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To cite this article: Thomas Röckmann et al 2024 Environ. Res. Lett. 19 064054

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RECEIVED 31 October 2023

REVISED 2 March 2024

ACCEPTED FOR PUBLICATION 25 April 2024

PUBLISHED 7 June 2024

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

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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 $\delta^{13}\mathrm{C}_{\mathrm{CO}_{\mathrm{amb}}}=-25\%$, 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.

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