Replies to Review #1 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 #1 (Received and published: 16 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: This paper presents atmospheric measurements of C4F8O along with laboratory studies of its IR spectrum and loss processes via photolysis and reaction with O(1D). The conclusion is that C4F8O is very long lived (> 3000 y) and has a GWP100 of the order of 12000.

Whereas the laboratory studies of the IR spectrum appear to be of high quality, the investigation of the UV spectrum and the reaction with O(1D) are rather disappointing. It is not clear if C4F8O absorbs in the 200-225 nm investigated (the authors do not present a Figure) and the O(1D) reaction appears to have been carried out with a reference reactant that reacts too rapidly with O(1D) to get a good number for the rate coefficient. The most disturbing aspect is that the authors calculate that Lyman-alpha absorption may actually dominate the atmospheric loss of C4F8O, but only an unfounded guesstimate of the cross-section is made. A measurement of the VUV spectrum of C4F8O would significantly improve the laboratory studies and the manuscript as a whole. In addition, no mention is made of loss via hydrolysis (ocean) or reaction on particles. If such loss processes can indeed be neglected, the authors should provide physical constants (e.g. solubility / hydrolysis rate constants from the literature) that support this. These issues should be addressed in a revised version, as should the comments below:

Reply: We address the individual concerns below where most of them are mentioned in a more specific form. With regard to losses other than atmospheric, we refer to the replies to reviewer 2, who has commented on similar issues. Note that research on this compound is extremely sparse, e.g. we have not found reasonable peer-reviewed solubility data, to further investigate other potential sink. This is also clearly out of the scope of this study.

Reviewer Comment: Acronyms: use of acronyms is fine if it improves readability. The term ABN appears only three times in the manuscript (the first time being its definition). I would encourage use of the full name Aurora Basin North (as used in Figure 1).

Reply: We agree with this suggestion and suggest to use the full name for Aurora Basin North in the main text. However, in the supplement, the term 'Aurora Basin North' appears many times, consequently we suggest to use the abbreviated form (ABN) there.

Reviewer Comment: P6L29 Some of the terms (A, I, L) need to be italicised as in the equation they refer to.

Reply: This is now fixed, also with regard to equation II.

Reviewer Comment: P6P6 Estimated accuracy of 1 %. Please state how this value is calculated.

Reply: This probably refers to P7L6, not P6L6. The estimated accuracy is based on the estimated uncertainty of the pressure measurements used in the preparation of the standard gas mixtures. These include the uncertainty in the sample pressure, the total mixture pressure, and the linearity of the pressure gauge (estimated to be 0.2%). On the basis of these estimates, we report an estimated accuracy of around 1%.
We suggest to revise the sentence on P7L5 "The dilute mixtures of *c*-C_4F_8O in a He (UHP, 99.999 %) bath gas was prepared manometrically in a 12 L Pyrex bulb with an estimated accuracy of 1 %." by "The dilute mixtures of *c*-C_4F_8O in a He (UHP, 99.999 %) bath gas were prepared manometrically in a 12 L Pyrex bulb with an estimated accuracy of 1%, as derived from the accuracy of the pressure measurements. The pressure measurement uncertainty includes the uncertainty in the sample pressure, the total mixture pressure, and the linearity of the pressure gauge (estimated to be 0.2%)."

Reviewer Comment: P7L15 What was the effective spectral resolution of the MC/CCD?

Reply: The resolution of the UV spectrometer was ~1 nm.
Actions Taken: P7L16, the sentence "…using a 0.5 m spectrometer equipped with a charge-coupled device (CCD) detector." will be replaced by "… using a 0.5 m spectrometer (1 nm resolution) equipped with a charge-coupled device (CCD) detector."

Reviewer Comment: P7L24 The chemical element O should not by italicised.

Reply: This is now fixed.

Reviewer Comment: P8L4 Why not use the terms k1a and k2a to define the rate coefficients for reactions 1a and 2a. Also in equation (II) ?

Reply: Yes, k_{1a} and k_{2a} are the reactive rate coefficients for the reaction of $O(^1D)$ with *c*-C_4F_8O and CHF_3, respectively. In the Equation (II), $k_{c\text{-}C4F8O}$ and k_{CHF3} are suggested as replacements for k_{1a} and k_{2a}, respectively.

Reviewer Comment: P8L3 replace "at times t0 and t" with "at times zero and t".

Reply: Done, it now reads 'at times zero (t_0) and t.

Reviewer Comment: P8L11 The chemicals element (O) should not be italicised

Reply: This is now fixed.

Reviewer Comment: P8L19 is the "dark" loss of C4F8O measured in the presence of O3 ?

Reply: Yes, under these experimental conditions, the loss of *c*-C_4F_8O in the absence of $O(^1D)$ production implies the dark loss of *c*-C_4F_8O under identical experimental conditions.
Actions Taken: The sentence "Experiments performed separately demonstrated that there was no significant loss of *c*-C_4F_8O or CHF_3 in the absence of $O(^1D)$ production." will be replaced by "Experiments performed separately demonstrated that there was no significant loss of *c*-C_4F_8O or CHF_3 under identical conditions in the absence of photolysis."

Reviewer Comment: P8L23 Figure 2 is mentioned before Figure 1. The numbering of the Figures needs adjusting.
Reply: This is now fixed, first-mentioned figure (IR spectrum) is now Figure 1.

Reviewer Comment: P8L28 Equation (I) describes absorption at any discrete wavelength, ï¿Aˇn and not over a range of wavelengths as the integrated band strength is calculated.

Reply: The reviewer is correct, and the revision is suggested for P8L27 by replacing the sentence "Absorption spectra were quantified using Beer's law" by "Absorption spectra, A(v) (base e), (or integrated band strengths) were quantified using Beer's law"

Reviewer Comment: P8L28 The uncertainty estimates need attention. How do the individual uncertainties of combine to result in 3% ? How about the 1 % uncertainty quoted previously for the dilution in He ?

Reply: The absolute uncertainty of the total integrated band strength was based on the root mean square analysis including the estimated uncertainties of the measured absorbance (±0.5%), the optical pathlength (±0.5%) and the concentration (±1%). The uncertainty of the concentration is directly related to the pressure uncertainty where a value of ±1% has been used for the calculation. This resulted to a total uncertainty of 2.1%. We assigned a conservative uncertainty of 3%. We suggest to leave the text unaltered and not include such detail of how the estimate was derived.

Reviewer Comment: P9L3 cross sectionS decreasing monotonically

Reply: This is now fixed, the word is pluralized.

Reviewer Comment: P9L7 An upper limit for the absorption cross section is presented. Please add a Figure (Supp. Inf) to clarify how this value was obtained.

Reply: The following figure will be added in the Supplement. At the end of P9L4, the sentence "(An example of the measured UV spectrum of the *c*-C_4F_8O sample is shown in the Supplement)" will be added.

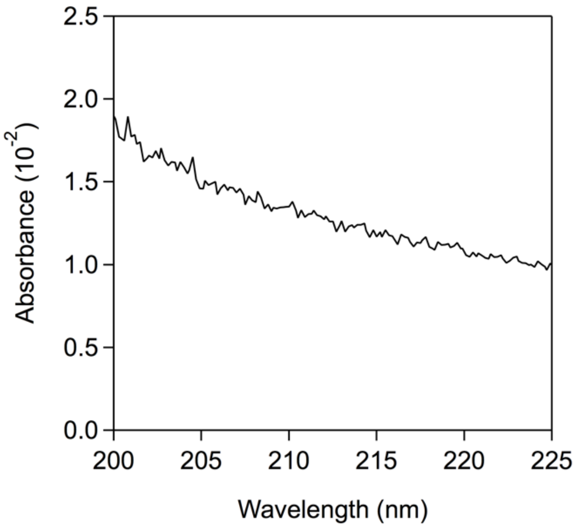

Figure S2. Measured 296 K gas-phase UV spectrum of the octafluorotetrahydrofuran (*c*-C_4F_8O) sample used in this study. The *c*-C_4F_8O concentration was 2.16□ x 10^{19} molecule cm^{-3}. Assuming no absorption from possible sample impurities, the *c*-C_4F_8O absorption cross section at 210 nm was found to be 6.25 x 10^{-24} cm^2 $molecule^{-1}$. As discussed in Section 3.2, such a low cross section is susceptible to overestimation due to the presence of impurities in the *c*-C_4F_8O sample. Therefore, this spectrum was considered as an upper-limit in our lifetime analysis.

Reviewer Comment: P9L16 The problem with this measurements of the relative rate coefficient is that while measureable amounts (up to 10 %) of CHF3 are removed, the changes in the C4F8O concentration are too low to measure reliably. Could this have been improved by a better choice of reference compound (i.e. one that reacts more slowly with O(1D)? Why was the experiment stopped after only 10% of CHF3 was depleted ? Which absorption bands of C4F8O and CHF3 were used to derive the fractional losses? Unless there are good arguments against, the authors should consider doing further experiments to nail down this number. Alternatively, they might consider using the correlation between ionisation potential and O(1D) rate coefficient that is frequently used to estimate the latter.

Reply: Regarding the $O(^1D)$ reaction, presently there is not a more reliable reference compound to be used. Note that it is extremely difficult to accurately measure small $O(^1D)$ rate coefficients. It is also worth noting that an improved measure of the $O(^1D)$ reactive rate coefficient for the furan reaction would not significantly alter our conclusions regarding the atmospheric loss of the furan. In this work, a conservative upper-limit rate coefficient was reported that can be refined in the future, if warranted.

Regarding the extent of reaction: The 248 nm photolysis of ozone was used as a source of $O(^1D)$ in the photochemical reactor. The introduction of ozone to the reactor was accompanied by an addition of molecular oxygen. After multiple ozone additions, the reaction of $O(^1D)$ by O_2 can dominate the $O(^1D)$ loss, making the $O(^1D)$ + furan and $O(^1D)$ + CHF_3 reactions less significant.

Regarding the absorption bands: The absorption bands used in this study were 1120-1000 and 1180-1120 cm^{-1} for *c*-C_4F_8O and CHF_3, respectively.

Regarding further laboratory studies of the $O(^1D)$ reaction: Based on our experimental data and analysis, the $O(^1D)$ reaction will have a minor impact on the furan global atmospheric lifetime. Therefore, at our current level of understanding of the atmospheric chemistry and modeling (i.e., lifetime determination for persistent compounds) further refinement of the $O(^1D)$ rate coefficient is not warranted at this time.

The sentence "the precision of the infrared spectral subtractions are the primary sources of uncertainty in the measurements." will be replaced by "the precision of the infrared spectral subtractions are the primary sources of uncertainty in the measurements. The low conversion of the *c*-C_4F_8O and CHF_3 achieved in these experiments was primarily due to the build up of O_2 associated with the addition of ozone to the reactor, making the loss of $O(^1D)$ by reaction with O_2 more significant than its reaction with *c*-C_4F_8O and CHF_3. The absorption bands used in this study were 1120-1000 and 1180-1120 cm^{-1} for *c*-C_4F_8O and CHF_3, respectively."

P9L16, at the end of the paragraph of the Section 3.3, the sentence "Given the small $O(^1D)$ rate coefficient for the reaction between $O(^1D)$ and *c*-C_4F_8O, a refinement of the measured $O(^1D)$ reactive rate coefficient will have a negligible impact to the total atmospheric loss of *c*-C_4F_8O." is suggested to be added.

Reviewer Comment: P9L24 The authors state that reaction with OH will not represent a loss of C4F8O in the atmosphere. I agree, but the authors should state why this is most likely to be the case. Will a perfluorinated furan react with OH like other fully fluorinated organics? What upper limit to the OH-rate coefficient would be necessary for OH reaction to compete with O(1D) induced losses?

Reply: As stated, the loss of *c*-C_4F_8O by reaction with OH radicals is most likely a negligible process. Due to laboratory challenges, it is not possible to measure values approaching 1×10^{-17} cm^3 $molecule^{-1}$ s^{-1} (equivalent to 3000 years lifetime). We estimate that our laboratory measurements would, at best, yield a rate constant upper-limit of $\sim 1 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}, which would be a gross overestimate of the true rate constant. Reporting such a rate constant would be very misleading and possibly misinterpreted by the community. We did not attempt to conduct OH reactivity measurements of this compound for these reasons. The expected low-reactivity of the furan is supported by its low O(1D) reactivity. To compete with O(1D) induced losses, the OH rate coefficient would be equivalent to >1 x 10^{-18} cm^3 molecule^{-1} s^{-1}.

Actions Taken: P9L22, the sentence "The loss of *c*-C_4F_8O via reaction with the OH radical is assumed to make a negligible contribution to the global lifetime and consequently we ignore the last term in Equation 4." is planned to be replaced by "The loss of c-C_4F_8O via the reaction with the OH radical is assumed to make a negligible contribution to the global lifetime in our analysis. the OH rate coefficient would need to be ~1 x 10^{-17} cm^3 molecule^{-1} s^{-1} (equivalent to a 3000 year lifetime) to make a significant global lifetime contribution. Such a low rate coefficient represents a significant challenge to current rate coefficient measurement methods. Additionally, an expected OH low-reactivity of the furan is supported by its low O(^{1}D) reactivity measured in this work. Additional laboratory studies that are beyond the scope of the present work would be needed to quantify the OH reaction."

Reviewer Comment: P10L3 The authors state that is reasonable to assume a Lyman-alpha cross-section of about 1x 10-17 as it is "roughly consistent" with highly fluorinated compounds. As the authors go on to conclude that this process has the shortest associated lifetime, I find this unacceptably vague. What is the physical basis for assuming that a fluorinated furan will absorb at 121.6 nm with the same cross section as non-heterocyclic, perfluorinated gases? Measurement of the cross section at this wavelength is not impossible. The NOAA lab certainly has VUV capability (e.g. for 185 nm measurements using Hg-lines) which could be extended to 121.6 nm. Surely even a rough experiment is better than a precarious assumption.

Reply: The Lyman-alpha absorption cross section was not measured as part of the present study. We are implying that it should be measured in future studies, which would refine our analysis. In the absence of experimental data, we surveyed available cross section data for highly fluorinated compounds and found that a cross section of 1 x 10^{-17} cm^2 molecule^{-1} would represent a reasonable cross section upper-limit. Using this cross section value in our lifetime analysis provides a Lyman-alpha photolysis lifetime of ~4500 years. Assuming a smaller or greater cross section would yield slightly longer or shorter lifetimes, although the relationship is not linear due to the dependence on the transport time to the mesosphere. Therefore, in the absence of experimental data, we believe our assumed cross section and lifetime is reasonable. Laboratory studies to measure VUV cross sections would help refine our analysis but not alter the primary conclusion from this work that the atmospheric lifetime of the furan is extremely long. Note that measuring VUV spectra in the laboratory is significantly different than measuring 185 nm cross sections and requires specialized equipment.

Actions Taken: P10L2, the sentences "It is reasonable to assume a Lyman-α cross section of 10^{-17} cm^2 molecule^{-1} for *c*-C_4F_8O which would be roughly consistent with values for highly fluorinated compounds (SPARC, 2013). The estimated lifetime due to Lyman-□α photolysis, $\tau_{Lyman-\alpha}$, is then ~ 4500 years (a smaller Lyman-α cross section would lead to a longer lifetime)." will be replaced by "The scope of the present study did not include a measurement of the Lyman-α cross section. It is however reasonable to assume a Lyman-α cross section of 10^{-17} cm^2 molecule^{-1} for *c*-C_4F_8O which is in the range of values for highly fluorinated compounds, (0.035 - 10) x 10^{-17} cm^2 molecule^{-1} (SPARC, 2013). Therefore, in the absence of experimental data, we consider the Lyman-α cross section, 1x10^{-17} cm^2 molecule^{-1}, used in our lifetime analysis as a reasonable estimate. Note that a smaller (larger) Lyman-α cross section would lead to a longer (shorter) photolysis lifetime, although the lifetime dependence on the cross section value is not linear due to the lifetime dependence on the transport time to the mesosphere."

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 "$k_{2a} = 2.4\times10^{-12}$ 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 $c\text{-}C_4F_8O$ should be in the main article

Reply: We agree on this and suggest to add text related to natural/synthetic $c\text{-}C_4F_8O$ 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 $c\text{-}C_4F_8O$."

Reviewer Comment: Technical corrections:
p 5 l7 use indices in $c\text{-}C_4F_8O$
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.

Abundances, emissions, and loss processes of the long-lived and potent greenhouse gas octafluorooxolane (octafluorotetrahydrofuran, c-C$_4$F$_8$O) in the atmosphere

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Abstract. The first observations of octafluorooxolane (octafluorotetrahydrofuran, c-C$_4$F$_8$O), a persistent greenhouse gas, in the atmosphere are reported. In addition, a ~~complimentary~~ complementary laboratory study of its most likely atmospheric loss processes~~and~~, its infrared absorption spectrum, and global warming potential (GWP) are reported. First atmospheric measurements of c-C$_4$F$_8$O are provided from the Cape Grim Air Archive (41°S, Tasmania, Australia, 1978–present), supplemented by two firn air samples from Antarctica, in situ measurements of ambient air at Aspendale, Victoria (38°S), and a few archived air samples from the Northern Hemisphere. ~~Atmospheric abundances~~ The atmospheric abundance in the Southern Hemisphere ~~have reached~~ has monotonically grown over the past decades and leveled at 74 ppq (parts per quadrillion, femtomol mol^{-1} in dry air) by ~~2017. However its growth rate~~ 2015–2018. The growth rate of c-C$_4$F$_8$O has decreased from a maximum in 2004 of ~~4.3~~ 4.0 ppq yr^{-1} to <~~0.15~~ 0.25 ppq yr^{-1} in ~~2017.~~ 2017 and 2018. Using a 12-box atmospheric transport model, globally averaged yearly emissions and abundances of c-C$_4$F$_8$O are calculated for ~~1951–2017~~1951–2018. Emissions, which we speculate to derive predominantly from usage of c-C$_4$F$_8$O as a solvent in the semiconductor industry, peaked at ~~0.16~~ 0.15 (±0.04, 2σ) kt yr^{-1} in 2004 and have after declined to <~~0.01~~ 0.015 kt yr^{-1} in ~~2017.~~ 2017 and 2018. Cumulative emissions over the full range of our record amount to 2.8 (~~2.6~~2.4–3~~.2~~.3) kt, which correspond to 34 Mt of CO$_2$-equivalent emissions. Infrared and ultraviolet absorption spectra for c-C$_4$F$_8$O as well as the reactive channel rate coefficient for the O(^{1}D) + c-C$_4$F$_8$O reaction were determined from laboratory studies. On the basis of these experiments, a radiative efficiency of 0.430 W m^{-2} ppb^{-1} (parts per billion, nanomol mol^{-1}) was determined, which is one of the largest found for synthetic greenhouse gases. The global annually averaged atmospheric lifetime, including mesospheric loss, is estimated to be >3 000 years. GWPs of 8 975, 12 000, and 16 000 are estimated for the 20, 100, and 500-year time-horizons, respectively.

1 Introduction

Halogenated organic substances are generally potent greenhouse gases and contribute significantly to climate change, despite their relatively low abundances in the atmosphere (Myhre et al., 2013; Carpenter and Reimann, 2014). Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), and nitrogen trifluoride (NF_3) are important anthropogenic greenhouse gases, which are included in the Kyoto Protocol to the United Nations' Framework Convention on Climate Change (UNFCCC). Although they ~~don’t~~ do not have the capacity to destroy stratospheric ozone (unlike e.g. chlorofluorocarbons), HFCs have also been added to the Montreal Protocol on Substances That Deplete the Ozone Layer through the recent Kigali Amendment so that emissions can be curtailed by the effective method of restricting HFC use (United Nations, 2016).

The topic of the present research is the heterocyclic and fully fluorinated compound octafluorooxolane (c-C_4F_8O, CAS 773-14-8), better known by its older name as octafluorotetrahydrofuran, from which it has recently been renamed to its present name by IUPAC (Favre and Powell, 2014). The compound is ~~not regulated under the above Protocols despite its potential long lifetime and high radiative efficiency.~~ 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. For example 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 CO_2-equivalent emissions are required for these submissions, a default GWP for fully fluorinated GHGs of 10 000 (100-yr time horizon) 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.

c-C_4F_8O has been under discussion in the recent literature foremost as a new Chemical Vapor Deposition (CVD) chamber cleaning agent in the semiconductor industry (Pruette et al., 2000; McCoy, 2000; Oh et al., 2001; Kim et al., 2002, 2004). It was evaluated against the widely used perfluoroethane (C_2F_6) and perfluoropropane (C_3F_8) in terms of cleaning effectiveness and reduction in greenhouse gas emissions. Its advantages over NF_3, another alternative cleaning agent, are stated as lower toxicity and a smaller adjustment to existing chamber cleaning structures using C_2F_6. However, its disadvantages are potential byproducts such as tetrafluoromethane (CF_4), which is another long-lived potent greenhouse gas (Beu, 2005). c-C_4F_8O has also been evaluated as part of a gas mixture to replace SF_6 in high-voltage gaseous insulation applications, again driven by the desire to reduce greenhouse gas emissions ~~(Dahl et al., 2014; Chachereau et al., 2016)~~(Dahl et al., 2014; Chachereau et al., 2016; Kočišek et al., 2018 Another niche application is the use as a radiator gas for Cherenkov detectors in large scale particle acceleration experiments (Artuso et al., 2006; Acconcia et al., 2014).

The above applications have emerged only within the last two decades. Whether c-C_4F_8O was used earlier than that is undocumented. Frick and Anderson (1972) patented a method to synthesize c-C_4F_8O for potential use as an inert solvent for highly reactive or corrosive halogenated materials in naval applications. However it remains unclear if this led to mass production of c-C_4F_8O at that time.

Little is known of ~~the~~ c-C_4F_8O ~~properties related to~~ related to its radiative properties and gas phase loss processes in the atmosphere. ~~As part of the above-mentioned evaluations, a greenhouse warming potential (GWP) is cited at a value~~ A GWP of 8 700 (with no reference to the time horizon) ~~and~~ has been reported, which was derived based on structural analogies to octafluorocyclobutane (c-C_4F_8), for which the GWP is known (3M company-internal analysis cited by Pruette et al. (2000)). A Material Safety Data Sheet for PFG-3480 (trade name for c-C_4F_8O), lists a GWP of 13 900 (100-yr time horizon) and a lifetime of <4 000 years (3M Company, 2007). It is unknown to us how these results were obtained. Information is also lacking on other potential loss processes for c-C_4F_8O, such as uptake by oceans and land. In addition, no atmospheric measurements~~or emissions estimates to the atmosphere~~, and consequently no atmospheric observation based (top-down) emissions estimates are presently available for c-C_4F_8O.

The present study aims to improve our knowledge on the chemical and radiative properties of c-C_4F_8O relevant to determining its atmospheric lifetime and to provide the first atmospheric measurements from which we derive estimated global emissions to the atmosphere. Measurements were made on atmospheric samples archived in canisters and Antarctic firn, and in modern air from in situ observations. From the derived historical record, emissions are estimated using a 12-box chemical transport model of the atmosphere (Cunnold et al., 1983; Rigby et al., 2013; Vollmer et al., 2016). We also conducted laboratory experiments to determine the infrared and ultraviolet (UV) absorption spectra of c-C_4F_8O, and the rate coefficient for the $O(^1D)$ + c-C_4F_8O reaction to estimate the atmospheric lifetime and GWP of c-C_4F_8O.

2 Methods

2.1 c-C_4F_8O in air samples

2.1.1 Measurements of c-C_4F_8O in archived and ambient in situ air

For the present study, archived and urban ambient air samples were analyzed at the Commonwealth Scientific and Industrial Research Organization (CSIRO) laboratory at Aspendale (Victoria, Australia) using Medusa gas chromatographic (GC) mass spectrometric (MS) techniques (Miller et al., 2008). The archived air samples consisted primarily of the Cape Grim Air Archive (CGAA) samples collected under clean air baseline conditions for archival purposes since 1978 at the Cape Grim Baseline Air Pollution Station (Tasmania, Australia 40.7°S, 144.7°E). These >100 samples were collected into 34 L internally electropolished stainless steel canisters (Essex Industries, USA) using cryogenic techniques (Fraser et al., 1991; Langenfelds et al., 1996, 2014; Fraser et al., 2016). The CGAA record was complemented with a few samples collected in the Northern Hemisphere (33°N–53°N) mostly using oil-free diving compressors.

Two firn air samples were also analyzed, which were collected at the Aurora Basin North ~~(ABN)~~ site in Antarctica (71.1°S, 111.4°E). The site is located 550 km inland from Australia's Casey station, at 2710 masl and has a low mean annual air temperature of −44°C. Samples were collected in December 2013; those for the halocarbon measurements were collected into internally electropolished stainless steel containers using a 2-stage teflon-coated viton diaphragm pump. Only two samples were available for the present study as other samples from this site were used for a different halocarbon study.

In situ measurements of c-C_4F_8O at Aspendale (38.0°S, 145.1°E) were started in February 2017. These samples are collected from the rooftop at CSIRO (at 11 m height from the ground) through a 3/8" OD Synflex 1300 tube (Saint-Gobain, France) using a continuous flow air sampling module (Miller et al., 2008) with a diaphragm sampling pump fitted with stainless steel heads and a neoprene membrane (KNF Neuberger, Germany).

All archived air samples were analyzed on the Medusa-GCMS “Medusa-9” in December ~~2016.~~ 2016 along with a suite of other trace gases. The instrument is based on the original design of the Medusa-GCMS used in the Advanced Global Atmospheric Gases Experiment (AGAGE) network (Miller et al., 2008; Prinn et al., 2018) but fitted with different chromatography columns (Vollmer et al., 2018). A GS-GasPro main capillary column (0.32 mm ID × 60 m, Agilent Technologies) was used for the main separation and a column of the same type (5 m) was fitted as a precolumn, allowing for a backflushing of late eluting compounds. In this GCMS setup (Agilent 6890 GC, 5975 MS) c-C_4F_8O was identified using a multi-component diluted mixture of known composition with the MS in scan and selected ion modes. The choice for the two fragments used in the analysis of our air samples was based on the mass spectrum, which we measured for c-C_4F_8O, to the best of our knowledge the first one published for this compound (see Supplement).

Analytes from the samples were cryogenically preconcentrated on a first microtrap of the GCMS and subsequently transferred to a second microtrap, both filled with HayeSepD and held at ~ -155 °C. During this process, water vapor was largely removed using nafion dryers; nitrogen, oxygen, and a large fraction of noble gases were removed due to their trap breakthroughs, and carbon dioxide was removed using a molecular sieve (4A) packed column between the traps. To enhance the signal size of the measured compounds, 3 L sample sizes were used for each measurement (compared to normally 2 L) and the MS electron multiplier voltage was increased by 50 V compared to what was given by the autotune algorithm. Analysis of a single sample lasted 65 min. Archived air sample measurements were bracketed by measurements of a standard (E-146S) to track and correct for MS sensitivity changes. This standard was air compressed into a 34 L tank at the remote Rigi-Seebodenalp station (Switzerland) using an oil-free compressor, and was additionally spiked with small amounts of c-C_4F_8O and other compounds, to enhance the GCMS peak size and signal-to-noise ratio. In general, three measurements of each archived air sample were made. For some, no standard measurement was made between the second and third sample to assess potential memory effects of the system. For c-C_4F_8O, no memory effect and no signal in the blank runs could be detected. Detection limits are estimated at 5 ppq (parts per quadrillion, femtomol mol^{-1}). Mean precisions (2σ) for the measurements of the archived air samples ranged 3–4 ppq (20–5 %) for the low (~15 ppq) to high (~70 ppq) mole fractions, respectively. Based on two different types of experiments, a linear system response for the relevant mole fraction range was found (see Supplement). In situ urban air measurements at Aspendale are based on 2 L samples and without alteration of the MS electron multiplier voltage. Consequently the precisions are slightly poorer for these measurements. These air precisions were estimated at ~12 ppq (~17 %, 2σ) under the assumption that c-C_4F_8O remains constant in the air measured in situ at Aspendale on a daily basis.

2.1.2 Absolute calibration and uncertainty estimates for air measurements

A primary calibration scale was prepared based on a commercially obtained multi-component mixture in dry synthetic air (Carbagas, Switzerland, HCP-04Carba), with a mole fraction of c-C_4F_8O at 10 ppm (parts-per-million, μmol mol^{-1}). This mixture was diluted manometrically and using a bootstrap technique, resulting in a primary calibration standard (EP-001) with c-C_4F_8O at 1.81 ppt (parts-per-trillion, picomol mol^{-1}). Three secondary standards were additionally prepared from ambient air compressed into cylinders (Essex Industries, USA) and spiked with small quantities of c-C_4F_8O resulting in mole fractions of $\sim$0.5 ppt. These secondary standards were the base for propagating the calibration scale to other calibration standards, in particular that used for the Cape Grim Air Archive measurements (E-146S). They define the Empa-2013 calibration scale for c-C_4F_8O on which our results are reported. The systematic uncertainty of the preparation of this primary calibration scale (including its propagation to the working standards), which defines its accuracy, is estimated at 15 % (2σ). Details of the dilution technique and the primary calibration scale are provided by Vollmer et al. (2015).

2.2 Models and inversion

2.2.1 Firn model

We use a numerical firn air model (Trudinger et al., 1997, 2013) to quantify the movement of c-C_4F_8O in firn air in order to determine the time period for which c-C_4F_8O in the firn samples is representative of the atmosphere. Vertical diffusion in the firn and other physical processes cause a tracer in a firn air sample to correspond to an age spectrum relative to the atmosphere, rather than a discrete age. Green's functions from the firn model represent the age spectrum of a tracer in each firn sample, and are used in this work to relate the measured mole fractions of ~~c-C4F8O~~ c-C_4F_8O in firn to the time-range of the corresponding atmospheric mole fractions.

For ~~ABN~~Aurora Basin North, the firn model uses an accumulation rate of 97 kg m^{-2} yr^{-1}, a temperature of −44°C, and pressure of 695 hPa. The density profile used was based on a spline fit to density measurements. Diffusion parameters in the firn model are calibrated for ~~the ABN site~~ Aurora Basin North using 12 tracers at between 5 and 11 depths each throughout the firn. ~~Vertical diffusion~~ Only molecular diffusion was used for the Aurora Basin North firn model calculations; eddy diffusivity is sometimes used in the CSIRO firn model in the ~~firn and other physical processes cause a firn air sample to correspond to an age spectrum rather than a discrete age. Green's functions from the firn model represent the age spectrum of each firn sample, and are used in this work to relate the measured mole fractions to the time-range of the corresponding atmospheric mole fractions~~deep firn but was not used here as the parameters were not well constrained by the available measurements. The diffusion coefficient used in this work for c-C_4F_8O in air, relative to CO_2 in air, (for a temperature of 253 K) is 0.460. This value was determined using Equation 4 from Fuller et al. (1966) with Le Bas volume increments (e.g. Table 1.3.1, Mackay et al. (2006)) and a multiplier for the Le Bas increments of 0.97 (this value minimizes the difference of calculated relative diffusion coefficients of a number of compounds from values measured by Matsunaga et al. (1993, 2002, 2005)).

2.2.2 12-box atmospheric model

We use the AGAGE 12-box atmospheric model (Rigby et al., 2013) to relate the atmospheric mole fractions to surface emissions. Briefly, in this model, the atmosphere is divided into four zonal bands, separated at the equator and at the 30° latitudes, thereby creating boxes of similar air masses. There are also vertical separations, at altitudes represented by 500 hPa and 200 hPa, resulting in the overall 12 boxes. Model transport parameters and stratospheric photolytic loss vary seasonally and repeat interannually (Rigby et al., 2013). We anticipate that variations in emissions dominate atmospheric trends, particularly over the longer (multi-annual) timescales that are our primary focus, so inter-annual variation in transport is not expected to be important here. 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. 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).

2.2.3 Global inversions

To estimate global emissions to the atmosphere from the mole fraction measurements, we employ an inverse calculation (inversion InvE2 from Trudinger et al. (2016), and termed "CSIRO" inversion in Vollmer et al. (2016, 2018)) that was developed to focus on sparse observations from air archives, and firn air and ice core samples that are associated with age spectra. The inversion ~~uses~~ combines Green's functions from both the firn model and AGAGE 12-box atmospheric model described above to relate firn and tropospheric mole fraction to c-C_4F_8O surface emissions. The Green's functions from the 12-box model were calculated using a constant distribution of emissions into the four zonal boxes at the surface, and for this we used the relative contributions 0.675, 0.325, 0.0, and 0.0, in the northern-most to southern-most zonal bands. Results are fairly insensitive to emissions distributions that have ~~all~~ most emissions in the Northern Hemisphere (see Supplement). The characteristics of sparse atmospheric, firn and ice core data necessitate the use of constraints on the inversion to avoid unrealistic oscillations in the reconstructed mole fractions or negative values of mole fraction or emissions. The inversion uses non-negativity constraints and favors relatively small changes in annual emissions between adjacent years over large, unrealistic fluctuations. A prior emissions history is needed as a starting point for the inversion~~,~~ ; then a non-linear constrained optimization method (~~*contrained*~~*constrained_min* routine in IDL (~~Exelis Visual Information Solutions, Boulder~~Harris Geospatial Solutions, Inc., Broomfield, Colorado) ~~)~~ is used to find the solution that minimizes a cost function consisting of the model-data mismatch weighted by the observation uncertainties, plus the sum of the year-to-year changes in emissions (Trudinger et al., 2016). Given the lack of industry-based bottom-up emission estimates for c-C_4F_8O, we use emissions derived from observations ~~,~~ of perfluorooctane, which was found present for many decades and at low abundances in the global atmosphere (Ivy et al., 2012). Because the prior is not based on information on c-C_4F_8O, we do not include the prior in the cost function. The emissions derived from the inversion are rather insensitive to the choice of the prior (see Supplement), because the prior is used here as a starting point for the inversion only, and not as a constraint. Our observations used in the inversion are the firn measurements and annual values of mole fraction from a smoothing spline fit (50 % attenuation at 10 years) to measurements of the CGAA and in situ measurements at Aspendale. Northern Hemisphere measurements were compared with the reconstructed mole fractions for that hemisphere, but were not used in the inversion. Uncertainties ~~for the CGAA and Aspendale annual means~~ in the emissions are estimated using a bootstrap method that incorporates temporally-correlated uncertainties in the annual values derived from the atmospheric data (see Supplement), uncertainty in firn measurements, uncertainty ~~in the calibration scale~~ of ±15 % in the calibration scale, and uncertainties in the firn model parameters through the use of an ensemble of firn Green's functions.

2.3 Laboratory studies

Laboratory studies to measure the infrared and UV spectra of c-C_4F_8O and the rate coefficient for the $O(^1D)$ + c-C_4F_8O reaction were conducted at the Chemical Sciences Division Laboratories at the National Oceanic and Atmospheric Administration (NOAA), Boulder, Colorado, USA. The apparatus and methods used in this work are described separately below.

2.3.1 Absorption spectra

Absorption spectra, $A(v)$ (base e), or integrated band strengths, were quantified using Beer's law

$$A(\lambda) = -ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \sigma(\lambda) \times L \times [c\text{-}C_4F_8O] \tag{I}$$

where ~~A~~ A is the measured absorbance at wavelength λ, ~~I(λ) and I$_0$(λ)~~ $I(\lambda)$ and $I_0(\lambda)$ are the measured light intensities with and without the sample present in the absorption cell, respectively, ~~L~~ L is the optical absorption path length, ~~σ(λ)~~ $\sigma(\lambda)$ is the infrared or UV cross section of c-C_4F_8O, and [c-C_4F_8O] is the concentration of c-C_4F_8O. In total, 11 independent absorption spectrum measurements were used in the linear least-squares fit. The c-C_4F_8O concentration was determined using the ideal gas law and absolute pressure measurements of either the pure compound or of a dilute mixture of the compound in a helium (He) bath gas.

The c-C_4F_8O sample was obtained from SynQuest Laboratories ~~(Inc. ,~~ Inc. (Alachua, Florida, USA, 99 % purity). For the experiments described below, c-C_4F_8O was introduced into the absorption cells as a pure sample or in a dilute mixture prepared off-line. The dilute mixtures of c-C_4F_8O in a He (UHP, 99.999 %) bath gas ~~was~~ were prepared manometrically in a 12 L Pyrex bulb with an estimated accuracy of ∼1 %, as derived from the accuracy of the pressure measurements. The pressure measurement uncertainty includes the uncertainty in the sample pressure, the total mixture pressure, and the linearity of the pressure gauge (estimated to be 0.2 %). Pressures were measured with 100 Torr and 1 000 Torr (130 and 1 300 hPa, respectively) capacitance manometers. Quoted uncertainties are 2σ.

Infrared absorption spectra were measured at 296 K using Fourier transform ~~infrared~~ infraRed (FTIR) spectroscopy over the 500–4 000 cm^{-1} spectral region at 1 cm^{-1} resolution with Boxcar apodization. The apparatus has been used extensively in previous studies (Bernard et al., 2017, 2018a). The FTIR was coupled to a 15 cm path length single pass absorption cell with potassium bromide (KBr) windows. A liquid-nitrogen cooled HgCdTe/B semiconductor detector was used. Infrared spectra were recorded in 100 or 500 co-added scans. Absorption spectra were recorded under static conditions using a dilute mixture of c-C_4F_8O in He with a 0.00180 mixing ratio. The c-C_4F_8O concentration used in the absorption measurements was in the range 1.75×10^{15} to 2.34×10^{16} molecule cm^{-3}. Integrated band strengths (IBS) were obtained from the measurement of 11 individual IR spectra.

The UV absorption spectrum of c-C_4F_8O was measured at 296 K using a 0.5 m spectrometer (1 nm resolution) equipped with a charge-coupled device (CCD) detector. The collimated output of a 30 W deuterium lamp passed through a 100 cm long and 2.5 cm diameter Pyrex absorption cell with quartz windows. Spectral measurements were made over the wavelength region 200–350 nm. The wavelength scale of the spectrometer was calibrated using the emission lines from a low-pressure Hg pen-ray lamp. c-C_4F_8O was added to the absorption cell in pure form from the original sample. Measurements were performed over a range of c-C_4F_8O concentrations from 2.51×10^{18} to 2.16×10^{19} molecule cm^{-3}. Eleven independent UV absorption spectrum measurements were used in the final linear least-squares fit.

2.3.2 O(^{1}D) reaction rate coefficient

The reactive rate coefficient, ~~k_R~~ k_1, for the reaction

$$O(^1D) + c\text{-}C_4F_8O \quad \rightarrow \text{Products} \tag{1a}$$

$$O(^1D) + c\text{-}C_4F_8O \quad \rightarrow c\text{-}C_4F_8O + O(^3P) \tag{1b}$$

i.e., the channel resulting in the loss of c-C_4F_8O, was measured at 294 K using a relative method (e.g. Baasandorj et al., 2013). The loss of c-C_4F_8O was measured relative to the loss of the reference compound CHF_3 during the same experiment:

$$O(^1D) + CHF_3 \quad \rightarrow \text{Products} \tag{2a}$$

$$O(^1D) + CHF_3 \quad \rightarrow CHF_3 + O(^3P) \tag{2b}$$

The recommended total rate coefficient for reaction 2, k_2 is $(9.60\pm0.5)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} and the recommended reactive channel branching ratio, k_{2a}/k_2 is 0.25, i.e., $k_{2a} = 2.4\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (Burkholder et al., 2015).

Provided c-C_4F_8O and the reference compound are removed solely by reaction with O(^{1}D), the rate coefficient for reaction 1a is related to the reference compound rate coefficient by the equation

$$ln\left(\frac{[c\text{-}C_4F_8O]_{t_0}}{[c\text{-}C_4F_8O]_t}\right) = \frac{k_{1a}}{k_{2a}}\left[ln\left(\frac{[CHF_3]_{t_0}}{[CHF_3]_t}\right)\right] \tag{II}$$

where $[c\text{-}C_4F_8O]_{t_0}$, $[CHF_3]_{t_0}$, $[c\text{-}C_4F_8O]_t$, and $[CHF_3]_t$ are the concentrations of c-C_4F_8O and CHF_3 at times zero (t_0) and t, respectively. The k_{1a} and k_{2a} are the reactive rate coefficients for the reaction of O(^{1}D) with c-C_4F_8O (1a) and CHF_3 (2a), respectively.

The Pyrex reactor, which was 100 cm long and with a 2.2 cm internal diameter, was coupled with a Teflon circulating pump to an absorption cell where the ~~loss~~ losses of c-C_4F_8O and CHF_3 ~~was~~ were measured using FTIR spectroscopy. The FTIR absorption cell was equipped a multi-pass cell (485 cm path length) with KBr windows. Spectra were recorded in 100 co-adds at a spectral resolution of 1 cm^{-1}.

$O(^1D)$ was produced by KrF (248 nm) excimer pulsed laser photolysis of ozone:

$$O_3 + h\nu\,(248\,\mathrm{nm}) \rightarrow O(^1D) + O_2(^1\Delta) \tag{3a}$$

$$\rightarrow O(^3P) + O_2(^3\Sigma) \tag{3b}$$

The yield of the $O(^1D)$ channel is 0.9 (Burkholder et al., 2015). After thoroughly mixing the gas mixture in the system, a time zero infrared spectrum was recorded. Ozone was then added slowly to the reactor with the photolysis laser and gas circulation on. The photolysis laser fluence was in the range ∼2–7.4 mJ cm^{-2} $pulse^{-1}$. The laser was operated at 10 or 20 Hz. The total pressure in the cell increased during an experiment by ∼300 Torr, mostly due to the addition of He carrier gas used to flush ozone into the reactor. Infrared spectra were recorded at regular intervals with approximately 10 spectra recorded over the course of an experiment. Experiments performed separately demonstrated that there was no significant loss of c-C_4F_8O or CHF_3 under identical conditions in the absence of ~~$O(^1D)$ production~~photolysis. The initial c-C_4F_8O and CHF_3 concentrations were in the range $6.4–6.8 \times 10^{14}$ molecule cm^{-3} and $4.5–5.0 \times 10^{14}$ molecule cm^{-3}, respectively.

3 Results and discussion

3.1 Infrared spectrum

The infrared absorption spectrum of c-C_4F_8O obtained in this study is shown in Fig. 1. Over the range of c-C_4F_8O concentrations used, the spectra obeyed Beer's law with high precision (∼0.2 %). Spectra recorded at different total pressures had identical band shapes, i.e., the spectrum was independent of the total pressure (He bath gas) over the range of 30–400 Torr.

The integrated band strength (IBS) over the spectral region 500–1 500 cm^{-1} was determined to be $(3.21 \pm 0.01) \times 10^{-16}$ cm^2 $molecule^{-1}$ cm^{-1}, where the quoted uncertainty is the precision of the linear least-squares fit of the data to Beer's law (Equation I). The absolute uncertainty in the c-C_4F_8O spectrum includes estimated uncertainties in the optical path length (±0.5 %), measured absorbance (±0.005), temperature (±1 K), and pressure (±0.2 %). The absolute uncertainty in the total integrated band strength is estimated to be 3 %.

3.2 UV absorption

UV absorption of c-C_4F_8O was observed between 200 nm and 225 nm, a range that is most critical for calculations of the c-C_4F_8O atmospheric photolysis rates. The spectrum is continuous, with cross ~~section~~ sections decreasing monotonically with increasing wavelength. The cross section measurements obeyed Beer's law with values of $(9.2 \pm 3.9) \times 10^{-24}$ and $(4.4 \pm 2.3) \times 10^{-24}$ cm^2 $molecule^{-1}$ cm^{-1} at 200 and 225 nm, respectively. An example of the measured UV spectrum of the c-C_4F_8O sample is shown in the Supplement. Overall, the cross sections of c-C_4F_8O were very low, and therefore, the measurements are susceptible to interference from even minor sample impurities. Therefore, we choose to assign a conservative UV cross section of $<2 \times 10^{-23}$ cm^2 $molecule^{-1}$ cm^{-1} over the 200–225 nm range.

3.3 O(^{1}D) reaction

We found the reactivity of c-C_4F_8O with O(^{1}D) to be low, which makes the determination of an accurate rate coefficient more challenging. The relative rate data are shown in Fig. 3 and tabulated in the Supplement. The precision of the three independent measurements is high with a fit precision of a few percent. However the agreement between the independent measurements is relatively poor. The low conversion of c-C_4F_8O, <2 %, and the precision of the infrared spectral subtractions are the primary sources of uncertainty in the measurements. The low conversion of c-C_4F_8O and CHF_3 achieved in these experiments was primarily due to the build up of O_2 associated with the addition of ozone to the reactor, making the loss of O(^{1}D) by reaction with O_2 more significant than its reaction with c-C_4F_8O and CHF_3. The absorption bands used in this study were 1120–1000 and 1180–1120 cm^{-1} for c-C_4F_8O and CHF_3, respectively. The spectral subtraction uncertainty is illustrated by the error bars included in Fig. 3. The average of individual measurements yields a rate coefficient ratio of 0.21±0.07. However, we recommend a conservative upper-limit of 0.5. Using the recommended O(^{1}D) + CHF_3 reactive rate coefficient, $(2.41\pm0.12)\times10^{-12}$ cm^3 molecule^{-1} s^{-1} (Burkholder et al., 2015) yields a c-C_4F_8O reactive rate coefficient of $<1.2\times10^{-12}$ cm^3 molecule^{-1} s^{-1}. Given the small O(^{1}D) rate coefficient of c-C_4F_8O, a refinement of the measured O(^{1}D) reactive rate coefficient will have a negligible impact to the total atmospheric loss of c-C_4F_8O.

3.4 Atmospheric lifetime

The global annually averaged atmospheric lifetime (τ) of c-C_4F_8O, is defined with respect to the individual partial lifetimes by the relationship:

$$\frac{1}{\tau} = \frac{1}{\tau_{\mathrm{O(^1D)}}} + \frac{1}{\tau_{h\nu}} + \frac{1}{\tau_{\mathrm{Lyman-}\alpha}} + \frac{1}{\tau_{\mathrm{OH}}} \qquad (4)$$

where the individual global loss processes are combined to derive the overall global lifetime. In the present analysis, only O(^{1}D), UV photolysis, and Lyman-α terms are considered. 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. The loss of c-C_4F_8O via reaction with the OH radical is assumed to make a negligible contribution to the global lifetime ~~and consequently~~ in our analysis. The OH rate coefficient would need to be $\sim1\times10^{-17}$ cm^3 molecule^{-1} s^{-1} (equivalent to a 3 000 year lifetime) to make a significant global lifetime contribution. Such a low rate coefficient represents a significant challenge to current rate coefficient measurement methods. Additionally, an expected OH low-reactivity of c-C_4F_8O is supported by its low O(^{1}D) reactivity measured in this work. Consequently, we ignore the last term in Equation 4. Additional laboratory studies, that are beyond the scope of the present work, would be needed to quantify the OH reaction.

The laboratory results for the O(^{1}D) reaction and UV photolysis obtained in this study are combined with an estimated Lyman-α lifetime to derive the lifetime utilizing the 2-D atmospheric model calculation parametrizations reported by ~~Bernard et al. (2018b)~~ The O(^{1}D) reaction represents a stratospheric loss process for c-C_4F_8O with a partial lifetime, $\tau_{\mathrm{O(^1D)}}$, estimated to be >30 000 years. This extremely long lifetime is a result of the low c-C_4F_8O reactivity combined with the turn-over time of the stratosphere. The UV photolysis lifetime, $\tau_{h\nu}$ is derived from the c-C$_4$F$_8$O UV cross section upper-limit of 10^{-23} cm^2 molecule^{-1} and an assumed quantum yield of unity for the 200–225 nm region, and is >15 000 years. Combining the estimated O(^{1}D) and UV photolysis lifetimes yields an estimated global lifetime for c-C$_4$F$_8$O >7 500 years.

Given the long atmospheric lifetime of c-C$_4$F$_8$O in the troposphere and stratosphere, upper atmospheric loss processes may contribute to the global atmospheric lifetime. Here, we consider loss due to Lyman-α photolysis, although other loss processes are possible. To date, the vacuum UV (VUV) absorption spectrum of c-C$_4$F$_8$O, which includes the Lyman-α absorption (121.567 nm), has not been reported. ~~It is~~ The scope of the present study did not include a measurement of the Lyman-α cross section. It is however reasonable to assume a Lyman-α cross section of $\sim 10^{-17}$ cm^2 molecule^{-1} for c-C$_4$F$_8$O which ~~would be roughly consistent with~~ is in the range of values for highly fluorinated compounds ~~(SPARC, 2013). The estimated lifetime due to~~ of $(0.035–10)\times10^{-17}$ cm^2 molecule^{-1} (SPARC, 2013). Therefore, in the absence of experimental data, we consider the Lyman-α ~~photolysis, $\tau_{\mathrm{Lyman}-\alpha}$, is then ∼4 500 years (a smaller~~ cross section 1×10^{-17} cm^2 molecule^{-1}, used in our lifetime analysis, as a reasonable estimate. Note that a smaller (larger) Lyman-α cross section would lead to a longer ~~lifetime)~~ (shorter) photolysis lifetime, although the lifetime dependence on the cross section value is not linear due to the lifetime dependence on the transport time to the mesosphere. On the basis of these assumptions, Lyman-α photolysis in the lower mesosphere could be the dominant atmospheric loss process for c-C$_4$F$_8$O. Including this Lyman-α photolysis lifetime yields a c-C$_4$F$_8$O globally averaged atmospheric lifetime of >3 000 years.

3.5 Global warming potential (GWP)

c-C$_4$F$_8$O has strong vibrational absorption bands within the Earth's atmospheric infrared transmission window (Hodnebrog et al. (2013), Fig. 4). We determine a radiative efficiency for c-C$_4$F$_8$O of 0.430 W m^{-2} ppb^{-1} using the parameterization for atmospherically well-mixed compounds given in Hodnebrog et al. (2013). c-C$_4$F$_8$O is therefore a potent greenhouse gas ~~. This radiative efficiency is~~ with a radiative efficiency greater than those of HFCs and chlorofluorocarbons (CFCs), which are typically less than 0.3 W m^{-2} ppb^{-1} (Myhre et al., 2013).

The GWP of c-C$_4$F$_8$O was calculated using the global atmospheric lifetime lower-limit of 3 000 years and the radiative efficiency determined in this work:

$$\mathrm{GWP(T)} = \frac{\mathrm{RE}_\tau(1-\exp(-\mathrm{T}/\tau))}{\mathrm{M}_{c\text{-}\mathrm{C_4F_8O}}\int \mathrm{RF}_{\mathrm{CO_2}}(\mathrm{T})} \tag{5}$$

where RE is the radiative efficiency, T is the time horizon (in years), $\mathrm{M}_{c\text{-}\mathrm{C_4F_8O}}$ is the molar weight of c-C$_4$F$_8$O~~-~~, and $\mathrm{RF}_{\mathrm{CO_2}}$ is the radiative forcing of CO$_2$. The GWPs are 8 975, 12 000, and 16 000 for the 20, 100, and 500-year time-horizons. Therefore, c-C$_4$F$_8$O is a potent radiative forcing agent due to the combination of its high radiative efficiency and long atmospheric lifetime. The GWPs for c-C$_4$F$_8$O are comparable to the values for long-lived perfluorocarbons (PFCs) that have GWP$_{100}$ values in the range 6 300–11 100 (Harris and Wuebbles, 2014).

3.6 Atmospheric observations and emissions of c-C_4F_8O

We observe a general increase of c-C_4F_8O in the atmosphere over the sample period starting in 1978 (Fig. 4). c-C_4F_8O was detectable in all samples but ~~abundances were~~ its abundance was low in the early record (<20 ppq) until about 1998, when its growth rate increased strongly. ~~Abundances~~ Its abundance increased rather steadily ~~to 75 ppq in 2015.~~ for more than a decade but has subsequently leveled at 73–75 ppq in 2015–2018. The growth rate was at a maximum of ~~4.3~~ 4.0 ppq yr^{-1} in 2004 and declined from ~~the maximum~~ that to <~~0.15~~ 0.25 ppq yr^{-1} in ~~2017. Consequently, its abundance has remained relatively constant~~ 2017 and 2018 as a consequence of the relatively constant abundance in the last few years.

The ~~few Northern Hemispheresamples show higher mole fractions compared to the CGAA at similar times, suggesting predominant Northern Hemisphere emissions.~~ 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. Most anthropogenic gases are released predominantly in the Northern Hemisphere, including gases released by the semiconductor industry. The assumption of mainly Northern Hemisphere emissions for c-C_4F_8O leads to higher mole fraction values in the Northern Hemisphere than in the Southern Hemisphere, and this is confirmed by comparison of the modeled Northern Hemisphere history with the few Northern Hemisphere samples 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.

The two firn air samples fit well into the CGAA record with the older sample at slightly lower mole fraction than the oldest CGAA samples. ~~This~~ Due to the very long lifetime, this suggests that c-C_4F_8O was below 10 ppq in the Southern Hemisphere before 1978, ~~however~~ and could only have been steady or increasing. 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, and 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 ~~is also~~ 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 situ measurements at Aspendale, which are available on a regular measurement basis since February 2017, show ~~constant abundances~~ a constant abundance of c-C_4F_8O at ∼74 ppq. This lack of growth is an indication of currently very small, if at all any, emissions of this compound. Also, pollution events are absent from this urban in situ record within the precision of these measurements, suggesting that c-C_4F_8O is not emitted within the airmass footprints of the site.

Emissions derived from the atmospheric observations were low during the first part of our record (Fig. 4). Until 1980, when the global mean abundance of c-C_4F_8O was ~~11~~ 10 ppq, cumulative emissions had reached ~~0.4~~ 0.38 kt. For the time after ∼1980, when observations became more frequent, emissions were 0.02–0.03 kt yr^{-1} for about a decade. From the mid 1990s, emissions increased strongly to a maximum of ~~0.16~~ 0.15 (±0.04, 2 σ) kt yr^{-1} in 2004. Surprisingly, emissions have declined since~~and have reached 0.01~~ , to <0.015 kt yr^{-1} by ~~2017.~~ 2017 and 2018. This rapid decline is suggestive of a ~~choice for other~~ switch to alternative compounds in large scale industrial ~~application~~ applications such as in the semiconductor industry~~.~~, or of a better containment in these applications or where c-C_4F_8O might be emitted as byproduct.

For the USA, reported bottom-up emissions of c-C_4F_8O under the GHGRP subpart “Fluorinated Gas Production” for 2011–2017 are surprisingly high (about half) compared to our top-down emissions estimates (Fig. 4c). It therefore appears unlikely that these bottom-up emissions derive entirely from fugitive emissions during c-C_4F_8O production, but they could, at least in partial, derive from emissions of c-C_4F_8O as a byproduct during the production of other fluorochemicals. Anyhow, they reveal a surprisingly similar relative decline compared to our top-down estimates.

Cumulative emissions until ~~2017~~ 2018 amount to 2.8 (~~2.6~~2.4–3~~.2~~.3) kt. If scaled with the GWP on a 100-yr time ~~horizons~~horizon, as derived below, they correspond to 34 Mt CO_2-equivalents. Despite the high GWP, these emissions are small compared to the major greenhouse gases but of similar magnitude to some of the other minor greenhouse gases such as minor perfluorocarbons and fluorinated inhalation anesthetics (Ivy et al., 2012; Vollmer et al., 2015). Whether these cumulative emissions remain at low levels will depend on potential future choices for c-C_4F_8O in large scale applications.

4 Conclusions

We provide first laboratory experiments of atmospheric loss processes and first atmospheric observations of c-C_4F_8O~~, a persistent greenhouse gas not regulated by the Montreal and Kyoto Protocols~~. We measured infrared and UV absorption spectra of c-C_4F_8O, and the rate coefficient for the $O(^1D)$ + c-C_4F_8O reaction. These experimental results suggest that c-C_4F_8O is an atmospherically persistent trace gas with an atmospheric lifetime of >3 000 years. In addition, its strong absorption in the “atmospheric window” results in a very high radiative efficiency, and when combined with the long atmospheric lifetime, yields a high ~~global warming potential~~ GWP of 12 000 (100-year time horizon), which is exceeded by only a few other ~~synthetic~~ greenhouse gases. We show an increase of c-C_4F_8O in the atmosphere to present mole fractions of ∼~~74~~ 75 ppq. Emissions, which were derived from these observations, have strongly declined after a peak in 2004. The ~~reason~~ reasons for this recent decline, and whether this is only a temporary feature, ~~remains~~ remain speculative. We hypothesize that the emissions decline ~~is~~ could be, at least in partial, a result of the industry’s choice for alternative substances for chemical vapor chamber cleaning, which ~~is~~ we assumed to have been its primary use in the last two decades. However, even if emissions were completely halted, it will, ~~due to the very long lifetime of~~ under the assumption of insignificant non-atmospheric sinks, take thousands of years for ~~the compound~~ c-C_4F_8O to be removed from the atmosphere.

Data availability: Data used in this study are available from the Supplement. Mention of trade names or commercial products does not constitute an endorsement or recommendation ~~by NOAA for use~~ for use by the authors’ affiliated organizations.

Author contributions: MKV, FB, PBK, LPS, SR, and JBB were responsible for the overall project design. RLL, LPS, PJF, BM, and PBK, and DME and MAJC provided the Cape Grim Air Archive and firn air samples, respectively, MKV, BM, and LPS provided the air sample measurements, FB and JBB provided the laboratory measurements and analysis, CMT provided the modeling part for the atmospheric observations. The manuscript was written by MKV and FB with contributions from all co-authors.

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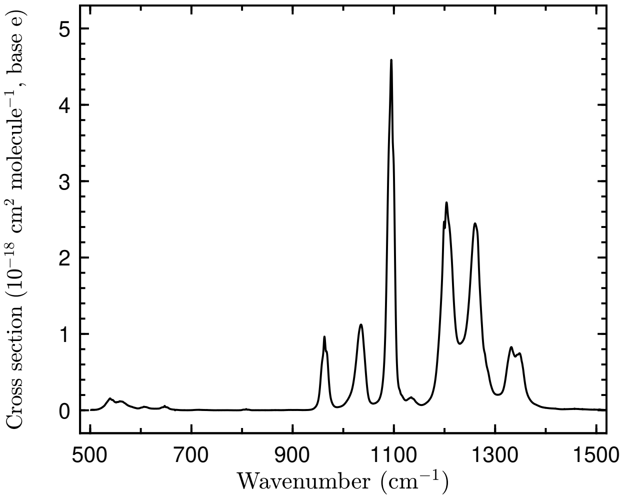
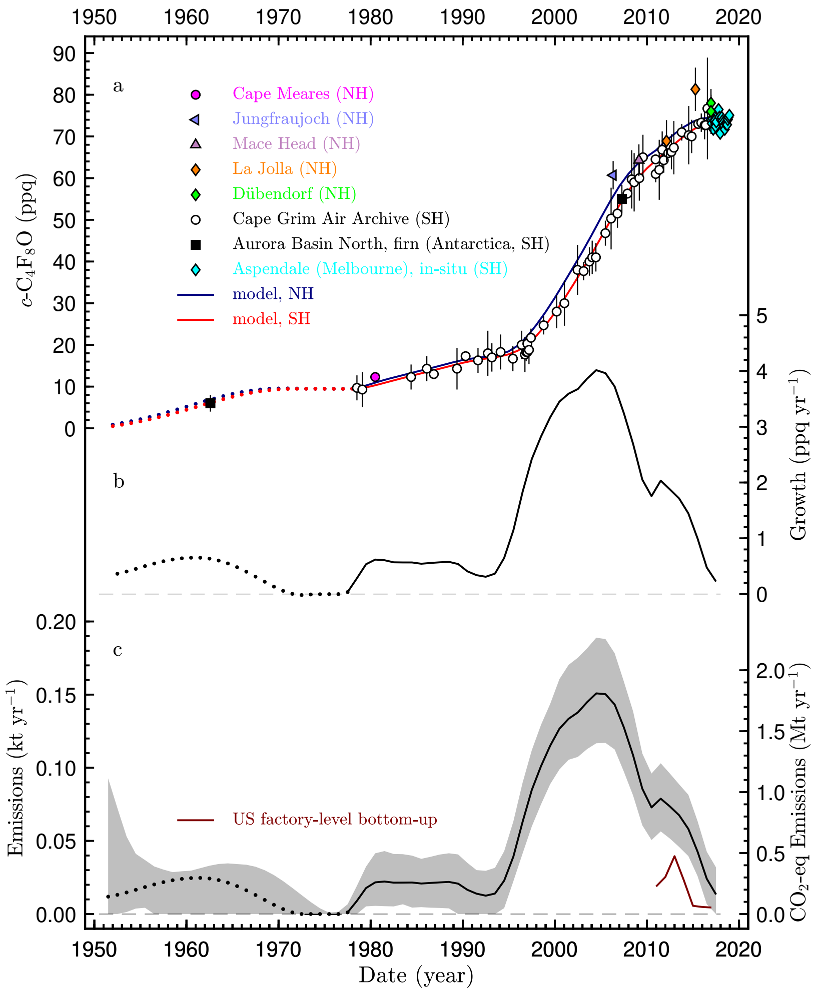


Figure 1. Infrared absorption spectrum of octafluorooxolane (c-C_4F_8O) measured in this work at 296 K at 1 cm^{-1} resolution.



~~Infrared absorption spectrum of octafluorooxolane () measured in this work at 296 K at 1 cm^{-1} resolution~~USA factory-level emissions are from URL: https://www.epa.gov/ghgreporting, accessed January 2019. The early history is shown as dotted lines to emphasize the greater uncertainties before 1978.

~~Infrared absorption spectrum of octafluorooxolane () measured in this work at 296 K at 1 cm^{-1} resolution~~USA factory-level emissions are from URL: https://www.epa.gov/ghgreporting, accessed January 2019. The early history is shown as dotted lines to emphasize the greater uncertainties before 1978.

Figure 2. Atmospheric observations (a), growth rates (b), and emissions (c) of ~~octofluorooxolane~~ octafluorooxolane (octafluorotetrahydrofuran, *c*-C$_4$F$_8$O). Abundances are given as dry air mole fractions in ppq (femtomol mol^{-1}) on the Empa-2013 primary calibration scale. Vertical bars denote the measurement precision (2σ) for the flask samples. Emission uncertainties are 2σ. Samples were collected in the Northern Hemisphere ~~(NH)~~ at Cape Meares (Oregon, 45.5° N, 124.0° W), Jungfraujoch (Switzerland, 46.5° N, 8.0° E), Mace Head (Ireland, 53.3° N, 9.9° W), La Jolla (California, 32.9° N, 117.3° W), and Dübendorf (Switzerland, 47.4° N, 8.6° E). Southern Hemisphere ~~(SH)~~ samples were mainly from the Cape Grim Air Archive collected at Cape Grim (Tasmania, 40.7° S, 144.7° E), two samples from the Aurora Basin North firn air sampling site (Antarctica, 71.2° S, 111.4° E), and in situ monthly means since February 2017 from Aspendale, Victoria, Australia (38.0° S, 145.1° E), with uncertainty bars for Aspendale omitted to aid visual clarity. Growth rates and emissions are globally averaged. Emissions (c) are shown with units on the left y-axis and ~~in~~ as CO$_2$~~equivalent~~ equivalent emissions based on a global warming potential of 12 000 (100-yr time frame), with units on the right y-axis.

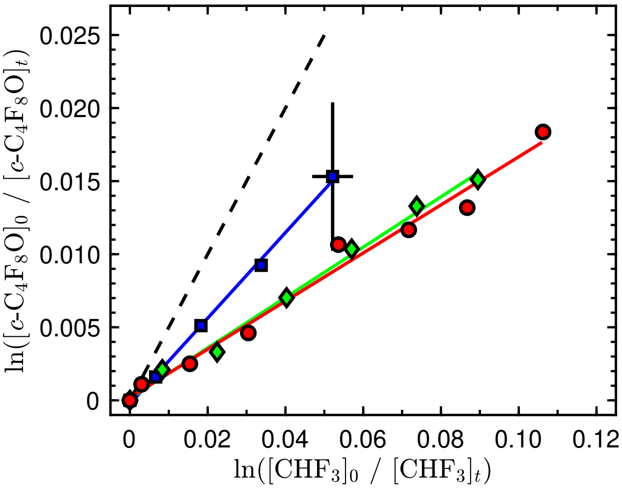


Figure 3. Relative rate data obtained in this work for the $O(^1D)$ + c-C_4F_8O reaction at 296 K. The different symbols are results from independent experiments and the solid lines are linear least-square fits to the data of the individual experiments. Representative estimated error bars from the infrared spectral analysis are included only on a single data point for improved clarity of the graph. The dashed line represents the upper-limit rate coefficient ratio recommended in this work.

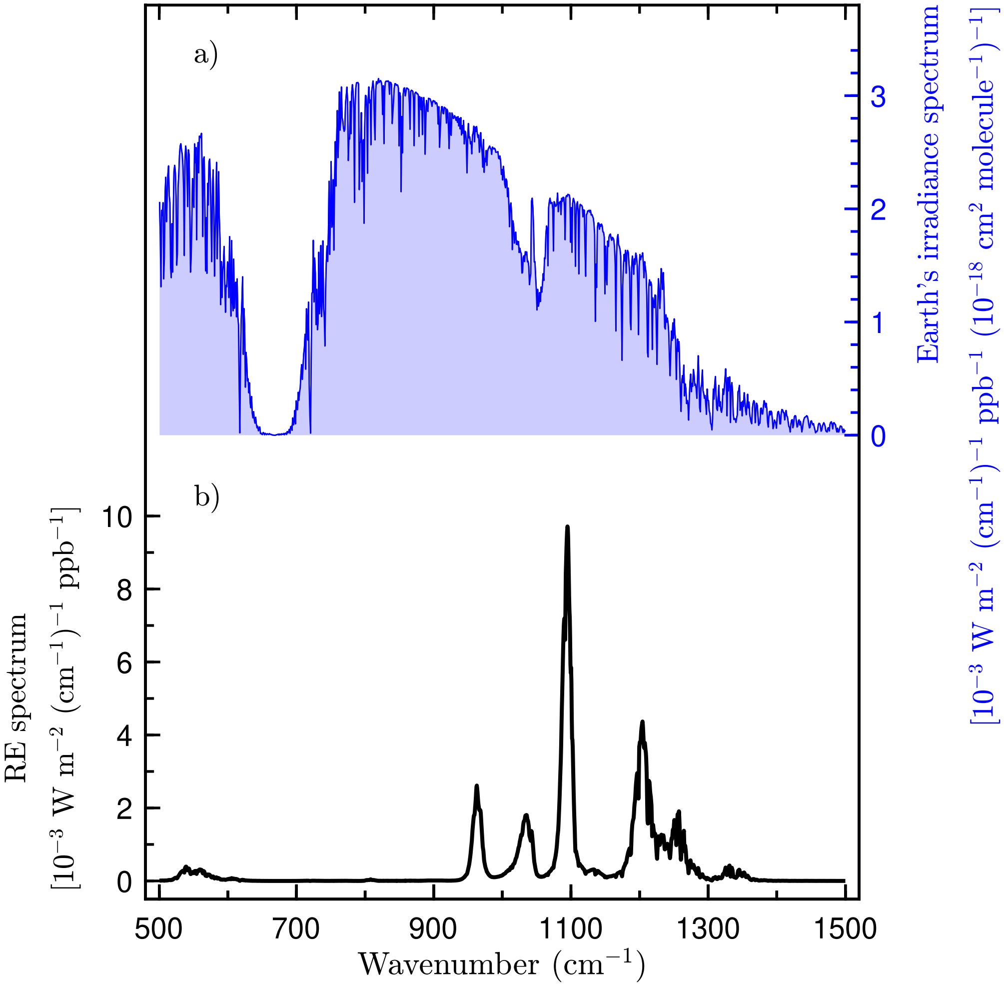


Figure 4. a) Earth's irradiance spectrum as reported by Hodnebrog et al. (2013) and b) radiative efficiency (RE) spectrum of octafluorooxolane (c-C_4F_8O).