Replies to Review #2 for

Interactive comment on "Abundances, emissions, and loss processes of the long-lived and potent greenhouse gas octafluorooxolane (octafluorotetrahydrofuran, *c*-C_4F_8O) in the atmosphere" by Martin K. Vollmer et al.
By Anonymous Referee #2 (Received and published: 25 October 2018)

Replies to the reviewer comments are added in blue color following each comment, and the revised text is in green.
We thank the reviewer for his/her input. We believe that with the suggested changes to these valuable comments, the manuscript will improve.

Reviewer Comment: General comments:
The article presents a large dataset and budget estimate for a newly detected compound in the atmosphere: *c*-C_4F_8O. Although its abundance is small (less than 0.1ppt) its radiative efficiency is strong and lifetime likely very high. It is still unregulated and sometimes viewed as a promising compound in terms of industrial applications (see for example Kočišek et al., 2018). I think that its scope and novelty make it adequate for a publication in ACP. I have some comments on the methodology and presentation.

Reviewer Comment: The Northern Hemisphere (NH) measurements are little described and commented (p 1 l5-6, p3 l14-15). The article should explain how the North Hemisphere trend (dashed line on Figure 1) was constrained and evaluate the uncertainty on emissions resulting from the lack of NH constraints.

Reply: Northern Hemisphere samples are planned to be better described in the Supplement as follows:
"S-2.5 Northern Hemisphere (NH) samples
The Southern Hemisphere Cape Grim Air Archive (CGAA) samples were complemented with a few archived air samples from the Northern Hemisphere (see also Table S3). Some of these samples were collected as whole air ambient background samples for original calibration purposes: UAN920470 at Cape Meares, Oregon, most likely cryogenic techniques; T-EMPA-1 and J-187 at La Jolla, California using an oil-free diving compressor (Rix Industries); EG-003 at Jungfraujoch, Switzerland, using cryogenic techniques. H-160 at Mace Head, Ireland, using an oil-free diving compressor. These samples were all collected in internally electropolished stainless steel canisters (Essex Industries, USA). Two samples collected at Dubendorf (DUE161216-D2 and DUE161216) were collected into 6-L internally electropolished cylindrical custom-fabricated containers (LabCommerce, California) using a diaphragm pump (KNF-N-022-ANE, Neuberger), for the specific purpose of this project. These two samples, and EG-003 and H-160 were shipped from Empa to CSIRO for analysis along with the CGAA samples under same measurement conditions."

We have now also better described how the NH trend was constrained. The text added is:
"The *c*-C_4F_8O measurements in the Southern Hemisphere provide a strong constraint on the trend in both hemispheres due to the very long lifetime of *c*-C_4F_8O in the atmosphere, the relatively rapid mixing of the atmosphere, and the expectation that most *c*-C_4F_8O emissions are in the Northern Hemisphere (NH). Most anthropogenic gases are released predominantly in the NH, including gases released by the semiconductor industry. The assumption of mainly NH emissions for *c*-C_4F_8O leads to higher mole fraction values in the NH, and this is confirmed by comparison of the modelled NH history with the few NH measurements that we do have. In the Supplement, we test the sensitivity of inferred global emissions and mole fraction in both hemispheres to the assumed spatial distribution of emissions, and show the uncertainty in inferred mole fraction in both hemispheres."

Reviewer Comment: Similarly, the mixing ratio and emission trends between 1950 and 1978 are mostly constrained by a single firn air data point undergoing a large age distribution, and having a mixing ratio (6 ppq, Table S4) very close to the detection limit (5 ppq, p4 l13). The article should explicitly discuss the constraints on the anthropogenic versus natural sources of c-C_4F_8O, as well as the little constrained early emissions.

Reply: We agree, and suggest to change the text in the results section to address these concerns: “This suggests that *c*-C_4F_8O was below 10 ppq in the Southern Hemisphere before 1978. However it is impossible to further pin down the first appearance of this compound in the atmosphere and the exact course of the abundance until ~1980 because our knowledge of *c*-C_4F_8O prior to the CGAA is based on only one firn sample measurement with air spanning several decades (see calculated Green's functions in the Supplement). Also, potential small contamination during firn air sampling by modern air or sampling devices cannot be fully excluded. Additionally, the measurement of the older firn air sample is close to the instrument's detection limit. Given these limitations, we are not able to draw any conclusions on any potential naturally-occurring *c*-C_4F_8O. Nevertheless, the two firn air sample measurements allow us to draw conclusions on storage stability of *c*-C_4F_8O in canisters. Given that the storage time of the two firn air samples in the canisters is much shorter than those of the older CGAA samples, the good agreement of the firn air results with those of the CGAA is supportive of storage stability of *c*-C_4F_8O in the CGAA tanks and confirms that the observed multidecadal record is not a simple artifact of degradation of *c*-C_4F_8O in canisters over time.”

In addition we suggest to show the early history with dotted lines rather than solid lines,to emphasize the greater uncertainty before 1978. See revised figure further below.

Reviewer Comment: However, for a well-mixed very long lived species, a reasonable estimate of global emissions can be obtained from a simple one box model calculation. Presenting this simple calculation and comparing it to the elaborate approach used would improve the description of the main uncertainties and be helpful to non-specialist readers.

Reply: We believe that adding another model calculation would be rather confusing than helping to understand the main uncertainties. The 12-box model has been used and validated many times in the past in numerous publications and doesn’t need to be re-assessed here. Nevertheless, we have made a quick intercomparison based on an 1-box model using the following assumption: 1.8E20 mol of air in the total atmosphere; well mixed (no delay in stratosphere); no sinks; using the fitted observations from the 12-box model. Admittedly, the latter assumption creates some degree of dependency to the 12-box model, but an independent fit through the observations would not significantly alter the results. The result is shown here in the subfigure c) as orange line. Some of the discrepancies to the emissions from the 12-box model is likely caused by the above assumption, in particular that of a uniform vertical atmosphere. In addition, we have calculated the cumulative emission in a 1-box model approach using the end-of record mole fractions of about 74.5 ppq. Again using 1.8 E20 mol of air in the total atmosphere and no sinks for *c*-C_4F_8O, we calculate 2.89 kt, which compares well with the 2.85 kt from the 12-box model. We propose to not mention these 1-box model results in the revised text for the reasons mentioned above.

Reviewer Comment: A first estimate of the lifetime of c-C_4F_8O is provided but some important assumptions should be better described: the basis for the estimated Lyman-α lifetime and OH reactivity (comparison with species having similar bonding structures?), the possible role of other unexplored sinks such as surface loss (to ocean and land) and heterogeneous processes should be discussed at least in terms of perspectives.

Reply: Thank you for addressing these points. We handle the comments regarding Lyman-alpha and OH reactivity as part of the replies to reviewer 1, and would like to refer to that reply.
With regard to other possible sinks, we suggest to add the following sentence to the Introduction (following the discussion on the lack of existing information on atmospheric loss of the compound): "Information is also lacking on other potential loss processes for *c*-C_4F_8O, such as uptake by oceans and land".

We also suggest to add the following sentence to the description of the 12-box model: "Loss processes other than those in the atmosphere, such as uptake by land and oceans, and potential natural sources, are not included in the model."

Further, we suggest to add the following sentences to the discussion of the 'Atmospheric Lifetime (3.4)':
"This study has focused primarily on the atmospheric loss processes of c-C_4F_8O*, i.e., potential deposition or heterogeneous loss processes of c-*C_4F_8O *were beyond the scope of this study. Deposition or heterogeneous loss processes, if significant, would lead to a shorter global lifetime for c-*C_4F_8O*."*

Ultimately we modified the last sentence in the conclusions to: "However, even if emissions were completely halted, it will, under the assumption of insignificant non-atmospheric sinks, take thousands of years for *c*-C_4F_8O to be removed from the atmosphere."

Reviewer Comment: Specific comments:

p2 l10-11: The Californian regulation could be mentioned (https://ww2.arb.ca.gov/resources/documents/semiconductor-regulation)
Reply: We have explored this a bit more. Rather than mentioning the Californian regulations, we have mentioned the US EPA regulations and IPCC. The revised text is suggested as

"The compound is listed in the Intergovernmental Panel on Climate Change (IPCC) 2006 guidelines in support of UNFCCC (IPCC, 2006, Volume 1, Chapter 8) as a compound, for which countries are encouraged to provide emissions estimates (on a mass unit until a published greenhouse warming potential (GWP) will become available). In the 2013 Revisions of the UNFCCC reporting guidelines (UNFCCC 2013), *c*-C_4F_8O is absent from the list of compounds with mandatory reporting. Additional reporting regulations exist on country or state levels. In the USA, large suppliers and emitters of *c*-C_4F_8O are required to report the amounts they supply or emit under the Greenhouse Gas Reporting Program (GHGRP, URL: https://www.epa.gov/ghgreporting, accessed January 2019). When CO2-equivalent emissions are required for these submissions, a default GWP for fully fluorinated GHGs of 10,000 is used due to the lack of a peer-reviewed GWP. Emissions have mainly been reported under the ``Fluorinated Gas Production'' subpart for 2011--2017 with a maximum of 40 t in 2013 and a subsequent decline to 4.5 t by 2017"

Reviewer Comment: p5 l11-14: As pumping out the interstitial air from deep firn can be difficult and induce contamination, more indications should be provided about the multi-species consistency of model results for the deep firn air sample used and the overall firn. For example, the RMSD/σ indicator used in Buizert et al. (2012) could be provided. The reason why so few depth levels were analyzed for c-C_4F_8O should be given, sample size issue?

Reply: The two ABN firn measurements play only a small role in this study. It is discussed above that the early history is not well constrained by the single deep firn measurement due to its age spread, and that contamination cannot be ruled out. Another publication is underway that will describe the ABN measurements and modelling in much greater detail, including showing how well the firn model fits all measurements used for calibration. The level of detail suggested by the reviewer is not seen as necessary for this study given the small role of the firn measurements, so no further change has been made.

We suggest to add the following sentence to explain why there were only 2 samples available for this project (in Methods).
"Only two samples were available for the present study as other samples from this site were used for a different halocarbon study."

Reviewer Comment p5 l14-18: The Trudinger et al. (2013) model uses both molecular and eddy diffusivity terms. As this has the same effect as modifying the diffusion coefficient, the relative roles of molecular and eddy diffusivity terms for the ABN firn should be commented.

Reply: We plan to comment on this by adding the following: "Only molecular diffusion was used for the ABN firn model calculations; eddy diffusivity is sometimes used in the deep firn but was not used here as the parameters were not well constrained by the available measurements".

Reviewer Comment: p5 l19-26: how were the North Hemisphere concentrations evaluated?
Reply: We are not clear about this comment. We assume that it is related to the first comment about the NH concentrations, and believe to have addressed this comment sufficiently there.

Reviewer Comment: p5 l29: Vollmer et al. (2016, 2018) used multi-depths firn air constraints from both hemispheres. The methodological adaptations to the lack of NH constraints should be described.

Reply: The method was not adapted from Vollmer et al (2016, 2018) due to the use of only SH constraints. As described above, the NH trends are well constrained by SH measurements due to the long lifetime and predominantly NH emissions.

Reviewer Comment: p6 l1: I do not understand what the Green’s functions from the 12-box model are and did not see an explanation in Vollmer et al. (2016, 2018)

Reply: To clarify this, we suggest to add the following text “Green’s functions derived from the 12-box atmospheric model relate atmospheric mole fraction in the high-latitude Northern and Southern Hemispheres to annual global emissions in preceding years, and are used in the inversion (Trudinger et al;, 2016).”

Reviewer Comment: p6 l11-13: The emission values in Ivy et al. (2012) start in 1980 (Table 3), how was the prior estimate designed for the 1950-1980 period and what impact does it have on the final solution for this weakly constrained period?

Reply: We suggest to add some text to correct for this shortfall. Although of importance, we consider it a detail that better fits into the supplement, in particular in relation to (original) Fig. S4, where we graphically show what we did. The suggested text is:
“We construct a *c*-C_4F_8O prior history from emissions of perfluorooctane because this compound has similarly low abundances and a long lifetime as *c*-C_4F_8O. For our standard case, we use perfluorooctane emissions published by Ivy et al. (2012) for the 1980 – 2010 period with the perfluorooctane 2010 value as a constant value for 2010 – 2017 and the 1980 value for perfluorooctane for the 1950 – 1980 period. We also test the sensitivity of our results to a number of other prior histories. a) the standard case doubled, b) the standard case halved, c) the standard case with emissions before 1980 extrapolated back to zero in 1950 and d) a small linearly increasing function (all shown in Fig. S4). Our analysis shows that the emissions derived for *c*-C_4F_8O are rather insensitive to the choice of the prior, because the prior is used as a starting point for the inversion only, and not as a constraint.”

Reviewer Comment: p7 l23 and after, including section 2.2 of the Supplement: a single notation should be adopted to name reaction rates, avoid using kR, then k1 (implicit) and k2, then kc-C_4F_8O.

Reply: We agree and suggest the following revision: “kR” will be replaced by “k_1”, and “$k_{c\text{-}C4F8O}$” and “k_{CHF3}” will be replaced by k_{1a} and k_{2a}, respectively in the Equation II. In the supplement, “k/k_{CHF3}” in Table S5 will be replaced by “k_{1a}/k_{2a}”. In the footnote of Table S5, “k_{CHF3} (O(^{1}D) + CHF_3) = 2.4×10^{-12} cm^3 $molecule^{-1}$ s^{-1}” has been replaced by “k_{2a} = 2.4×10^{-12} cm^3 $molecule^{-1}$ s^{-1}”.

Reviewer Comment: p10 l9: Figure 4 is little commented, it could be shifted to the Supplement or combined with Fig. 2

Reply: We prefer the Figure 4 to remain in the manuscript. It shows how IR absorption bands fall within the atmospheric window qualitatively and quantitatively. It is also used as a basis for Radiative Efficiency calculations and the discussions on GWP (p. 10 L. 9–13).

Reviewer Comment: p10 l26-27: circular argument, the calculated growth rate is small because the measured concentration trend is weak (in recent years), not the contrary.

Reply: Thank you for spotting this. We suggest to change the sentence(s) to: “The growth rate was at a maximum of 4.3 ppq/yr in 2004 and declined from that to <0.15 ppq/yr in 2017 as a consequence of the relatively constant abundances in the last few years.”

Reviewer Comment: p11 l6-9: the important Aspendale dataset (thousands of measurements) is briefly summarized in Table S3 and very briefly commented. A more in-depth discussion of c-C_4F_8O variability at various sub-annual time scales and recent trend, as well as a plot (at least in the Supplement) would be useful.

Reply: We plan to address this comment by providing an additional section in the supplement including a figure showing the high-resolution data set from in-situ measurements at Aspendale. There is no in-depth discussion on sub-annual time scales and trends, as there is no variability for this record, which we have already stated in the main text.
The revised text and figure is suggested as follows:

"S-2.6 In-situ measurements of *c*-C_4F_8O at Aspendale
Regular measurements of *c*-C_4F_8O in ambient air at Aspendale were started in February 2017. These were conducted on a 2-hourly basis whereas each air measurement is bracketed by standard measurements. Results are shown in Fig. S4. A few ambient air measurements were also made in late 2016 during the CGAA measurement phase. These were made from 3 L samples (vs the regular 2 L samples) and show improved precisions compared to the remaining record. The 2-year record shows constant *c*-C_4F_8O mole fractions within the precisions of the measurements. There is no sign of any pollution events in this record suggesting that there are no significant sources of *c*-C_4F_8O within the footprint of the site. Furthermore and given the long atmospheric lifetime of the compound, the absence of a significant trend is suggestive of the absence of major global emissions in the last years."

Figure S4. Ambient air measurements of c-C4F8O at Aspendale (Victoria, Australia, 38.0 °S, 145.1 °E). The measurements are expressed as dry air mole fraction in parts-per-trillion on the Empa-2013 calibration scale. Results show constant *c*-C_4F_8O within the precision of the measurement.

Reviewer Comment: p11 l26: the wording "a few other synthetic greenhouse gases" implicitly assumes that *c*-C_4F_8O is purely anthropogenic but this is not discussed in the article

Reply: The reviewer is correct. We suggest to remove the word 'synthetic'.

Reviewer Comment: p12 l6: due to the high cost of Antarctic field operations, research programs and logistic institutions financing them are usually explicitly named.

Reply: While we agree with the reviewer on the large-scale operations of the Antarctic field programs, this has to be also viewed in ratio to other contributions and be somewhat balanced. For example, compared to the two firn air samples, the input from the general AGAGE operation is large, AGAGE is a very large and costly long-term network and yet we cannot acknowledge all of its sub-contributions and funding agencies.

Reviewer Comment: pS7 l16 of the Supplement: the chosen 1 ppq uncertainty seems small compared to the stdv values in Table S3, this choice should be further commented.

Reply: The 1 ppq uncertainty is the magnitude of the uncertainty in the smoothed annual values, that come from the smoothing spline fit to the measurements. The uncertainties are much less than the stdv values of individual measurements, but relate to the uncertainty from the smoothing spline.

Reviewer Comment: pS10 l6-10 of the Supplement: this discussion of background / non anthropogenic level of c-C_4F_8O should be in the main article

Reply: We agree on this and suggest to add text related to natural/synthetic c-C_4F_8O in the main text of the manuscript, see replies to one of the above general comments by the reviewer. The key sentence there is: "Given these limitations, we are not able to draw any conclusions on any potential naturally-occurring c-C_4F_8O."

Reviewer Comment: Technical corrections:
p 5 l7 use indices in c-C_4F_8O
Reply: This is now fixed an the chemical formula is written with indices.

p 5 l11-14 repeats l4-8
Reply: Thank you for spotting this error, we plan to remove the second mentioning

p 5 l16 and 18 suppress))
Reply: We believe that both closing parentheses are necessary.

p 6 l12 from observations of
Reply: Fixed, we removed the erroneous comma.

New references:
Reply: We have now added the Kočišek et al. (2018) reference, we did not need to add the Buizert et al. (2012) reference.