Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-267-AC1, 2019

Atmospheric Chemistry and Physics
Discussions
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EGU

Interactive comment on "Perfluorocyclobutane (PFC-318, c-C_4F_8) in the global atmosphere" *by* Jens Mühle et al.

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Received and published: 9 July 2019

We thank reviewer 1 for the overall positive reviews and helpful suggestions. Below we repeat the comments, questions, and suggestions from reviewer 1 in italic and add our replies in bold. If we quote sentences from the manuscript, modified parts will be bold, while unmodified parts will not be bold. We have submitted revised main figures and revised Supplement text, figures, and tables in a zip file.

Reviewer 1:

The authors have brought together an impressive data set for atmospheric observations and modelling of PFC-318, which is global, long-term and consistent. The manuscript is well written but perhaps lacking succinctness a bit, which could be helped

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Discussion paper

by moving some rather technical aspects that are not essential for the narrative to the supplement. A general concern is that the authors focus very much on their hypothesis of PTFE production as the main source of PFC-318 to the atmosphere. Other sources are barely mentioned let alone discussed, whereas the observations in my opinion point to a much more complex picture of emission sources (including unknowns). This should be given some more consideration. Other points are listed below.

We thank the reviewer for the overall positive assessment of our work. We agree that more technical aspect can be moved in the Appendix. In our detailed replies and our revisions to the manuscript we now point out more strongly the limitations of the inversion. Foremost, the further away emissions occur, the more likely the regional inversion method will allocate these emissions to a general diffuse region, rather than identify individual *c*-C_4F_8 point sources. For the Indian subcontinent, the limited number of samples taken onboard the aircraft contributes further to the problem. This needs to be kept in mind when interpreting the inversion results for East Asia and India. We also now emphasize that we cannot categorically exclude an unknown industrial source (Abstract, Section 5.3.5, Summary and Conclusion) and changed or added several statements (Abstract, Sections 5.3.1 and 5.3.5, and Summary and Conclusion), but the data and the inversion results are consistent with the hypothesis that production of TFE/HFP/PTFE/FEP and other fluorochemicals, both historically in developed countries and today in developing countries are likely the main source for *c*-C_4F_8. *c*-C_4F_8 is a by-product of the production of the needed TFE and HFP monomers via the pyrolysis of HCFC-22, industry experts confirm the practice to vent *c*-C_4F_8 from this process into the atmosphere (historically in developed countries and currently in China), emissions are not correlated with population density, and the semi-conductor industries in South Korea, Japan, Taiwan, and Europe do not emit significant amounts of *c*-C_4F_8. We hope that our added explanations and revisions address the concerns of the reviewer.

L119 I don't think a personal communication can be counted as evidence

In hindsight, the evidence was weak and it seems that *c*-C_4F_8 was not used significantly in this application. Lacking other references, we removed this part of the sentence from the Introduction. The evidence for use as geohydrological tracer is also rather weak and we chose to add "perhaps used as a geohydrological tracer"**.**

L169-178 Have the authors ascertained that their calibration system has a linear response behaviour over a relevant mole fraction range? How was the calibration scale uncertainty estimated?

As explained in the last paragraph of Section 2.1, the linearity of the analytical system was assessed "with a series of diluted air samples (parent tank at 1.252 ppt, dilutions from 100 % to 6.25 %, Ivy et al., 2012) and a series of different volumes of a working standard (parent tank at 1.60 ppt, sample volumes from 200 % to 5 % of usual 2 L volume). A small deviation from linearity was observed for the most diluted samples and the smallest volumes probably due to a memory or blank of $\sim$0.014 ppt on Medusa 9 was corrected for. Medusa 7 showed an effect of $\sim$0.008 ppt, but as this was just below the detection limits and within the typical precisions, we chose not to correct for this."**. We hope that the reviewer agrees that these tests are sufficient to establish linearity.**

The calibration scale uncertainty was estimated conservatively based on the purity of the reagent, the reproducibility of the dilution technique to prepare the mixtures, measurement precisions, and propagation uncertainties as outlined in Prinn et al., 2000, 2001, and 2018 which we added at the end of the second paragraph of Section 2.1.

L187 "perhaps slightly better"?

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We tried to express that the 5975 series MSDs showed slightly better detection limits than 5973 series MSDs. As the range of ∼0.01-0.03 ppt includes detection limits estimated for both 5973 and 5975 series MSDs, we changed the sentence to “Detection limits . . . . were ∼0.01–0.03 ppt **for both types of** MSDs.”**.**

L210 “perhaps”?

We agree with the reviewer and removed “perhaps”. It was redundant as the slight uncertainty in the estimated effect of ∼0.008 ppt is already reflected in the approximate sign (∼).

L214-249 It is commendable that the authors have carried out these tests. However, the high number of statistical outliers is worrying and casts some doubt on the derived longterm trends, in particular the early parts. Adding uncertainty ranges to the fits based on a) the samples that were included but showed discrepancies between Medusas and b) the sparsity of the measurements, might help here. In addition, I recommend moving this rather technical paragraph to the supplement.

We understand the reviewer’s concern, which perhaps arises in part from the lengthy description of the tests we performed to verify that measurements at CSIRO and SIO agree, intermingled with the description of the filtering of the actual air archive measurements. We have now moved the discussion of the tests performed at CSIRO and SIO as well as some of the other details into the Supplement (at the beginning). Following the reviewer’s suggestion, this considerably shortened Section 2.2 and streamlined the description of the archive data filtering. As suggested by the reviewer, we have also added the 95% confidence bands to the fits in Fig. 1. It is correct that the “early part” of the record, from the mid-1970s to the late 1970s, is more uncertain as no Cape Grim Air Archive

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(CGAA) data were available, but we would like to point out that the reconstruction of the "early part" of the record, from the late 1970s until in-situ data became available, is dominated by the frequent and well behaved CGAA data. The less frequent, filtered NH tank data play a rather unimportant role. In the fits in Fig 1, this was achieved as described in the text by guiding the NH fit with the CGAA data. Note that, in the CSIRO inversion, the same effect was essentially achieved by using larger data uncertainties for the NH data, so that the inversion fits more closely to the SH data. When the NH tank data are left out of the CSIRO inversion, the reconstructed mixing ratios and emissions do not change significantly (see Fig. S3a for the emissions, and we now include the sensitivity test results for the reconstructed mixing ratios as well in a modified Fig. S3b). Moreover, it should be pointed out that most of the filtered NH tanks were filled in 2003 and later, typically many tanks on one or two days in a given year, which would add little information to the reconstruction given the onset of in-situ data at multiple stations in 2011 and the high quality of the CGAA data used to guide the filtering. We added this explanation to the revised text in Section 2.2.

L225 "eigth"

We fixed this typo to "eighth" **and the text has been moved to the beginning of the Supplement.**

L267 "a"

We removed this orphan "a" from Section 2.3.

L513 How high is the interhemispheric gradient and how has it evolved over time? This might e.g. reveal information on changes in emission latitudes. There is a lot of space

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Discussion paper

in Figures 1 and 4 to show this.

We believe that the IH gradient before the onset of in-situ data is too dependent on the more scattered and uncertain NH archive data to draw defendable conclusions. From 2011 to 2017, when full in-situ datasets are available, the IH gradient increased from ∼0.05 ppt to ∼0.09 ppt, in line with increasing predominantly NH emissions. We added a new inset to Fig. 1 to show this, modified the caption, and added corresponding text to Section 5.1. Unfortunately, we do not believe that we can draw conclusions about changes in emission latitudes from the IH gradient with the 12-box atmospheric model and annually-repeating transport parameters.

L523 Define "good agreement". There are no uncertainty ranges given for the two estimates in Figure S7.

We felt that the old Fig. S7 would be too busy if we had included the uncertainty bands, but we agree with the reviewer that we need to show them. Therefore, we created a new Fig. S7 which shows the reconstructed mole fractions by the two inversions including 2 uncertainty bands, demonstrating the good agreement of the two inversions. We reference this new Fig. S7 in Section 5.1. We also included the uncertainties of the mean ages (before 1965) and effective ages (after 1965) for the firn samples in the new Fig. S7 with respect to the question of reviewer #1 about L1256. (Note, the old Fig. S7 is now new Fig. S8 and so forth. Due to the insertion of new Fig. S12, old Fig. S11 is now Fig. S13 and old. Fig. S12 is now new Fig. S14.)

L537-538 Again, are these discrepancies within uncertainties?

Yes, the discrepancies in global emissions are within uncertainties as can be

seen in Fig. 5. Emissions prior to 1980 rely on archive data that are predominantly NH, relatively sparse and of poor quality compared to later decades (see Sec 2.2), and, in the case of the CSIRO inversion, firn data that comprises atmospheric air spanning a range of ages of typically about 40 years. To make this more clear to the reader and to also follow reviewer #1's comment on the same sentence, we modified this sentence at the beginning of Section 5.2 to “The Bristol inversion initially reconstructs lower emissions, but **the differences are within the estimated uncertainties for the reconstructed histories (see Fig. 5).”**

L555 GWP-100?

The reviewer is correct. We clarified the text at the end of Section 5.2 accordingly. The use of GWP$_{100}$ was actually specified in the caption of old Fig. S8/new Fig. S9, but now we also added the GWP$_{100}$ for each compound as well as a citation.

L571-574 Given that the largest emissions appear to occur near the sea, is there scope for some emissions being related to ships or submissions? What fraction of emissions did the model initially assign to have occurred over the ocean?

We are wondering if there is a misunderstanding here. Old Fig. S10/new Fig. S11 shows the cumulative footprint map for 2010-2017 for the Gosan station. This is the sensitivity to potential emissions from each area of the grid box on the map, not the emission strength at any given grid box. The sensitivity to potential emissions is related to how often air originates from a certain grid box according to meteorological models. It reflects how much information about distant sources is collected at the receptor site (in this case Gosan station).

The model assigns no emissions over sea a priori, and the inversion does not allow emissions to be placed there, see Fig. 7. The inversion actually infers a

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Discussion paper

spatially resolved scaling of the a priori emissions field, therefore by setting 0 emissions then no matter how it is scaled, the resultant emissions will always be 0 over sea.

L590-591 This appears to be in disagreement with the statement in L576-578.

We actually disagree, but our wording in Section 5.3.1 was probably not clear. On L590-591 we compare a) the combined regional emissions in East Asia with our global emissions estimate and b) the Eastern Chinese emissions with our global emissions estimate. On L576-578, however, we compare Eastern Chinese emissions determined by our inversion with the a-priori emissions for Eastern China estimated from Saito et al. Therefore, the statements are not in disagreement. To make this clearer, we have changed the sentence near the end of the first paragraph of Section 5.3.1 to “The a priori emissions for eastern China of 0.185 Gg yr^{-1} are based on the Saito et al. (2010) estimate for all of China for November 2007 to September 2009, **but the inversion suggests emissions that are** ∼62 % **higher** in 2010 and more than tripl**e** in 2017.**”.**

L603 FABS?

We thank the reviewer for catching that we did not define the FABS at the first appearance in the text. We now defined it as “semiconductor fabrication plants (FABS)**”. It had been defined in the caption for Figure 7.**

L631-638 Please add information such as measurement precisions, observed mole fraction ranges, ions used for identification and quantification, etc. on the HFP measurements to the manuscript. Please provide quantitative evidence instead of “associated with” and “virtually absent”.

We apologize for not including more details on the HFP measurements. We now added the new Fig. S12 with a detailed caption. We also modified the main text at the end of Section 5.3.1 and refer to this new Figure. HFP is measured on m/z 131 and 150. On the Porabond Q column it elutes after HFC-125 and before CFC-115. We confirmed the identify of HFP with a spike of ∼10 ppt HFP (87,422 area counts) measured at SIO. The working standard used at that time had a small HFP peak equivalent to ∼0.03–0.04 ppt (270–380 area counts), while ambient air samples contained ∼0.01 ppt HFP (98–123 area counts), just around the estimated detection limit of ∼0.01 ppt (3 times baseline noise). The small abundance of HFP in the working standard led to poor precisions of ∼20%. From Nov. 2018 until present, ambient air measurements at SIO typically showed 0–0.5 times (0–150 area counts) the response of the working standard used, reaching at most 2.5 times, indicating continuing miniscule ambient mixing ratios. HFP measurements at Aspendale (ASA) have not been calibrated, but the peak responses in ambient air sampled from Feb. 2017 until present were almost always small (ranging from 0 – 300 area counts), indicating similarly small ambient mixing ratios as at SIO. Only occasional small pollution events have been observed at ASA as discussed in Section 5.3.3. HFP measurements at Gosan and Shangdianzi (SDZ) were not calibrated, but several working standards showed significant peak responses (up to 2,500 and 4,000 area counts, respectively). From Aug. 2018 until present, *c*-C_4F_8 pollution events at SDZ always coincide with HFP pollution events. The new Fig. S12 shows the ratios of the area response in ambient air samples relative to the working standard (RL (reported)) for *c*-C_4F_8 (PFC-318), HFP, and HFC-23. Good correlations among the three compounds are evident. We removed references to other compounds from the text for brevity. We changed the wording from “associated with” **to “coincide with” and added a reference to the new Fig. S12 which clearly shows the correlations. As requested we clarified the second sentence to** “virtually absent (**≤0.01 ppt)”.

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Discussion paper

L639-641 Consistent with emissions from many of these facilities, but clearly not all (as stated in L610-612). Given the problems with associating these sources can the authors confirm that the ratios between m/z 131 and 101 during pollution events were consistent with those observed in clean air? This would help to rule out interferences during pollution events.

We can confirm that even during the highest pollution events measured at Gosan, the ratios of the mass over charge ratios m/z 131 over m/z 100 show no deviation from those observed in bracketing standards or during background conditions.

L661 How much smaller?

We thank the reviewer for pointing out this omission at the end of Section 5.3.2, which made us also realize that we had not defined the list of countries for the North Western European emissions given in this Section. We have now added this information and we also reran the European inversion as a mistake had been found. This leads to a slight upward revision of the emissions (from 0.02 ± 0.01 Gg yr^{-1} to 0.026 ± 0.013 Gg yr^{-1}) and an updated Fig. 8. We adjusted the wording in Section 5.3.2 to reflect the updated results. We have also added that "The inversion is broadly consistent with emissions from PTFE/FEP production and FABS, but emissions from other industrial sources may also play a role". As requested, we have now added UNFCCC and bottom-up emissions for comparison: 0.0007 Gg yr^{-1} (UNFCCC, 2013–2014) and 0.0017 Gg yr^{-1} (Bottom-up emission inventories, Section 3, 2013–2014)) for the inversion domain.

L697 That is a very optimistic way of looking at that Figure.

The sensitivity of the emissions generally decreases with distance from the mea-

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Discussion paper

surement location, which leads to increased uncertainty in the inversion, both in the spatial distribution of emissions and their overall magnitude. The further away emissions occur, the more likely the regional inversion method will allocate these emissions to a general diffuse region, rather than identify individual *c*-C_4F_8 point sources. We added this explanation to Section 4.4 to point out more clearly the limitations of the regional inversion method. Due to the limited number of samples taken onboard the aircraft, the regional inversion for the Indian subcontinent may have more difficulty identifying individual point sources (which also may not be emitting at all times). We added this information in Section 4.6. We modified the sentence in Section 5.3.5. to stress these limitations “Given the limitations of the inversion method to identify distant point sources from a relatively small number of samples (see Sections 4.4 and 4.6), the posterior emissions . . . **”. As pointed out in the text “**Emissions predominantly occur outside of the Indo-Gangetic plain, the most densely populated region of India” **and we now add** “**, which excludes potential sources that scale with population. Instead the inversion allocates emissions in a much less densely populated region in which multiple likely industrial point sources for *c*-C_4F_8 are located.” We hope that these additional explanations address the reviewer’s concern with respect to Fig. 9 and Section 5.3.5.**

L706-707 This is not very clear from the Figure, which is rather indicating an unknown source.

Given that all the potential PTFE/FEP producing facilities we found in India are located within the emissive region identified by the inversion (Fig. 9), while none are in the heavily populated Indo-Gangetic Plain, and keeping the limitations of the inversion in mind (see our reply above), we are confident that the inversion results support our hypothesis that production of PTFE/FEP and other fluorochemicals is the likely dominant source of *c*-C_4F_8 emissions. Still, we modified

the sentence to “While we cannot categorically exclude an unknown industrial source, these results **are consistent with the chemistry of** PTFE/**FEP** production as dominant emission source of *c*-C_4F_8**.”. We also modified two sentences in the Summary and conclusions section accordingly following the reviewer’s advice. Based on new information, we also added “Note, that one of the facilities in western India (Navin Fluorine International, Surat, Gujarat) is known to also produce HFO-1234yf since 2016, using a process which starts out with the same chemistry, that is the pyrolysis of HCFC-22 to TFE and HFP, with *c*-**C_4F_8 **as potential by-product (see Supplement)”. We added a short section in the Supplement with citations about HFO-1234yf. We also added a similar sentence in Section 5.3.1 about the PTFE production facilities of the Juhua Group Corporation in Zhejiang province which also produce HFO-1234yf since 2016. Other facilities licensed by Honeywell to produce HFO-1234yf using this route with potential *c*-**C_4F_8 **emissions may exist in East Asia, but any such production is relatively recent and cannot explain historic *c*-**C_4F_8 **emissions.**

L713 What is the main purpose of this direct c-C_4F_8 *production?*

The main purpose *c*-C_4F_8 **produced is unfortunately not listed on the HaloPolymer website. We contacted the company, but received no reply. The website broadly states that “R318C is used in air-conditioners, heat pumps and energy units. It is also used for synthesis of fluororganic compounds”. The website lists** CF_4**,** C_2F_6**, *c*-**C_4F_8**,** SF_6**, and** WF_6 **as “specialty gases (that) are organic and inorganic fluorinated gases widely used as dielectrics and fire extinguishing agents, in dry etching processes during production of microelectronics.”, but does not specify for which of these applications exactly *c*-**C_4F_8 **is used. The only use that was not included in the Introduction is “for synthesis of fluororganic compounds”. When searching for chemical reactions on scifinder.cas.org, several reactions can be found in which *c*-**C_4F_8 **is used to introduce -**CF_3 **group into**

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Discussion paper

larger organic molecules. The reaction of *c*-C_4F_8 with TFE to HFP, as described in the Introduction, is also found. Three other reactions are described which lead to a variety of products, including desired products such as the hydrofluoroolefin HFO-1234yf, a fourth generation refrigerant used in newer mobile air conditioners (MACs) or HFP, but also various other products. While it is not clear which of these, or other reactions, using *c*-C_4F_8 as feedstock are commercially important, we added this new information to the Introduction. We have also added short discussions on possible *c*-C_4F_8 emissions from HFO-1234yf production in recent years.

L729 Which ones did PFC-318 correlate best with (also for other pollution events in Asia etc)?

The best correlation was observed between PFC-318 (*c*-C_4F_8) and HFC-23 at ZEP. Other compounds, such as HCFC-22, CFC-13, CH_2Cl_2, $CHCl_3$, or TCE showed weaker correlations. We added Fig. S15 to show PFC-318 (*c*-C_4F_8), HFC-23, and HCFC-22 concentrations at ZEP and now refer to this figure. We also added Fig. S12 which shows the good correlations between PFC-318 (*c*-C_4F_8), HFP, and HFC-23 enhancements at SDZ.

L740-741 How much larger?

We have modified the sentence and added this information in the main text: "These global emissions are significantly larger **than what can be compiled from available** bottom-up inventory information **(70 ± 17 times, 1990–1996, 29 ± 5 times, 1997–2010, 15 ± 1 times, 2011–2014)".**

L1236 Figure 1 is mostly demonstrating quality assurance purposes and one cannot *see most station data anyway as it is on top of each other. As the long-term trend is shown again in Figures 3 and 4 I suggest moving it to the supplement.*

We believe that demonstrating data quality assurance and showing the underlying raw data is very important. Moreover, as requested we have added the confidence bands and the interhemispheric gradients to Fig. 1 and therefore would like to retain Fig. 1 in the main text.

L1256 Is it necessary to show years from 1900 if the first data point is after 1930? What is the uncertainty of the calculated effective ages?

As *c*-C_4F_8 mixing ratios are not much different from zero in the early decades of the 1900s, we have changed Fig. 3 to show mixing ratios reconstructed by the CSIRO inversion from 1930. We would like to point out though that firn measurements are not associated with discrete age values, rather they relate to atmospheric mole fraction from a range of times in the atmosphere. The oldest data point is from South Pole and has a mean age of 1890 (it is mentioned in the Fig. 3 caption that it is not plotted). The data point with mean age 1933 reflects a mix of air from about 1900–1950. So although the measurements do contain information about mole fraction before the 1930s, there is not much change occurring in mole fraction or emissions.

Effective ages before about 1965 are very uncertain, as they depend on the growth rate of *c*-C_4F_8 in the atmosphere which itself is quite uncertain and small at this time. However, as described at the end of the second paragraph in Section 4.3.1, mean ages are shown in Fig. 3 (and the new Fig. S7) for firn data that would have an age before 1965 (for the best case estimate). Effective ages after 1965 are also dependent on the atmospheric growth rate, but this is known quite well from the inversion. Note that the firn data are shown versus mean or effective age in Fig. 3 and new Fig. S7 for illustrative purposes only; the CSIRO inver-

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Discussion paper

sion uses Green's functions (also called age distributions) from the firn model to characterize the age of the air in each firn sample, with the ensemble of Green's functions used to incorporate uncertainty (as described in Section 4.3.1). Therefore uncertainty in effective age is only relevant for the comparison in Fig. 3 and new Fig. S7 and not for the CSIRO inversion. The 2 sigma range for effective ages varies between about ±0.2 and ±4 ppt, with a mean value of ±1.4 ppt (see new. Fig S7).

Supplement

Figure S1 The caption is actually an entire section and should perhaps have its own heading.

We now give the Section its own heading "Details on the tuning of the CSIRO firn model for the Summit13 site" and moved the heading "Supplemental Figures" and Fig. S1 just below this Section.

Figure S3 There is quite some uncertainty in the 1960s and 70s. Has this been reflected in the emission uncertainties?

Yes, uncertainty in the diffusion coefficient for *c*-C_4F_8 relative to CO_2 is included in the Green's function ensemble that is used in the bootstrap method to calculate uncertainties in emissions inferred by the CSIRO inversion. To clarify this, we modified the last sentence of the first paragraph of Section 4.3.1 to "... different firn model parameters **including relative diffusivity** (Trudinger et al., 2013, ...)**".**

Figure S7 Please also show the published observational data set of Saito et al.

Note, old Fig. S7 is now new Fig. S8. As requested, we added the baseline trends

given in Saito et al., 2010. However, we would like to point out that these data had calibration drift problems, see our reply to L547 below, which is why we did not include them in the inversion. We also believe that the baseline algorithm used for these data did not work as well as the AGAGE baseline algorithm, perhaps exacerbated by the significant pollution observed and worse precisions. Therefore, the seemingly large differences between the Saito et al. trend lines themselves and the AGAGE and Oram et al. data are misleading. Note, we also added citations for Saito et al. and Oram et al. under new Fig. S8.

Table S3 RoW is not explained and web pages should be cited with the date on which they were accessed.

We thank the reviewer for this comment as it made us revisit Tables S3 and S4. We realized that we made mistakes with the references and corrected those. We now include the names of the two market reports and when each of the three sources was accessed. We also include definitions of RoW (Rest of the World). For the two market research reports, RoW includes the market share for India and Russia. For www.qianzhan.com**, North America and Europe are also included in RoW as they could not be separated.**

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-267/acp-2019-267-AC1-supplement.zip

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Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-267, 2019.