into the IRMS using dual inlet systems. The advantage of this was that many samples could also be analyzed for ¹⁴CO using accelerator mass spectrometry (Brenninkmeijer 1993). After the development of continuous-flow IRMS (Merritt et al 1994), stable isotope measurements of CO became much less labor intensive since the analysis using such systems only requires about 100 ml of air (Mak and Yang 1998, Pathirana et al 2015, Vimont et al 2019, Kirago et al 2023). The CO isotope system at Utrecht University has been described in Pathirana et al (2015), and the isotope scale is linked to the calibration scale established in earlier studies, e.g. (Brenninkmeijer 1993, Brenninkmeijer and Röckmann 1997) via a high concentration CO isotope calibration gas stored in a high pressure cylinder.

Van Herpen et al (2023) simulated the release of Cl from Marine Dust - Sea spray Aerosol interaction (MDSA), and its subsequent reaction with CH₄, on $\delta^{13}C_{CO}$. They implemented a simplified MDSA parameterization in the global 3D Community Atmosphere Model with Chemistry (CAM-Chem) (Lamarque et al 2012, Tilmes et al 2016, Li et al 2023, Saiz-Lopez et al 2023, Van Herpen et al 2023). The MDSA mechanism (Wittmer and Zetzsch 2016, Van Herpen et al 2023) involves photocatalytic cycling of iron ions (Fe(III)—Fe(II)) and Cl in mixed MDSAs. The parameters in the model were chosen to match observed aerosol composition measurements in the North Atlantic. Details are provided in (Van Herpen et al 2023). The reaction of the released Cl with CH₄ is calculated online in the model, and the effect on $\delta^{13}C_{CO}$ is then calculated knowing the isotopic composition of the ambient and the formed CO (equations (3) and (4)). We present previously unpublished data from these simulations for the southern hemisphere to evaluate the impact of the Cl from MDSA on δ^{13} CO in Baring Head, New Zealand.

3. Results

3.1. $\delta^{13}C_{CO}$ —based detection of Cl in the stratosphere

In the stratosphere, the reaction of CH₄ with Cl that is produced from photolysis of CFCs in the ozone layer

contributes strongly to CH₄ removal, which affects the radiative effects of stratospheric CH₄ and water vapor (Saiz-Lopez *et al* 2023). This leads to a welldocumented and large ¹³C enrichment with altitude and latitude (Wahlen *et al* 1987, Brenninkmeijer *et al* 1995, Sugawara *et al* 1997, Rice *et al* 2003, Röckmann *et al* 2011). These observations can be reproduced in atmospheric models when the laboratory-based kinetic isotope effect in the Cl + CH₄ reaction is included (McCarthy *et al* 2003, Eichinger *et al* 2015, Thanwerdas *et al* 2022, Chandra *et al* 2024), demonstrating that the effect is well understood.

Brenninkmeijer *et al* (1996) were the first to show that the ¹³C enrichment in CH₄ is accompanied by a very strong depletion of ¹³C in stratospheric CO. Figure 1 shows extremely low $\delta^{13}C_{CO}$ values in stratospheric air when the CO mole fraction decreases below 35 ppb. The symbols are color-coded by the concentration of ¹⁴CO, an ultra-trace molecule that is formed in the upper troposphere and lower stratosphere from ¹⁴C produced by cosmic radiation (Mak *et al* 1994). Higher ¹⁴CO levels indicate a higher stratospheric character of the air mass, and it is evident that $\delta^{13}C_{CO}$ drops very strongly as the stratospheric character of the air mass increases.

3.2. $\delta^{13}C_{CO}$ —based detection of Cl in the troposphere: ozone depletion events (ODEs)

Tropospheric Cl is much more difficult to detect and quantify than stratospheric Cl, because tropospheric Cl concentrations are extremely low, between 10^2 and 10^5 cm^{-3} . Nevertheless, the $\delta^{13}C_{CO}$ method has been successfully used to detect and quantify elevated Cl levels associated with ODEs (ozone depletion events) in the Arctic (Röckmann et al 1999). Figure 2 shows an example of an ODE, when O₃ levels drop from ambient values of ~ 40 ppb to values near zero within hours. The black symbols show $\delta^{13}C_{CO}$ during normal O₃, and the long-term trend reflects part of the seasonal cycle of $\delta^{13}C_{CO}$. During ODE episodes, $\delta^{13}C_{CO}$ drops by about 1‰ relative to background levels (red circles in figure 1 relative to black circles, interpolated by black line). Note that the O₃ destruction during ODEs is largely caused by brominecatalyzed O₃ destruction (Herrmann et al 2022) with additional contributions from iodine (Benavent et al 2022). However, the depletion in $\delta^{13}C_{CO}$ (and hydrocarbon ratios (Jobson et al 1994, Ariya et al 1998)) confirms that also Cl is produced in these events at levels that facilitate oxidation of roughly 1 ppb of CH₄ upwind of the measurement location.

3.3. $\delta^{13}C_{CO}$ —based detection of Cl in the tropical troposphere

Are such negative $\delta^{13}C_{CO}$ deviations also observable at other locations where Cl levels increase temporarily? The number of CO isotope observations made in the past is rather limited, but more than 20 years ago, Mak *et al* (2003) reported unexpected

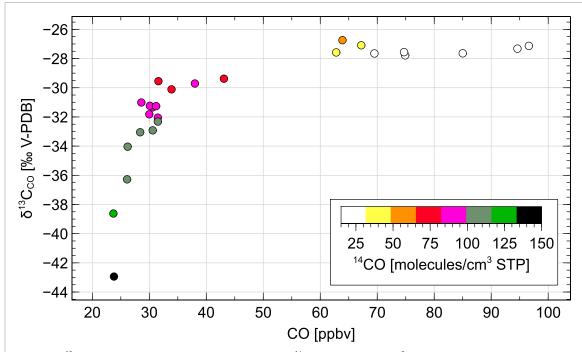
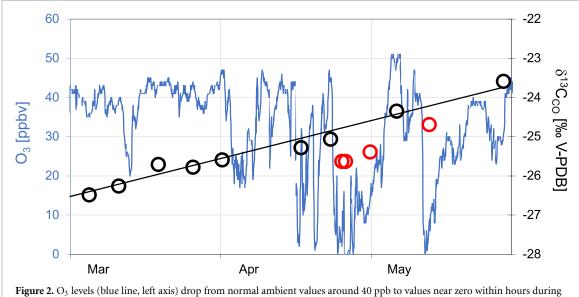
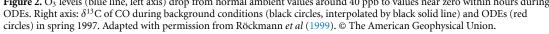


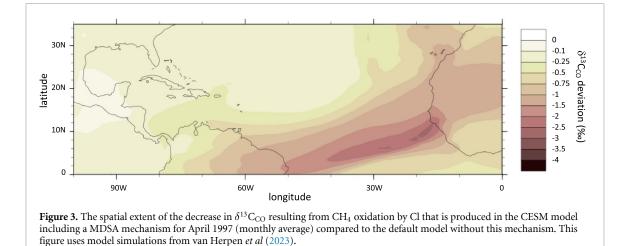
Figure 1. $\delta^{13}C_{CO}$ versus CO mole fraction, with a colour code of ¹⁴CO (in molecules cm⁻³ at standard temperature and pressure (STP)) for air samples collected on a C130 aircraft platform during flights in the southern polar lower stratosphere between New Zealand and Antarctica in October 1993. Adapted with permission from Brenninkmeijer *et al* (1996). © The American Geophysical Union.





 $\delta^{13}C_{CO}$ variability, including very depleted values, at Barbados. At other stations, much smoother seasonal evolutions and higher values of $\delta^{13}C_{CO}$ are generally observed (Brenninkmeijer 1993, Röckmann *et al* 1998, 2002, Mak and Kra 1999, Kato *et al* 2000, Mak *et al* 2000, Gros *et al* 2001). Mak *et al* (2003) already suggested that the low $\delta^{13}C_{CO}$ values could originate from the reaction Cl + CH₄, but at that time no source was known which could produce the relevant amounts of Cl in this region.

Van Herpen *et al* (2023) recently suggested that Cl could be liberated photocatalytically when ironcontaining mineral dust mixes with sea spray aerosol above the Atlantic. When a corresponding Marine Dust - Sea spray Aerosol (MDSA) mechanism was implemented in a global atmospheric model, sufficient Cl was produced in the model to oxidize



ppb-level quantities of CH₄ during the passage of the air parcel over the Atlantic. Figure 3 shows the expected deviation in $\delta^{13}C_{CO}$ originating from this ¹³C-depleted CO source (equation (3)) compared to a model without the MDSA mechanism for April 1997 from van Herpen *et al* (2023). In the model, the strength and location of these isotope signals varies with season.

To further confirm the MDSA hypothesis, air sampling programs have been recently initiated on several Atlantic islands, and on commercial ships. According to the modeling of MDSA performed in van Herpen *et al* (2023), the $\delta^{13}C_{CO}$ depletion should be strongest at around 30°W longitude, with negative shifts in $\delta^{13}C_{CO}$ of up to 4 ‰ (figure 3). The dust chemistry should lead to slightly lower $\delta^{13}C_{CO}$ depletions at the permanent stations compared to the ship track, based on the location of the aerosol dust plume during this period.

Figure 4 shows CO and $\delta^{13}C_{CO}$ data from air samples collected during two ship tracks that transected a large Sahara dust plume on 6-7 April 2023 (around 30° W, 7-11° N, Maersk Visby, back triangles) and 4-9 April 2023 (7-27 °W, 29-1 °N, Cap San Augustine, grey circles). We also include data from our fixed stations at Tenerife, Cape Verde and Barbados that were taken during the same period, and samples from the Southern Hemispheric station Baring Head. The air samples collected on the Visby between April 5 and 10 and by the San Augustine between April 6 and 9 were collected in a period associated with high levels of Saharan dust. Figure 4 shows that during these days the $\delta^{13}C_{CO}$ of samples collected on the Visby was much lower than the reference data from San Augustine, Barbados, Tenerife and Cape Verde. The Visby samples had relatively higher CO concentrations (figure 4(b)), likely due to an extra source from combustion, either technological or forest burning. This is evident from the high δ^{18} O values that are indicative of combustion

CO (Brenninkmeijer and Röckmann 1997). However, combustion derived CO cannot explain the ¹³C depletion in these samples, as CO from combustion sources has a similar or higher ¹³C content than the ambient CO (Brenninkmeijer et al 1999). CO in the dust-associated Visby samples between 5-10 April is depleted in ¹³C by more than 2 ‰ (average value of -31.6 ‰ compared to the reference average of -29.4 %). Such low values are found in the Southern Hemisphere (see data from Baring Head in figure 4), but the CO mole fraction and δ^{18} O values are too high to reflect Southern Hemispheric air. The addition of a very small amount of strongly ¹³C-depleted CO from the Cl + CH₄ reaction in the middle of the Atlantic can explain the negative δ^{13} C excursions in the Visby samples. The $Cl + CH_4$ signal is weaker at the island stations and the San Augustine locations that are further outside the dust plume, in line with the model prediction by van Herpen et al (2023).

4. Global scale considerations

Allan et al (2001, 2005, 2007) used the seasonal covariation of CH₄ and $\delta^{13}C_{CH4}$ (referred to as phase ellipses) at high southern latitudes to quantify the possible role of Cl. They showed that the slopes of the phase ellipses are much larger than the one expected from the kinetic isotope effect in the removal of CH₄ by OH (i.e. 3.9‰ according to Saueressig et al (1995) and 5.4‰ according to Cantrell et al (1990)). They concluded that this can only be caused by a significant contribution of tropospheric Cl to the sink, with a seasonal amplitude of 6×10^3 cm⁻³. From a similar analysis, Platt et al (2004) estimated that the contribution of Cl to the tropospheric CH₄ sink could be as high as 3.3%, or 19 Tg CH_4 yr⁻¹. A weakness of their argument is that the slope of the phase ellipse also exhibits strong interannual variation. In particular over the first years of the record, it varied from 17 ‰ in 1997 to 6 ‰ in 1999. This would

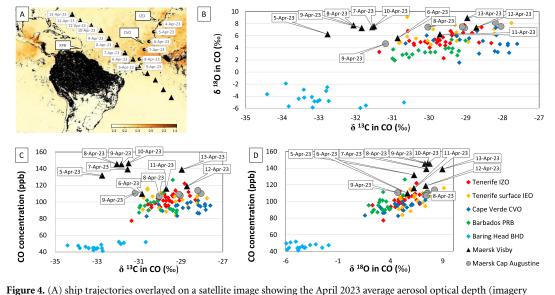


Figure 4. (A) ship trajectories overlayed on a satellite image showing the April 2023 average aerosol optical depth (imagery produced by NASA based on data provided by the MODIS Atmosphere Science Team, NASA Goddard Space Flight Center). (B) ship data compared with fixed stations shows ¹³C depletions for dust-associated locations. (C) $\delta^{13}C(CO)$ vs. CO. (D) $\delta^{18}O(CO)$ vs. CO. We only analyze northern hemisphere ship flasks, because the isotopic composition of CO in the Southern Hemisphere is very different (see data from Baring Head, New Zealand).

correspond to a change in the Cl contribution of several percent, and if this was caused by Cl, it should also have affected the overall δ^{13} C of atmospheric CH₄ to a degree that is incompatible with atmospheric observations.

Gromov et al (2018) illustrated this issue from the perspective of the reaction product CO. They argue that large interannual variations in Cl-based oxidation of CH4 in the Extra Tropical Southern Hemisphere (ETSH) would necessarily result in strong corresponding variations of $\delta^{13}C_{CO}$ as the CO produced in this reaction is strongly depleted in ¹³C (equation (1)). However, corresponding variations in $\delta^{13}C_{CO}$ in the ETSH have not been observed. Interpreting the available atmospheric model results, they put an upper limit of $n_{\rm Cl} = 0.9 \times 10^3 \text{ cm}^{-3}$ on the variation of mean Cl levels in the ETSH, far less than the levels proposed by Allan and co-workers. Moreover, they argue that a large Cl source in the ETSH would lead to even lower background $\delta^{13}C_{CO}$ values, which are already hard to reconcile with the understanding of the global CO cycle.

Nevertheless, the argument for high Cl based on the $\delta^{13}C_{CH4}$ phase ellipses has been supported by recent model analyses of the temporal and spatial trends in $\delta^{13}C_{CH4}$, which can only be reproduced in atmospheric models that use a strong isotope fractionation in the removal of CH₄ (Lan *et al* 2021, Basu *et al* 2022, Thanwerdas *et al* 2022). This requires either a high fractionation in the OH sink or a large contribution of Cl to the total sink. Whitehill *et al* (2017) reported 6.1 ‰ for the fractionation in the OH sink, higher than the previous reported values of 3.9‰ (Saueressig *et al* 1995) or 5.4‰ (Cantrell *et al* 1990). A stronger fractionation in the OH sink would require a small contribution from Cl, whereas a weaker fractionation in the OH sink would require a much larger contribution from Cl to explain the atmospheric observations.

Is it possible that a large source of Cl from MDSA near South America can provide enough Cl to explain the phase-ellipses observed by Allan et al (2001, 2005, 2007), but not affect $\delta^{13}C_{CO}$ at the Baring Head and Scott Base sites in a corresponding way? We examined the CESM model output from van Herpen et al (2023), which included an extrapolation to the global scale. The model output shows an additional strong Cl source near South America, and a modest source of Cl near Australia. Between July 1996 and June 1998, the modelled monthly average $n_{\rm Cl}$ in the southern hemisphere varied between 400 and 2200 atoms cm⁻³, resulting in $\Delta n_{\rm Cl}$ exceeding 2×10^3 cm⁻³, which is of the order of magnitude suggested by Allan et al (2007). At Baring Head, the model output shows a $\delta^{13}C_{CO}$ of less than 0.3 ‰, in line with the analysis made by Gromov et al (2018). The inter-annual variation in the model output is even less pronounced. Note, however, that the model setup used in van Herpen et al (2023) was not targeted at the global scale, in particular it does not include a polar halogen source module (Fernandez et al 2019).

These results suggest that a large regional Cl source, far away from the remote observatories in the SH could at the same time provide a high average [Cl] exposure to explain the phase ellipses for CH₄, without causing a large effect on $\delta^{13}C_{CO}$. In addition, a large and previously unaccounted-for source of Cl in the NH could potentially alleviate difficulties in

modeling the rather small interhemispheric gradient in $\delta^{13}C_{CO}$, which was previously attributed to a possibly unrealistically low yield of CO from CH₄ oxidation (Manning *et al* 1997, Bergamaschi *et al* 2000), one of the key parameters of the tropospheric CO budget that is yet rather uncertain (Gromov *et al* 2018). Further modeling is needed to confirm the global scale relevance and implications of this potentially large Cl source.

5. Implications

Measurements of the carbon isotopic composition of CH₄ have been widely used to quantify the relative contribution of emissions from different source sectors to the observed variations in the growth rate of CH₄ over the past decades (Nisbet et al 2016, 2019, 2023, Schaefer et al 2016, Worden et al 2017, Lan et al 2021, Basu et al 2022, Thanwerdas et al 2022). The kinetic isotope effect in the total removal of CH₄ is a key parameter influencing this partitioning. An error in the assumption of its value will invariably translate to an error in the partitioning between fossil fuel related and biogenic source categories. Basu et al (2022) identified the uncertainty in the fractionation (both related to the uncertainty in the fractionation of the CO + OH reaction, and the contribution of Cl) as the single most important parameter precluding a more reliable separation between the different source sectors. Consequently, it is important to reduce this uncertainty using new measurement techniques, such as $\delta^{13}C_{CO}$. Finally, we note that measurements of $\delta^{13}C_{CO}$ may be a valuable tool to quantify the efficiency of possible future CH4 mitigation policies that may involve accelerating Cl-based destruction of CH₄.

Data availability statements

The new CO isotope data used in this publication are included in the supplemental material to this paper. The Aqua/MODIS AOD data shown in figure 4 were obtained from https://neo.gsfc.nasa. gov/view.php?datasetId=MYDAL2_M_AER_OD& date=2023-04-01.

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgments

We are very grateful to OceansX for logistical support to our flask sampling program, including the seafarers and their maritime organizations that are sampling flasks on many routes of interest, through their program 'Xploration Seafarers and Scientists'. We thank Peter Sealy for collecting the air samples at Barbados.

Funding

This research is part of the ISAMO project funded by Spark Climate Solutions. The sampling at Tenerife was supported under the European Union's Horizon 2020 research and innovation programme through the ATMO-ACCESS Integrating Activity under Grant Agreement No 101008004.

Conflict of interest

The authors declare no competing interest.

ORCID iDs

Thomas Röckmann b https://orcid.org/0000-0002-6688-8968

Sergey Gromov () https://orcid.org/0000-0002-2542-3005

Ignacio Mármol © https://orcid.org/0009-0007-2475-9125

Jesús M Arrieta () https://orcid.org/0000-0002-0190-6950

Matthew S Johnson lo https://orcid.org/0000-0002-3645-3955

References

- Allan W, Lowe D C, Gomez A J, Struthers H and Brailsford G W 2005 Interannual variation of ¹³C in tropospheric methane: implications for a possible atomic chlorine sink in the marine boundary layer *J. Geophys. Res.* **110** D11306
- Allan W, Manning M R, Lassey K R, Lowe D C and Gomez A J 2001 Modeling the variation of δ^{13} C in atmospheric methane: phase ellipses and the kinetic isotope effect *Glob. Biogeochem. Cycles* **15** 467–81

Allan W, Struthers H and Lowe D C 2007 Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: global model results compared with southern hemisphere measurements *J. Geophys. Res.* **112** D04306

- Alvarez R A *et al* 2018 Assessment of methane emissions from the U.S. oil and gas supply chain *Science* **361** 186–8
- Ariya P A, Jobson B T, Sander R, Niki H, Harris G W, Hopper J F and Anlauf K G 1998 Measurements of C2-C7 hydrocarbons during the Polar Sunrise Experiment 1994: further evidence for halogen chemistry in the troposphere *J. Geophys. Res.* 103 13169–80
- Basu S *et al* 2022 Estimating emissions of methane consistent with atmospheric measurements of methane and δ^{13} C of methane *Atmos. Chem. Phys.* 22 15351–77
- Benavent N *et al* 2022 Substantial contribution of iodine to Arctic ozone destruction Nat. Geosci. **15** 770–3
- Bergamaschi P, Hein R, Brenninkmeijer C A M and Crutzen P J 2000 Inverse modeling of the global CO cycle: 2. Inversion of ¹³C/¹²C and ¹⁸O/¹⁶O isotope ratios J. Geophys. Res. 105 1909–27

Brandt A R et al 2014 Methane leaks from North American natural gas systems *Science* **343** 733–5

- Brenninkmeijer C A M 1993 Measurement of the abundance of ¹⁴CO in the atmosphere and the ¹³C/¹²C and ¹⁸O/¹⁶O ratio of atmospheric CO, with application in New-Zealand and Antarctica J. Geophys. Res. 98 10,595–10,614
- Brenninkmeijer C A M, Lowe D C, Manning M R, Sparks R J and Velthoven P F J V 1995 The ¹³C, ¹⁴C, and ¹⁸O isotopic composition of CO, CH₄ and CO₂ in the higher southern

latitudes lower stratosphere *J. Geophys. Res.* **100** 26,163–26,172

- Brenninkmeijer C A M, Müller R, Crutzen P J, Lowe D C, Manning M R, Sparks R J and Velthoven P J V 1996 A large ¹³CO deficit in the lower Antarctic stratosphere due to "ozone hole" chemistry: part 1, observations *Geophys. Res. Lett.* 23 2125–8
- Brenninkmeijer C A M and Röckmann T 1997 Principal factors determining the ¹⁸O/¹⁶O ratio of atmospheric CO as derived from observations in the southern hemispheric troposphere and lowermost stratosphere J. Geophys. Res. **102** 25477–85
- Brenninkmeijer C A M, Röckmann T, Bräunlich M, Jöckel P and Bergamaschi P 1999 Review of progress in isotope studies of atmospheric carbon monoxide *Chemosphere* 1 33–52
- Cael B B and Goodwin P A 2023 Global methane pledge versus carbon dioxide emission reduction *Environ. Res. Lett.* **18** 104015
- Cantrell C A, Shetter R E, McDaniel A H, Calvert J G, Davidson J A, Lowe D C, Tyler S C, Cicerone R J and Greenberg J P 1990 Carbon kinetic isotope effect in the oxidation of methane by the hydroxyl radical *J. Geophys. Res.* **95** 22455–62
- Chandra N *et al* 2021 Emissions from the oil and gas sectors, coal mining and ruminant farming drive methane growth over the past three decades *J. Meteorol. Soc. Jpn.* **99** 309–37
- Chandra N, Patra P K, Fujita R, Höglund-Isaksson L, Umezawa T, Goto D, Morimoto S, Vaughn B H and Röckmann T 2024 Methane emissions decreased in fossil fuel exploitation and sustainably increased in microbial source sectors during 1990–2020 Commun. Earth Environ. 5 147
- Eichinger R, Jöckel P, Brinkop S, Werner M and Lossow S 2015 Simulation of the isotopic composition of stratospheric water vapour—part 1: description and evaluation of the EMAC model *Atmos. Chem. Phys.* **15** 5537–55
- Fernandez R P *et al* 2019 Modeling the sources and chemistry of polar tropospheric halogens (Cl, Br, And I) using the CAM-Chem global chemistry-climate model *J. Adv. Model. Earth Syst.* **11** 2259–89
- Gromov S, Brenninkmeijer C A M and Jöckel P 2018 A very limited role of tropospheric chlorine as a sink of the greenhouse gas methane *Atmos. Chem. Phys.* **18** 9831–43
- Gros V *et al* 2001 Detailed analysis of the isotopic composition of CO and characterization of the air masses arriving at Mt. Sonnblick (Austrian Alps) *J. Geophys. Res.* **106** 3179–93
- Herrmann M, Schöne M, Borger C, Warnach S, Wagner T, Platt U and Gutheil E 2022 Ozone Depletion Events in the Arctic spring of 2019: a new modeling approach to bromine emissions Atmos. Chem. Phys. 22 13495–526
- Hossaini R, Chipperfield M P, Saiz-Lopez A, Fernandez R, Monks S, Feng W, Brauer P and Von Glasow R 2016 A global model of tropospheric chlorine chemistry: organic versus inorganic sources and impact on methane oxidation *J. Geophys. Res.* **121** 14–271
- Jobson B T, Niki H, Yokouchi Y, Bottenheim J, Hopper F and Leaitch R 1994 Measurements of C_2 – C_6 hydrocarbons during the Polar Sunrise 1992 Experiment: evidence for Cl atom and Br atom chemistry *J. Geophys. Res.* **99** 25355–68
- Kato S, Kajii Y, Akimoto H, Bräunlich M, Röckmann T and Brenninkmeijer C A M 2000 Observed and modeled seasonal variation of ¹³C, ¹⁸O and ¹⁴C of atmospheric CO at Happo, a remote site in Japan, and a comparison with other records J. Geophys. Res. 105 8891–900
- Kirago L et al 2023 Sources and long-term variability of carbon monoxide at Mount Kenya and in Nairobi Atmos. Chem. Phys. 23 14349–57
- Kleinen T, Gromov S, Steil B and Brovkin V 2021 Atmospheric methane underestimated in future climate projections *Environ. Res. Lett.* 16 094006
- Lamarque J-F *et al* 2012 CAM-Chem: description and evaluation of interactive atmospheric chemistry in the Community Earth System Model *Geosci. Model Dev.* **5** 369–411

- Lan X *et al* 2021 Improved constraints on global methane emissions and sinks using δ^{13} C-CH₄ *Glob. Biogeochem. Cycles* **35** E2021gb007000
- Lan X, Thoning K W and Dlugokencky E D 2023 Trends in globally-averaged CH₄, N₂O, and SF₆ determined from NOAA global monitoring laboratory measurements. Version 2023–10 (https://doi.org/10.15138/P8xg-Aa10)
- Li Q *et al* 2023 Global environmental implications of atmospheric methane removal through chlorine-mediated chemistry-climate interactions *Nat. Commun.* **14** 4045
- Mak J E, Brenninkmeijer C A M and Tamaresis J 1994 Atmospheric ¹⁴CO observations and their use for estimating carbon monoxide removal rates *J. Geophys. Res.* **99** 22915–22
- Mak J E and Kra G 1999 The isotopic composition of carbon monoxide At Montauk Point, Long Island *Chemosphere Glob. Change Sci.* **1** 205–18
- Mak J E, Kra G, Sandomenico T and Bergamaschi P 2003 The seasonally varying isotopic composition of the sources of carbon monoxide at Barbados, West Indies *J. Geophys. Res.* **108** 4635
- Mak J E, Manning M R and Lowe D C 2000 Aircraft observations of δ^{13} C of atmospheric methane over the Pacific in August 1991 and 1993: evidence of an enrichment in (CH₄)-¹³C in the Southern Hemisphere *J. Geophys. Res.* **105** 1329–35
- Mak J E and Yang W B 1998 Technique for analysis of air samples for ¹³C and ¹⁸O in carbon monoxide via continuous-flow isotope ratio mass spectrometry *Anal. Chem.* **70** 5159–61
- Manning M R, Brenninkmeijer C A M and Allan W 1997 Atmospheric carbon monoxide budget of the southern hemisphere: implications of ¹³C/¹²C measurements *J. Geophys. Res. Atmos.* **102** 10673–82
- McCarthy M C, Boering K A, Rice A L, Tyler S C, Connell P and Atlas E 2003 Carbon and hydrogen isotopic compositions of stratospheric methane: 2. two-dimensional model results and implications for kinetic isotope effects *J. Geophys. Res.* 108 4461
- Merritt D A, Brand W A and Hayes J M 1994 Isotope-ratio-monitoring gas chromatography-mass spectrometry: methods for isotopic calibration *Org. Geochem.* 21 573–83
- Nisbet E G *et al* 2016 Rising atmospheric methane: 2007–2014 growth and isotopic shift *Glob. Biogeochem. Cycles* **30** 1356–70
- Nisbet E G *et al* 2019 Very strong atmospheric methane growth in the 4 years 2014–2017: implications for the Paris agreement *Glob. Biogeochem. Cycles* **33** 318–42
- Nisbet E G *et al* 2023 Atmospheric methane: comparison between methane's record in 2006–2022 and during glacial terminations *Glob. Biogeochem. Cycles* **37** e2023GB007875
- Ocko I B, Sun T, Shindell D, Oppenheimer M, Hristov A N, Pacala S W, Mauzerall D L, Xu Y and Hamburg S P 2021 Acting rapidly to deploy readily available methane mitigation measures by sector can immediately slow global warming *Environ. Res. Lett.* **16** 054042
- Oh Y *et al* 2022 Improved global wetland carbon isotopic signatures support post-2006 microbial methane emission increase *Commun. Earth Environ.* **3** 159
- Pathirana S L, Van Der Veen C, Popa M E and Röckmann T 2015 An analytical system for stable isotope analysis on carbon monoxide using continuous-flow isotope-ratio mass spectrometry Atmos. Meas. Tech. 8 5315–24
- Platt U, Allan W and Lowe D 2004 Hemispheric average Cl atom concentration from ¹³C/¹²C ratios in atmospheric methane *Atmos. Chem. Phys.* **4** 2393–9
- Rice A L, Tyler S C, McCarthy M C, Boering K A and Atlas E 2003 carbon and hydrogen isotopic compositions of stratospheric methane: 1. High-precision observations from the NASA ER-2 aircraft *J. Geophys. Res.* **108** 4460
- Rigby M *et al* 2017 Role of atmospheric oxidation inrecent methane growth *Proc. Natl. Acad. Sci. USA* **114** 5373–7
- Röckmann T, Brass M, Borchers R and Engel A 2011 The isotopic composition of methane in the stratosphere: high-altitude

balloon sample measurements *Atmos. Chem. Phys.* **11** 13287–304

- Röckmann T, Brenninkmeijer C A M, Crutzen P J and Platt U 1999 Short term variations in the ¹³C/¹²C ratio of CO as a measure of Cl activation during tropospheric Ozone Depletion Events in the Arctic J. Geophys. Res. 104 1691–7
- Röckmann T, Brenninkmeijer C A M, Saueressig G, Bergamaschi P, Crowley J, Fischer H and Crutzen P J 1998 Mass independent fractionation of oxygen isotopes in atmospheric CO due to the reaction CO + OH *Science* 281 544–6
- Röckmann T, Jöckel P, Gros V, Bräunlich M, Possnert G and Brenninkmeijer C A M 2002 Using ¹⁴C, ¹³C, ¹⁸O and ¹⁷O isotopic variations to provide insights into the high northern latitude surface CO inventory *Atmos. Chem. Phys.* 2 147–59
- Saiz-Lopez A *et al* 2023 Natural short-lived halogens exert an indirect cooling effect on climate *Nature* **618** 967–73
- Saueressig G, Bergamaschi P, Crowley J N, Fischer H and Harris G W 1995 Carbon kinetic isotope effect in the reaction of CH₄ with Cl atoms *Geophys. Res. Lett.* 22 1225–8
- Saunois M 2020 The global methane budget 2000–2017 Earth Syst. Sci. Data **12** 1561–623
- Schaefer H *et al* 2016 A 21st-century shift from fossil-fuel to biogenic methane emissions indicated by (CH₄)-¹³C Science 352 80–84
- Shindell D et al 2021 Global Methaneassessment: Benefits And Costs Of Mitigating Methane Emissions (United Nations Environment Programme; United Nations Environment Programme And Climate And Clean Air Coalition)
- Smiley W G 1965 Note on a reagent for oxidation of carbon monoxide Nucl. Sci. Abstr. 3 391
 Smith D. Bow D. and Smith L 2021 Activultural methods on activity
- Smith P, Reay D and Smith J 2021 Agricultural methane emissions and the potential for mitigation *Phil. Trans. R. Soc.* A **379** 20200451
- Stavropoulou F *et al* 2023 High potential for CH_4 emission mitigation from oil infrastructure in one of EU's major production regions *Atmos. Chem. Phys.* **23** 10399–412
- Stevens C M and Krout L 1972 Method for the determination of the concentration and of the carbon and oxygen isotopic composition of atmospheric carbon monoxide *Int. J. Mass Spectrom. Ion Phys.* 8 265–75
- Stevenson D S, Derwent R G, Wild O and Collins W J 2022 Covid-19 lockdown emission reductions have the potential to explain over half of the coincident increase in global atmospheric methane *Atmos. Chem. Phys.* **22** 14243–52 Sugawara S, Nakazawa T, Shirakawa Y, Kawamura K, Aoki S,

Machida T and Honda H 1997 Vertical profile of the carbon

isotopic ratio of stratospheric methane over Japan *Geophys. Res. Lett.* **24** 2989–92

- Thanwerdas J, Saunois M, Berchet A, Pison I and Bousquet P 2023 Investigation of the post-2007 methane renewed growth with high-resolution 3D variational inverse modelling and isotopic constraints *EGUsphere* 2023 1–50
- Thanwerdas J, Saunois M, Pison I, Hauglustaine D, Berchet A, Baier B, Sweeney C and Bousquet P 2022 How do Cl concentrations matter for the simulation of CH₄ and δ^{13} C(CH₄) and estimation of the CH₄ budget through atmospheric inversions? *Atmos. Chem. Phys.* 22 15489–508
- Tilmes S *et al* 2016 Representation of the Community Earth System Model (CESM1) CAM4-Chem within the Chemistry-Climate Model Initiative (CCMI) *Geosci. Model Dev.* **9** 1853–90
- Turner A J, Frankenberg C, Wennberg P O and Jacob D J 2017 Ambiguity in the causes for decadal trends in atmospheric methane and hydroxyl Proc. Natl. Acad. Sci. USA 114 5367–72
- van Herpen M *et al* 2023 Photocatalytic chlorine atom production on mineral dust-sea spray aerosols over the North Atlantic *Proc. Natl. Acad. Sci. USA* **120** E2303974120
- Vimont I J, Turnbull J C, Petrenko V V, Place P F, Sweeney C, Miles N, Richardson S, Vaughn B H and White J W C 2019 An improved estimate for the δ^{13} C and δ^{18} O signatures of carbon monoxide produced from atmospheric oxidation of volatile organic compounds *Atmos. Chem. Phys.* **19** 8547–62
- Wahlen M, Tanaka N, Henry R and Yoshinari T 1987 ¹³C, D and ¹⁴C in methane *EOS Trans. Am. Geophys. Union* **68** 1220
- Wang J, Ciais P, Smith P, Yan X, Kuzyakov Y, Liu S, Li T and Zou J 2023 The role of rice cultivation in changes in atmospheric methane concentration and the Global Methane Pledge *Glob. Change Biol.* 29 2776–89
- Whitehill A R, Joelsson L M T, Schmidt J A, Wang D T, Johnson M S and Ono S 2017 Clumped isotope effects during OH and Cl oxidation of methane Geochim. Cosmochim. Acta 196 307–25
- Wittmer J and Zetzsch C 2016 Photochemical activation of chlorine by iron-oxide aerosol J. Atmos. Chem. 74 187–204
- Worden J R, Bloom A A, Pandey S, Jiang Z, Worden H M,
 Walker T W, Houweling S and Röckmann T 2017 Reduced biomass burning emissions reconcile conflicting estimates of the post-2006 atmospheric methane budget *Nat. Commun.* 8 2227
- Zhang Q L, Chang T L and Li W J 1990 A calibrated measurement of the atomic-weight of carbon *Chin. Sci. Bull.* **35** 290–6
- Zhang Z *et al* 2021 Anthropogenic emission is the main contributor to the rise of atmospheric methane during 1993–2017 *Natl. Sci. Rev.* **9** nwab200