

University of Groningen

## Stable isotopes in stratospheric carbon monoxide

Hooghiem, Joram

DOI:  
[10.33612/diss.195700524](https://doi.org/10.33612/diss.195700524)

**IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.**

*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
2021

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*  
Hooghiem, J. (2021). *Stable isotopes in stratospheric carbon monoxide*. University of Groningen.  
<https://doi.org/10.33612/diss.195700524>

### Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

### Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

---

# Discussion and Outlook

---

This thesis aimed at novel CO isotope measurements in the stratosphere, understand the isotope budget, and explore the potential of CO isotope observations as tracers for the stratospheric CH<sub>4</sub> sink. In Chapter 2, the development of a new sampler was described, a sampler that made it possible to obtain sufficient air for stable isotope analysis in CO. The measurement campaigns and observations were presented in Chapter 3. In that same chapter, the data is used to assess two different GCMs, as part of a validation of the tagged chemistry scheme used in Chapter 5. Chapters 4 and 5 present the stable isotope observations of <sup>13</sup>CO and C<sup>18</sup>O, the first with a focus on the lowermost stratosphere and the identification of NH wildfire smoke in the stratosphere. Chapter 5 focuses on the stratosphere above 380 K potential temperature. New constraints on unknown source signatures are obtained, and the general budget of CO stable isotopes in the stratosphere is well understood. Indeed, a potential is found in the use of stable isotope source signatures of CO, but also complications are identified. The main results are discussed in a broad context in this chapter.

## 6.1 Observations of stratospheric tracers

The sampler developed in Chapter 2 has proven to be a viable method, performing several flights, and subsequent multi tracer analysis of both mole fractions and challenging stable isotope measurements, as summarised in Section 3.2.1. Conform to one of its design requirements the sampler is cheap compared to other methods. The sampler itself costs little under 1000 Euro, where the pump is the most expensive part. Launching the sampler can be done by a single skilled person, with the right equipment. Thus, reducing the cost of personnel for a launch. Trajectory forecasts can be made with free web-based tools such as habhub, and a balloon launch doesn't require any authorisation in many countries when flying under the weight limit specified by the local authorities. During several intensive campaigns, nine flights were performed within a total of fewer than five weeks, obtaining 35 air samples. When weather is favourable, like in September 2017, a flight was performed every day for three days in a row; the whole campaign lasted less than a week. This dissertation thus shows that routine soundings of the stratosphere are possible, at relatively low costs.

The low cost of a single launch makes a valuable alternative to other whole air samplers. Goto et al., 2017, reported 43 samples obtained using the cryogenic methods described in Morimoto et al., 2009, and Honda et al., 1996, of which 28 were usable, which is less than two samples per year, where the LISA sampler provided on average 11 samples per year, over the three-year period it was operational. The LISA sampler, however, does provides a significantly smaller amount of air, a cumulative total of 21 l over three years, where the cryogenic technique is capable of delivering that amount in a single sample. High altitude aircraft have that same advantage. Heidt et al., 1989, communicated the design of the whole air sampler for NASA ER-aircraft, later adapted for Global Hawk (Jensen et al., 2017), and a similar system is operated on the M55 Geophysica. These on the other hand, rarely provide data above 20 km.

The sampler here is optimised to obtain as much air as possible. It was tested for a specific set of trace gases. However, the general design can be easily adapted to meet other scientific requirements. For example, smaller samples with a higher resolution can be obtained, and potentially more than four samples can be obtained. When is considered for other trace gases, it is recommended to first test the suitability of the sample container.

For the work presented in this dissertation, observations of CO<sub>2</sub>, CO, CH<sub>4</sub>, and N<sub>2</sub>O have been obtained using LISA. Thus providing in situ observations that are useful for the evaluation of GCMs. Besides, stable isotope analysis of CO and CO<sub>2</sub> on single samples is possible, which provides measurements of  $\delta(^{13}\text{C})$  in CO and CO<sub>2</sub>,  $\delta(^{18}\text{O})$  in CO and CO<sub>2</sub>, and  $\delta(^{17}\text{O})$  in CO<sub>2</sub>. This proves that multi tracer analysis on small samples is now possible, and no longer require high-altitude aircraft or heavy payload balloon flights. The sampler provides a good complementary method to the AirCore sampling method. The latter provides very accurate measurements, but provides less air. Also, the altitude at which the sample was taken is not accurate, thus imposing uncertainties in the mole fraction as a function of the altitude coordinate,  $y(p)$  or  $y(z)$ . Samples obtained with the LISA sampler do not suffer from that, but are, on the other hand, an integrated sample. Nevertheless, multi tracer analysis can be provided on a well-defined grid.

A bottom up estimate of the uncertainty of mole fractions was presented for CO<sub>2</sub>,

$0.12 \mu\text{mol mol}^{-1}$ ,  $\text{CH}_4$   $3 \text{ nmol mol}^{-1}$ , and  $\text{CO}$   $1.4 \text{ nmol mol}^{-1}$ . This estimate includes the stability of trace gases  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  in the sampling container. This does not meet the WMO compatibility goals for  $\text{CO}_2$  and  $\text{CH}_4$ , however is comparable to in situ airborne measurements presented by Filges et al., 2015, which uses the same analyser as this work.

In a direct comparison with high-resolution AirCore measurements a significant bias was found in  $\text{CO}_2$  mole fraction measurements on LISA samples, of about  $0.8 \mu\text{mol mol}^{-1}$ . To this day no cause of this bias is found. The diffusion of trace gases into the bag was shown to be insignificant during the relevant storage period of a few hours. Potential sources that have been hypothesised are as follows. It could be that surface interaction with the bags is more profound for a smaller sample size. Secondly, the individual components of the sampling system have been tested. The pump, however, is not tested and may be a potential source, even though the EPDM diaphragm is deemed inert. Another possibility is that the bias lies with the AirCore measurements. The AirCore was fully validated down to atmospheric pressures of 300 hPa, Karion et al., 2010, noted that full validation to lower atmospheric pressure is still necessary.

Most stratospheric measurements of  $\text{CO}$  are made in situ from aircraft and show the same structure, to which LISA measurements compare well. Measurements from Flocke et al., 1999; Homan et al., 2010; Pommrich et al., 2014, made in the tropics, and Hoor et al., 2004, obtained in the extra-tropical UTLS, show the general decrease of  $\text{CO}$  with altitude. In the latter values decrease to  $25\text{--}30 \text{ nmol mol}^{-1}$ , wherein the tropical stratosphere  $\text{CO}$  mole fractions decrease to  $10\text{--}15 \text{ nmol mol}^{-1}$ . Moreover, the observed variability on isentropes of about  $5\text{--}10 \text{ nmol mol}^{-1}$ . Observations from the LISA samples show the same general features, possibly with a larger variation at higher altitudes. The only recent measurements at these high altitudes are provided by the AirCore as shown in this work. In general good agreement was found between these instruments. Interesting are the older results by Engel et al., 2006, that identified mesospheric air identified by  $\text{CO}$  and  $\text{SF}_6$ . This is very similar to the feature observed by the LISA sampler in April 2017, although the mole fractions presented in Engel et al., 2006, are larger, up to  $600 \text{ nmol mol}^{-1}$ . On the other hand, the LISA sampler observations were made at the end of April, and the observation by Engel et al., 2006, were made in January and near the end of March. The mixing and chemical processes could have had a profound impact.

Carefully planned additional laboratory tests can be designed to answer the unresolved bias issue. It is recommended that these are carried out to improve either sampling instrument. Developments with the Global Hawk (Jensen et al., 2017) provide promising opportunities for further validation of the sampler, and AirCore. Not only does the Global hawk provide air samples that could be used for stable isotope analysis. A system similar to (Filges et al., 2015) for high accuracy mole fraction measurements of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  has been developed (Jensen et al., 2017).

## 6.2 Accuracy and uncertainty of $\text{CO}$ measurements

In the introduction, it was mentioned that care was taken to determine qualitatively good measurements. The analysis in this work so far show excellent results for the

$y(\text{CO})$  measurements. This work possibly shows the lowest CO mole fraction measurements of the stratosphere on record. The accuracy of CO measurements was ensured by the calibration strategy discussed in Chapter 2, and the total uncertainty, a combination of type A and type B uncertainties, of CO measurements was determined to be  $1.4 \text{ nmol mol}^{-1}$ . The long-term stability of the scale was tested regularly, and no significant drift was found. In addition, the extrapolation of the scale to low stratospheric measurements was assessed, and the associated uncertainty was found to be small. Measurements with a CO scrubber were also used to determine the absolute zero point of the instrument during the field campaign in Traînou. These measurements indicate a small potential bias,  $\leq 1 \text{ nmol mol}^{-1}$  in the scale, which encourages further investigation of the use of Sofnocat in the calibration strategy for atmospheric CO measurements, in particular, the stratosphere.

Stability of CO in air sample containers is a general concern, and therefore attention was paid to test the containers used in this study. A short term storage stability test was performed during the development phase of LISA, reported in Chapter 2. A small effect was found for CO, and included in the original uncertainty analysis reported in the publication Hooghiem et al., 2018. The direction of the drift however did not indicate diffusion, and this observation motivated additional research. A long-term storage test with the same container followed, and this indeed showed that drift is small, and random, allowing for an updated estimate of the uncertainty presented in Chapter 2. A third storage test was performed over a longer period of 2 a, with the glass flasks for transport and storage of the samples. The drift of  $0.05 \text{ nmol mol}^{-1} \text{ d}^{-1}$  was found, which potentially resulted in a bias of the stable isotope measurements performed, a bias which could not be constrained.

The uncertainty of CO measurements is better than most in situ measurements. Cairo et al., 2010, reports an uncertainty of the COLD instrument (Viciani et al., 2008) of  $3 \text{ nmol mol}^{-1}$ , which was further reduced in the second version (Viciani et al., 2018). An uncertainty of  $3 \text{ nmol mol}^{-1}$  is also reported for the balloon-borne spectrometer (Moreau et al., 2005). Flocke et al., 1999, reports a  $0.7 \text{ nmol mol}^{-1}$  precision and an accuracy of 5%. Very few Measurements of CO on whole air samples have been presented. (Engel et al., 2006) presented measurements of CO from the cryogenic sampler, but no uncertainty was specified.

The long storage period of the samples, unfortunately, has resulted in a potential bias in the stable isotope measurements. Apart from that, a good analytical uncertainty was achieved, on relatively small samples. The storage time of three to seven months may have resulted in a bias in the stable isotopes. As mentioned in the previous paragraph, the mole fractions showed a significant increase over time. The drift rate was used to estimate the expected isotope drift which could have been significant and not constraint. In future work, the stability of the stable isotope composition should be quantified for the container used, for low mole fractions of CO. The storage test results from tests with the sampling bags also encourage the investigation of the potential long term storage of CO for stable isotope measurements relevant in other fields.

In addition,  $\delta(^{13}\text{C})$  is biased due to the interference of  $^{17}\text{O}$  on the measurements using the IRMS technique. The isotope budget of CO contains a mass-independent oxygen component, MIF. An estimate was provided in Chapter 5 using  $\delta(^{18}\text{O})$  observations and the known processes that may lead to mass-independent fractionation. The

**Table 6.1:** Four main sources of CO and their isotopic source signatures, the same as Table 1.2 in Chapter 1, updated with the results of this work. <sup>a</sup>(C. M. Stevens et al., 1972), <sup>b</sup>(C. A. M. Brenninkmeijer, 1993), <sup>c</sup>(C. M. Stevens and Wagner, 1989), <sup>d</sup>(Bergamaschi et al., 1998), <sup>e</sup>(Saurer et al., 2009), <sup>f</sup>(Manning et al., 1997), <sup>g</sup>(C. A. M. Brenninkmeijer and Röckmann, 1997), and <sup>h</sup>(Vimont et al., 2019). Table is based on the most recent compilation of source signatures by Vimont et al., 2019. <sup>i</sup>This work; oxidation through the reaction  $\text{CH}_3 + \text{O}_2$ . <sup>j</sup>This work; oxidation through reaction  $\text{CH}_4 + \text{O}(^1\text{D})$ . <sup>k</sup>This work.

Source	$^{13}\text{C}$ (VPDB)	Uncertainty	$^{18}\text{O}$ (VSMOW)	Uncertainty
Fossil fuel combustion <sup>a,b</sup>	-27.5 ‰	≤ 1 ‰	23.5 ‰	≤ 1 ‰
Biomass burning <sup>c,d,e,f</sup>	-25–-12 ‰	1–3 ‰	10–18 ‰	1–3 ‰
$\text{CH}_4$ oxidation <sup>f,g</sup>	-52.6 ‰	1–3 ‰	0 ‰	> 3 ‰
$\text{CH}_4$ oxidation <sup>i</sup>	variable	1–3 ‰	12–15 ‰	6 ‰
$\text{CH}_4$ oxidation <sup>j</sup>	variable	1–3 ‰	> 91 ‰	95 ‰
$\text{CO}_2$ photolysis <sup>k</sup>	-30 ‰	14 ‰	31–34 ‰	3 ‰
NMHC oxidation <sup>c,g,h</sup>	-32 ‰	1–3 ‰	0–4 ‰	> 3 ‰

estimated effect bias in the reported  $\delta(^{13}\text{C})$  is at most 0.3 ‰. This is small and comparable to the effect on typical tropospheric measurements (Röckmann and C. A. M. Brenninkmeijer, 1998). Quantification of  $\delta(^{17}\text{O})$  is possible and recommended, to avoid the additional uncertainty related to assumptions made in the model to estimate MIF.

### 6.3 Source signatures of CO

Chapter 5 has provided an estimate or an updated estimate of four stable isotopic source signatures in CO. The first estimate of the source signature  $\text{CO}_2$  photolysis of both  $\delta(^{13}\text{C})$  and  $\delta(^{18}\text{O})$  was derived using the Keeling method Chapter 4. Furthermore, using an inverse model of CO isotopes,  $\delta(^{18}\text{O})$  values of the primary source of the oxygen atom in CO in the stratosphere were computed. In addition to a second estimate of  $\text{CO}_2$  photolysis  $\delta(^{18}\text{O})$ , these are  $\text{CH}_4 + \text{O}(^1\text{D})$  and  $\text{CH}_3 + \text{O}_2$  where it was shown that essentially all  $\text{CH}_3$  is produced from  $\text{CH}_4$  in the stratosphere at high latitudes. Table 6.1 lists an updated version of Table 1.2, presented in Chapter 1 and Table 1.2, with CO source signatures now including the results obtained from this work.

The isotope budget of CO was discussed. There are two pathways of  $\delta(^{13}\text{C})$  into CO, photolysis of  $\text{CO}_2$  and  $\text{CH}_4$ . Through two different dissociation channels of the reaction of  $\text{O}(^1\text{D})$  with  $\text{CH}_4$ , there are three different sources of oxygen. One relates to oxygen through the reaction of  $\text{CH}_3$ . The second is  $\text{O}(^1\text{D})$ , which attains its oxygen isotope signature from ozone. Finally,  $\text{CO}_2$  photolysis becomes an important source of  $^{18}\text{O}$  enrichment in the upper stratosphere, though it is likely produced in the mesosphere.

A computation using the measured rate parameter of the competing reactions of  $\text{O}_3$ ,  $\text{O}(^3\text{P})$ , and  $\text{O}_2$  with  $\text{CH}_3$  show that the resulting oxygen isotope composition of stratospheric CO derived from  $\text{CH}_3$  is primarily determined by the reaction with  $\text{O}_2$ . Only in unusual cases with a very high ozone abundance or an unusual temperature may the effect of  $\text{O}_3$  be significant. Yet, it would be still hard to differentiate with the techniques employed in this work. In addition to the calculation, the tagged chemistry model showed that at high latitude nearly all  $\text{CH}_3$  is derived from  $\text{CH}_4$

oxidation. These two results provide evidence that stratospheric CO derived from CH<sub>4</sub> has distinct apparent isotopic signatures in the produced CO. This may be different from the troposphere, where the intermediate CH<sub>2</sub>O can be removed by wet deposition or turned into CO<sub>2</sub> once dissolved in water droplets.

The source signature of CO<sub>2</sub> is a new addition to Table 6.1 presented by Vimont et al., 2019, and references therein, and of primary interest in middle atmospheric chemistry, applicable to the Earth's atmosphere. The two estimates presented in Chapter 5 agree well for  $\delta(^{18}\text{O})$ . The fractionation does not necessarily disagree with the laboratory work performed by Mahata and S. K. Bhattacharya, 2009; Mahata and S. Bhattacharya, 2009, because the chosen wavelengths presented in their work is not representative for the broadband photolysis in the upper stratosphere and mesosphere. On the other hand, estimated enrichment, based on calculations by J. A. Schmidt et al., 2013, appear to be an overestimation compared to the estimates obtained from the atmospheric observations in this work, under the assumption that CO<sub>2</sub> photolysis in the atmosphere does not occur for  $\lambda \leq 160$  nm.

The first estimate of the oxygen isotopic source signature of atmospheric CH<sub>4</sub> oxidation was presented by C. M. Stevens and Wagner, 1989, based on atmospheric measurements and a value of  $\delta(^{18}\text{O}) = 15$  ‰ was obtained. This result was contradicted by C. A. M. Brenninkmeijer, 1993; C. A. M. Brenninkmeijer and Röckmann, 1997, who obtained a figure close to 0 ‰. The data presented here do support the former, within the quoted uncertainty. As previously mentioned, the removal of CH<sub>2</sub>O by wet deposition may be a reason for a somewhat more variable apparent source signature in the troposphere.

## 6.4 Uncertainties in the budget of isotopic signatures of stratospheric CO

The isotope budget is well understood with the source signatures discussed in the previous paragraph. CO is produced from CH<sub>4</sub> and CO<sub>2</sub> in the middle atmosphere. The tagged chemistry results showed that part of the seasonality in  $\delta(^{18}\text{O})$  is explained by the unusual enriched CO derived from the ozone enrichment in the stratosphere via CH<sub>4</sub> + O(<sup>1</sup>D), which is also responsible for an increase with altitude when O(<sup>1</sup>D) is more abundant. At high altitude both  $\delta(^{13}\text{C})$  and  $\delta(^{18}\text{O})$  are more enriched through CO<sub>2</sub> photolysis derived CO transported from the mesosphere.

In addition, the measurements of  $y(\text{CO})$  and isotope composition have proven to be useful tracers of unusual sources of CO in the stratosphere. In Chapter 4, primarily the  $\delta(^{18}\text{O})$  proved to be a powerful tracer to identify wildfire smoke in the stratosphere. Then, Chapters 3 and 5 showed that increasing mole fractions and the isotopic signature of photolysis can be used to trace CO<sub>2</sub> to lower locations in the stratosphere.

In principle, the encounter with wildfire smoke has been a chance encounter, nevertheless, the isotope composition measurements have been proven invaluable, confirming the contamination source, based on in situ measurements. The methods outlined to determine the source signature as in Chapter 4, specifically the Monte Carlo simulation results would benefit from more frequent measurements in the troposphere. This is further corroborated by the results in Chapter 5, which suggest that part of the

seasonal cycle observed in the stratospheric CO isotopes can be traced back to its tropospheric origin. As such, utilisation of stable isotope measurements of CO in the lowermost stratosphere require observations of its tropospheric origin as well.

As an example of the point made in the previous paragraph, redoing the Monte Carlo simulations changing the uncertainty of the tropospheric and stratospheric isotope composition to 0.5 ‰, and the uncertainty of the stratospheric measurements of the mole fraction to less than  $0.5 \text{ nmol mol}^{-1}$ , which is not unthinkable if routine measurements were to be made, the uncertainty of the estimated fractions of stratospheric and tropospheric air reduces from 18 % to 15 %.

It is unknown whether the increase in  $y(\text{CO})$  observed at larger altitudes is only a feature at the poles or whether this is global. Mid-latitude vertical profiles of  $y(\text{CO})$  obtained by and AirCore do suggest that higher  $y(\text{CO})$  is present, and two different models predict the existence of the somewhat enhanced  $y(\text{CO})$ , though there appears to be an altitude discrepancy between observations and model predictions. This is not present in most of the observations obtained from previous work, where  $y(\text{CO})$  in general decreases, though it may be that those platforms did not reach the altitude where the CO starts increasing. Observations of the stable isotope composition could aid in identifying the origin of CO.

So far, all of these estimates are derived from atmospheric observations, assuming equilibrium between sources and sinks, and using the known fractionation in the latter. This is a mere practical requirement, and at least 2-dimensional modelling is required otherwise. Where this approach does provide a qualitative satisfactory explanation for the observed records, they do not provide enough information to evaluate the temperature dependence predicted from the computation of the fractionation (Weston, 2001). Secondly, as pointed out in the aforementioned works, the assumption of a steady-state is questionable, given the average atmospheric lifetime of CO, and the seasonal changing mean OH abundance. Minschwaner et al., 2010, concluded that photochemical loss of CO dominates production at atmospheric pressure between 0.02–10 hPa, which argues against a steady-state.

To assess the effect of OH when a steady-state does not apply, the CO species continuity equation was solved under restrictive boundary conditions in Chapter 4. To investigate the effect a wide range of OH abundance was investigated. Although successful in providing a distinct range of source signatures possible that allowed identification of the origin of the pollution source, it also illuminates the fact that the typical OH abundance can have a significant impact on the isotope composition of CO. This shows that any assumption on equilibrium should be treated with care. In this particular case, the observed pollution appeared to be only mildly fractionated.

In Chapter 5 on the other hand, the total effective fractionation was computed to be larger than expected based on a simple equilibrium. Consequently, the estimated source signatures in CO<sub>2</sub> photolysis would have been underestimated without the proper correction for fractionation in the sink. This may have also affected source signatures obtained in past work. Most likely the oxygen source signature of CO from CH<sub>4</sub> oxidation is underestimated. When interpreting remote atmospheric observations of CO stable isotopes, care has to be taken that the appropriate correction is applied, as this work has shown that this can be variable in space and time. Currently, this can only be provided by 3D modelling and potentially 2D modelling, using the method employed by Manning et al., 1997, and Bergamaschi et al., 2000, which was also

employed in this work.

This work showed that potentially very enriched CO is derived from the reaction of CH<sub>4</sub> + O(<sup>1</sup>D). Even though the uncertainty of the estimate presented here is large, the effect is so large that it is significant. Subsequently, measurements of δ(<sup>18</sup>O) and δ(<sup>13</sup>C) in CO provide direct insight in the importance of O(<sup>1</sup>D) to the CH<sub>4</sub> sink. In addition, the exceptionally large effect is better reconciled with the known isotope composition of the primary source of O(<sup>1</sup>D), if the O(<sup>1</sup>D) sink of CH<sub>4</sub> is larger. This is promising, and laboratory measurements of this particular reaction and the isotope effects are recommended. Although not conclusive, the results here would support the use of a higher rate, as suggested by Vranckx et al., 2008, for the reaction of CH<sub>4</sub> + O(<sup>1</sup>D).

## 6.5 The stratospheric CH<sub>4</sub> sink

Röckmann et al., 2011, showed that the sink partitioning of the three stratospheric methane sinks using the stable isotopes of CH<sub>4</sub> is complicated by the fact that the effective fractionation is pathway-dependent. In principle, the isotope composition of the more short-lived CO should reflect the local production. Thus, <sup>13</sup>C is determined by the three different fractionation pathways shown in the Chapter 1. In addition, the oxygen budget of CO is relatively simple, consisting of two sources: O<sub>2</sub> and O(<sup>1</sup>D). The latter is a direct tracer for the O(<sup>1</sup>D) sink. This qualitatively explains where certain sinks are more important.

Yet, numerical sink partitioning is complicated for several reasons. First, the 3D modelling results show that there is always a significant non-methane component to the observed CO which would add additional unknown terms to the mass balance. This results in an unknown term that can not be resolved. Secondly, for simple calculations, an important assumption necessarily to solve the mass balance is that of equilibrium. As discussed in the preceding paragraphs, there is conclusive evidence that a steady-state does not exist, and that a simple correction for the sink fractionation is not possible. The latter is complicated further by the lifetime of CO in the stratosphere. The horizontal and vertical structure of the stratospheric CH<sub>4</sub> sink can thus not be identified.

As a simple example of the above, consider the oxygen budget in the stratosphere. This can provide a soft upper limit to the fraction of O(<sup>1</sup>D) as the CH<sub>4</sub> sink. Under the assumption that a local steady-state exists, the oxygen isotope composition to a first approximation, is:

$$\delta(^{18}\text{O})_o + \varepsilon_{\text{OH}} = f_{\text{O}_2} \delta(^{18}\text{O})_{\text{O}_2} + f_{\text{O}(\text{}^1\text{D})} \delta(^{18}\text{O})_{\text{O}(\text{}^1\text{D})}, \quad (6.1)$$

with  $f_{\text{O}_2} + f_{\text{O}(\text{}^1\text{D})} = 1$ , this can be solved to yield  $f_{\text{O}(\text{}^1\text{D})}$ . Making use of the constant branching ratio of this channel,  $b = 0.25$ , the total fraction of CO from CH<sub>4</sub> + O(<sup>1</sup>D) can be computed. In this model, other sources of CO are neglected, which is an assumption that cannot be made. Under the assumption that the local lifetime of CO is much shorter than the vertical transport timescale, this value than represents an upper limit estimate of O(<sup>1</sup>D) + CH<sub>4</sub>. This estimate however, will be biased high, first because of the typical other sources of CO with high enrichments, i.e. tropospheric air and CO<sub>2</sub> derived CO. Secondly, equilibrium fractionation may over or underestimate the effective  $\varepsilon_{\text{OH}}$ .

On the other hand, the relatively simple processes that make up the CO budget can be easily simulated. Stable isotope analysis of CO, therefore, does provide very useful observations, which can be used to constrain stratospheric chemistry models that include a detailed CH<sub>4</sub> oxidation scheme. The stable isotope observations can provide an indirect constraint on the CH<sub>4</sub> sink through isotope enabled chemistry scheme, as was successful in identifying Cl as an important sink under ozone hole conditions (Müller et al., 1996).

Although the focus of this work has been stratospheric CO, the intimate relation of CO with CH<sub>4</sub> in the stratosphere naturally led to the exploration of implications of these results the CH<sub>4</sub> sink in the stratosphere. This work does not provide direct evidence to support any claims about the CH<sub>4</sub> sink, and its potential has been discussed above. However, it does provide strong pointers which may lead to fruitful results for future research.

First, the analysis in Chapter 3 showed that the overestimated vertical mass transport, due to a cold bias present in many models, is counterbalanced by underestimated CO production from CH<sub>4</sub>. The bias in CO that should be visible in the stratospheric mole fractions is not observed by comparing the model observations with mole fraction measurements. The overestimated mass transport is clearly visible in profiles of CH<sub>4</sub> and CO<sub>2</sub>.

A second indication for underestimated CH<sub>4</sub> sink was presented in Chapter 5. The oxygen isotope signature in the reaction between CH<sub>4</sub> and O(<sup>1</sup>D) could be better explained if the relative contribution of O(<sup>1</sup>D) to the overall CH<sub>4</sub> sink is larger. Indeed, recent measurements of the kinetics of the reactions suggest that the reaction is underestimated by as much as 26 %. Which in turn, would have an effect on the stratosphere chemistry.

These two effects combined suggest that at high latitudes the CH<sub>4</sub> sink in the stratosphere is potentially underestimated by 10 %. It is also worthwhile to note that if this were to be confirmed, this potentially changes the distribution of CH<sub>4</sub> in the stratosphere, and also the production of stratospheric H<sub>2</sub>O. As O(<sup>1</sup>D) is strongest in the tropical pipe, this may also change the distribution of stratospheric water vapour. Secondary, the OH produced from this reaction may also have profound secondary effects on ozone chemistry.

## 6.6 Outlook and recommendation

In summary, this dissertation reports novel CO isotope measurements performed on air samples from the stratosphere. The samples are obtained using a newly developed sampler named the LISA sampler. In addition to the stable isotope measurements, air samples are analysed for a suite of greenhouse gas mole fractions, namely CO<sub>2</sub>, CO, CH<sub>4</sub>, and N<sub>2</sub>O. The results are used to evaluate the performance of two general circulations models with online chemistry, CAMS reanalysis and EMAC. Aided by tagged chemistry modelling performed with EMAC, the most important in situ pathways of CO are traced, to understand the isotope budget of CO. Estimates of unknown source signatures from two important atmospheric sources relevant for the stratosphere, oxidation of CH<sub>4</sub> and CO<sub>2</sub> photolysis, are obtained. CO<sub>2</sub> photolysis occurs primarily in the mesosphere and not in the stratosphere, thus its signature can be used to trace

air from the mesosphere where it is the dominant source of CO. In addition, CH<sub>4</sub> oxidation inherits an oxygen signature from O<sub>2</sub>. A secondary source is the reaction of CH<sub>4</sub> with O(<sup>1</sup>D), providing a route for the exceptionally high oxygen enrichment in ozone into CO. It is also shown, however, that the potential to directly constrain the CH<sub>4</sub> sink is limited. Stable isotopes can, however, be used to identify non-stratospheric air. Both enhanced CO mole fractions from the mesosphere and tropospheric pollution, wildfire smoke, showed distinctly different CO isotope enrichments, compared to the background.

The results obtained in this work provide several directions for future research. Continuation of validation and comparison of LISA against other methods is recommended. In addition to AirCore, Global Hawk and balloon-borne platforms such as Spirale, could provide additional validation for the sampler. This would further validate the capabilities of , or show yet unknown problems. Then, experiments aimed at the determination of the exact enrichments obtained from broadband wavelength-dependent CO<sub>2</sub> photolysis and the oxidation of CH<sub>4</sub> are highly encouraged. Especially the details of CH<sub>4</sub> + O(<sup>1</sup>D) could provide unique information on that reaction, and add to the potential use of these reactions as a constraint on the CH<sub>4</sub> sink. Also, future observations of atmospheric CO and its isotope composition would benefit from a more fundamental understanding of the processes underlying the budget. The simplicity of the budgets as discussed in this work could be confirmed. Then observations of the isotope composition could provide an excellent way to constrain GCMs. Finally, the effect of the temperature bias and stratospheric transport properties on the kinetics of the carbon chemistry in the stratosphere should be evaluated. Computation performed in this work shows that a potential bias in the stratosphere may exist. This is supported by the isotope observations in this work.