Atmos. Chem. Phys. Discuss., 12, C556–C563, 2012
www.atmos-chem-phys-discuss.net/12/C556/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emissions halted of the potent greenhouse gas SF_5CF_3" *by* W. T. Sturges et al.

W. T. Sturges et al.

w.sturges@uea.ac.uk

Received and published: 13 March 2012

We thank all the reviewers and public commentators for their very positive comments. Their comments (in italics) are responded to individually below (plain text). Responses are given by the lead author on behalf of all authors.

Anonymous Referee #1 Received and published: 24 January 2012

The paper describes the temporal development of global emission of SF_5CF_3 derived from its long-term measurements from a Southern hemisphere air archive, from Northern hemisphere firn air and from aircraft sampling. It continues the discussion on the atmospheric occurrence and sources of this compound, which was started by the same group around a decade ago. I am very much in favor of publishing the manuscript in

ACP after the corrections/ suggestions have been addressed.

Major issue

I am not very much in favor of the following statement in the abstract: "It is concluded that this is due to the cessation of global production of perfluorooctyl sulfonate-based fluorochemicals". I think there is evidence that this was the global source but this is not 100% certain. So I would suggest that authors should weaken the statement so that if new findings show up they don't have to revise this statement.

Authors. This has been changed to: "The timing of this decline suggests that emissions of this gas may have been related to the production of certain fluorochemicals, production of which has also been recently phased out."

Minor issues

Page 870 Line 2: I would avoid the term "super", the paper is worth to be published also without pushing it in this direction.

Authors. This is not, in fact, our invention; it comes from a paper by Jo Francisco's team at Purdue University: M. F. Gerstell, J. S. Francisco, Y. L. Yung, C. Boxe, and E. T. Aaltonee, Keeping Mars warm with new super greenhouse gases, PNAS, 2001, 98 (5), 2154-2157, doi:10.1073/pnas.051511598. These authors had been developing their paper, unaware that we were about to publish the discovery of one of their hypothetical terraforming "super greenhouse gases" in Earth's atmosphere. The fact that this gas has been considered for its theoretical suitability to induce a powerful artificial greenhouse on Mars – however far-fetched and "sci-fi" this may appear – I think speaks volumes for the potential danger posed by unconstrained release of such a gas. The term "super greenhouse gas" has subsequently been adopted by other authors investigating the physical properties of SF_5CF_3, such as Richard Tuckett, University of Birmingham. However, we have replaced two occurrences of this term, and now merely make note in passing about the coining of this term in Gerstell's paper.

Page 870 Line 11: I would mention the aircraft measurements together with the other measurement platforms in the beginning.

Authors. We take the point, but the first line refers to long-term measurements (Cape Grim and firn air), whereas the aircraft provides latitudinal distribution. It therefore follows on from the initial discussion of time trends. I tried changing it as requested, but it just did not look right. I would prefer not to change it.

Page 871 : I would suggest that the authors give a short overview on the content of the paper at the end of the introduction, in addition to their preparing the ground for exchanging the proposed source from co-production of SF_6 to production of perfluorooctyl sulfonate-based fluorochemicals.

Authors. We have added: "We have updated our time series of atmospheric measurement from our original publication, and find that concentrations of SF_5CF_3 have ceased to increase, whereas the abundance of SF_6 has continued to rise unabated. This clearly demonstrates that. . .".

Page 872: A short description of the standard is needed in the methods section.

Authors. We have added: "The air standard used here is the same as that calibrated for the original study (Sturges et al., 2000) and comprises ambient air filled in the Colorado Mountains by the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado. The calibration of this high pressure cylinder is detailed in the foregoing study."

Anonymous Referee #2 Received and published: 31 January 2012

This is a succinct, carefully written, and complete manuscript. The authors capture the issue and address details sufficiently for the reader to understand the message on first time through. Nice – I don't see that often. I recommend publication without significant change.

Authors. We are very grateful for the kind comments

Suggested alterations: Title: Since this manuscript is on a report on emissions, per se, but rather a top down view of what the end result looks like, the authors may want to insert the word "apparent" in the title. Emissions are deduced from observations here, not directly measured.

Authors. We do see what the referee means, but are struggling to find a way to phrase it elegantly. I think the fact that the atmospheric lifetime is unarguably (after many independent laboratory studies, and our own stratospheric measurements) hundreds of years long, then the fact that concentrations are no longer increasing, and the interhemispheric gradient is now nil, seems to inevitably lead to the conclusion that emissions have stopped; the major conclusion of our paper. We are prepared, however, to change it to "Growth of the potent greenhouse gas SF_5CF_3 in the global atmosphere has halted". We defer to the advice of the Editor on this.

Abstract: The authors addressed "what we did, why it's important, what we found, and what it means" and did it in as few sentences as possible. No changes recommended.

Introduction: All good.

Methods: page 5, line 3. Stating "the" GasPro column suggests that the authors had described it already, but I don't see that.

Authors. We are grateful to the Referee for noting this omission. I have extended an earlier line to: "..samples were preconcentrated on a Hayesep D-packed trap cooled to -780C and separated on an Agilent GS-GasPro capillary column." Now the "the" later on makes sense.

P.S. I am struggling to find "Page 5" – the pages are 869 – 885 in the on line manuscript.

Page 5, line 5. "time trend" is redundant. "trend" says it all.

Authors. Agreed, deleted.

Pages 5-6, section on atmospheric modeling. I'm not too sure that a 2D model was

necessary for this analysis; it seems like overkill for such a long-lived compound. Back of the envelope, global mass balance works fine and gets the same result.

Authors. This is interesting, and I would have agreed with the Referee until we made this study, and indeed this is how we originally derived the emissions in our 2000 paper. I initially did the same thing here for the updated measurements, and then used this as input to the 2-D model. Instead of mapping back on to the Cape Grim measurements, the fit obtained was less-than perfect and even more so when the same trend was used to drive the firn model at NEEM. Again, close but not perfect. This was a surprise. The 'direct' inversion, i.e. the first derivative of the time series, has been used by others, albeit with a greater degree of sophistication and careful application of corrections for, e.g., stratospheric gradients (see the SF_6 study by Levin et al., 2010; referenced in our paper). I think in the latter case this is possible because there is a reasonably monotonic increase in abundance for most of the time record, whereas SF_5CF_3 concentrations 'turn-over' and flatten. As a result, the stratospheric gradient that existed while atmospheric abundances increased (note our measured stratospheric profiles in Sturges et al., 2000) will diminish and disappear a few years after the growth stops. The model even shows a small gradient in SF_5CF_3 in the upper troposphere in mid to high northern latitudes during the period of growth. The interhemispheric gradient also disappears (as the aircraft measurements demonstrate) which can further affect the 'back of envelope' calculation. A further benefit of the modelling approach is that it provides an estimate of the concentration series at the latitude appropriate to NEEM, which can then be used as input to the firn model. In this way we are able to determine consistency between southern hemispheric ambient air observations (Cape Grim), and northern hemispheric firn air measurements NEEM). The appropriate NH trend is not obtained by simply lagging the Cape Grim trend by an interhemispheric exchange time, as can be seen from the modelled Cape Grim and NEEM trends given in the supplement. I am, therefore, fully convinced of the necessity for carrying out the full 2-D modelling exercise.

Page 6, line 7. "time trend" again. Results: Page 7, line 1. "time period" – again, redundant.

Authors. Deleted both.

Page 9, line 21, ff. the aircraft latitudinal gradient gives strength to the overall case. Are there other surface sites to put in with this? Conclusion: All good. Figures: All informative. Nice work.

Authors. No, unfortunately we do not have time series measurements from other sites.

Public comment; M. Vollmer Received and published: 10 February 2012

This is a very nice paper and a great continuation of the SF_5CF_3 story. I have a couple of comments.

1) I strongly encourage the authors to publish their measurement results, in particular the Cape Grim data (and maybe the emissions) in numerical form, for example as supplementary material. Easy and long-lasting access to such long-term records is important for upcoming work on greenhouse gases by other groups and for larger reports ('climate reports').

Authors. We think this is an excellent suggestion, and we will do exactly this: provide a supplement with the numerical data along with the revised manuscript.

2) Like one of the reviewers mentioned, I was a bit irritated by the use of the expression 'super' greenhouse gas. Is this an official term, I have never heard of it. I think the paper is very strong, it doesn't need catchy terms like 'super' greenhouse gas.

Authors. Please see reply to Anonymous Referee 2.

3) In the analytical section, I'd like to see a statement/reference to what primary calibration scale was used and what the accuracy of that scale is.

Authors. Please see reply to Anonymous Referee 2.

4) p. 876, l 14ff. It is stated that the model doesn't produce a significant latitudinal gradient for the years 2005 onward. But what about the 1990s where the emissions seem to have grown rapidly. With all the emissions set to the northern hemisphere (if I understand p. 874 l 13ff correctly), the model should compute a significant latitudinal gradient for that period.

Authors. Yes this is so. For the year 1996 the model shows higher north polar abundances than in the Antarctic. By 2004 there is no modelled difference. Just to be clear, I have amended the text to read: "While atmospheric abundances were rising, e.g. during the 1990s, the model computes significant global latitudinal concentration gradients, and significant altitudinal gradients in the northern hemisphere. For example, for the year 1996 the model predicts 21

5) Even though Rosiek et al., 2007 make a similar statement as the authors of this paper (p. 875, l. 26) about agreement of various measurements, the term 'broadly consistent' seems to be rather stretched when comparing this work with that of Rosiek et al., 2007. The Krakow record shows no sign of flattening, it appears to be in missmatch with the Concordia Dome results, and the absolute concentration nearly reach 170 ppq, while the present study shows SH values around 150 to 155 ppq (Fig. 1 inset), which given the lack of an interhemispheric gradient, should be the same for the NH.

Authors. This is a very good point and we thank the commentator for noting it. I had erroneously compared the 'flattening' of the trend at Cape Grim with that in Krakow, without taking in to account interhemispheric lag times. The 2-D model suggests that the northern hemispheric trend began to turn over in 2001, and had definitely flattened by 2002 – 2003. This is seemingly contrary to the Krakow observations of Roseik et al. By the same argument our results are perhaps not entirely in agreement with Busenberg and Plummer either, in that their measurements suggest an increase in mixing ratios over the USA after 2003, before flattening by 2005. However, their measurements, like those of Roseik et al., have very large uncertainties and within these it is

difficult to draw definite conclusions.

I have, however, redrafted the statement as: "Rosiek et al. (2007) reported an upward trend in SF_5CF_3 (measured by gas chromatography with a modulated electron capture detector) between 2001 and 2003 in Krakow, Poland that is not consistent with the timing of the 'turn over' in northern hemispheric abundances from this study. The 2-D model used here, tuned to the Cape Grim record, suggests that growth in the northern hemisphere would have stopped after about 2001. Measurements by Busenberg and Plummer (2008) of the growth of SF_5CF_3 (also by electron capture detector) since the late 1980s from various sites in North America are in broad agreement with our measurements, and also suggest a possible turn over in concentrations since 2000, although it is difficult to be certain given the relatively large scatter in their reported measurements. It is not clear if analytical methodologies might have contributed to some of the discrepancies noted between these different studies."

6) Minor: p. 870, l. 18: Reference 'Levine' without an 'e', 'Levin, et al., 2010' Ref Rosiek: Change page numbers from 235 to 235 – 242.

Authors. Corrected, thanks.

I hope that some of these comments may further improve this already excellent paper.

Authors. Thank you.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 869, 2012.