Response to reviewers' comments on the manuscript "Satellite observations of stratospheric hydrogen fluoride and comparisons with SLIMCAT calculations" by Jeremy J. Harrison et al.

We thank the reviewers for their comments. These comments are reproduced below in bold text, followed by our responses.

Reviewer #1:

This is a nice and generally well written paper adding more evidence to the role of dynamics for trends of trace gases in the stratosphere. The authors use here observations of the gas HF and its source gases to compare them with results of the SLIMCAT model. As shown in previous papers with a similar purpose, the sophisticated interplay of dynamics and chemistry does not allow to relate observed stratospheric trends directly with tropospheric emission scenarios. Instead, applying a full chemistry transport model as a first step allows to test if or not data are, in a statistical sense, in agreement with a model simulation. The gas HF allows to study this question for a rather long period, as global observations date back to the HALOE instrument.

On the other hand, I have some comments to the paper which the authors may consider for an improved version:
As a major comment, it is somewhat unclear for me what the original contribution of the authors to the content of the paper is.
We are unsure what point the reviewer is trying to make here, particularly as the author contributions are listed in the 'Author contribution' section of the manuscript. We suspect the reviewer is asking for a clearer statement of the new science in the paper, which we will provide.

A rather long part of the paper deals with the description of the ACE-FTS HF observations and some discussion of the error budget. Tables 1-3 also add to the impression, that the authors here present for the first time the version 3.0/3.5 retrieval of the HF data.
ACE-FTS HF v3.0 data have appeared in the literature several times before. However, this is the first paper dedicated to investigating an almost complete ACE time series (2004 to 2012), and providing detailed comparisons with a state-of-the-art CTM. We believe this is the first paper to present v3.5 HF data (data from October 2010).
This paper is a sequel to a previous paper on COF_2, and in keeping with this previous paper it was decided to provide a similar amount of detail on the retrieval. Note that the HF and COF_2 retrievals are distinct, with different microwindow sets and different interferers, so this is not simply repetition.

The inclusion of the HALOE dataset on the other hand directs to the presentation of a new combined dataset. Indeed, the authors present here for the first time (as I understand) the GOZCARDS data set of HF, but which is from version 2.2 of ACE-FTS.
Yes, we are presenting the GOZCARDS HF data for the first time. We will mention this point in the text.

For the model simulation, there is a similar question if the data presented in the paper are from the same run as used in the paper Harrison et al., 2014, or if a different setup has been used. So my strong suggestion would be to state clearly what original new contributions have been made for this paper and how this differs to previous work.
This work does use SLIMCAT data from a new run. The most important update for this new run is that the photolysis scheme now uses modelled ozone profiles in each grid box instead of climatological ozone profiles. We will describe these differences, but note that the effects are small and this is not a major scientific point.

In this line, the paper is in my opinion undecided over its focus. In case the data are in the focus, I would expect to see more of validation work or the construction of a new combined data set. In case atmospheric processes is in the focus, I would expect to see a deeper discussion of the relation between HF and its direct precursos COF2 and COClF (eg. seasonal plots), as an extension of the correlation plots. In case the evaluation of atmospheric transport is in the focus, comparison with tracers of transport (at least for the model) and their discussion would be necessary.
The focus of this work is not 'data'. We will include more of a discussion on model COF_2 and COFCl for completeness. The main science we will expand upon is on the stratospheric transport (see response to Reviewer #2).

Minor comments:
As solar occulation data are sparse, there may be selection effects when comparing zonal means from different data sets and model. This effect may be especially important in high latitude spring when strong azonal structures may develop. Does this explain the higher seasonal amplitude at high latitudes? In principle, one could, as a first step, use co-located data from model and observations. Have you checked if this would change the trend analysis?
This will be checked.

The SLIMCAT model has an upper boundary of 60 km. The stratospheric maximum may not be well presented in the model and HF depleted mesospheric air in polar spring cannot be reproduced by the model. Do you see such effects and does it have any implication for your analysis?
According to Ricaud and Lefevre (referenced in the manuscript), some HF is transported up into the mesosphere, where its mixing ratio remains constant up to high altitudes. At the poles, data are only available up to ~ 50 km. If HF were depleted high up via dissociation, when the air descended the F atoms would simply reform HF. At the 50 – 60 km level, we see no evidence for any depletion.

p34380 l 17: In Fig. 6, at 44.5 km model and HALOE converge, esp. at high lat, meaning that they have a different trend. In Fig 7. they seem to agree perfectly. This looks like more than just a bias shift.
There are some differences in how the data have been filtered, so there can be differences between the plots other than a simple bias shift. Although the reviewer is exaggerating when claiming 'they seem to agree perfectly', we will check that there have not been any errors in compiling the plot.

p34375 l11: compare lifetime of COClF with p34365 l13. Did you re-determine its value here?

Yes, it has been re-calculated for this work. The COF_2 SLIMCAT lifetime has also been updated (due to the photolysis change) and will be included in the manuscript.

p34371 l24: see Waymark et al., 2013, ANNALS OF GEOPHYSICS, 56, Fast Track-1, 2013; 10.4401/ag-6339
There is nothing new in the Waymark paper. The information is taken directly from the Duchatelet paper, which we reference.

Typos or similar:
p34366 l17: Jungfraujoch observations are remote sensing, too. l23: the "however" sounds strange for me when it relates to the space shuttle.
The language will be tidied up here. Although there are some measurements from the space shuttle, these do not provide global coverage over long time periods.

Reviewer #2:

In this manuscript, the authors combine the two multi-year satellite infrared solar occultation data sets available for hydrogen fluoride (HF), the main stratospheric reservoir of fluorine, in order to determine its global distribution and trend over the 1991-2012 time frame. The version 19 set (the latest release to my knowledge) derived from the HALOE (HALogen Occultation Experiment) observations and covering the 1991-2005 period is used, complemented with several subsets (v2.2, v3 and v3.5) derived from the ACE (Atmospheric Chemistry Experiment)-FTS instrument, in operation since 2004.
We wish to point out that the GOZCARDS HF data product was not created specifically for this work. Here we only make use of *existing* HF datasets.

Furthermore, ACE-FTS data available for the main F-bearing source gases (CFC-12, CFC-11 and CFC- 113) and two intermediates of their degradation (COF2 and COClF) are presented. Model results by the TOMCAT/SLIMCAT 3D Chemical Transport Model are included for comparison with the observations and to support the interpretation of the results.
The manuscript is generally clear and well written (although some figures (as Fig. 6) remain tiny and of limited use), the data sets and the results are important and the subject is clearly of relevance for this journal. In my opinion, there are however a few drawbacks that need to be fixed before publication. They are identified and listed below, together with suggestions for improvement.

While one of the aim of this paper is to characterize and understand the evolution of HF over two decades or so, with two different instruments (already a challenge with only a few months overlap between the two missions...), three -possibly inconsistent!- versions of the ACE-FTS data are used, version 2.2, version 3 and 3.5. Moreover, these versions are incompletely described, with e.g., Table 1, 2 and 3 providing information as to the settings for v3 and v3.5, but nothing for v2.2. There is no effort to characterize a possible systematic bias (because different HF lines might be used, the interferences accounted for might be dissimilar...) and to merge the ACE data sets.
All ACE v3.0 data from October 2010 suffer from problems in the P and T supplied by the Canadian Meteorological Centre, and are therefore unusable. V3.5 remedies this problem by using the correct P and T; in this work we use v3.5 data for measurements taken from

October 2010. The retrieval schemes are identical. We will explain this more clearly in the manuscript.
It is not possible to characterise a systematic bias between these datasets, only a relative bias. There is no bias between v3.0 and v3.5, but there is a bias between v3.0/v3.5 and v2.2. We will calculate the bias between the HALOE and HALOE-GOZCARDS datasets and use this to derive an approximate bias between ACE HF v3.0/v3.5 and v2.2 – it should be around 5%, as stated in our paper.
We believe that v3.0/v3.5 is an improvement relative to v2.2. There are undoubtedly biases between the nineteen different HALOE data versions, but it is considered that the latest, v19, is the most reliable. We do not understand how merging different ACE datasets will be beneficial; it is not something that is generally done.

The same is true for the combination of ACE-FTS with HALOE results, despite a well-known bias. The authors state (section 3.2, page 34371): "There have been no detailed comparisons in the literature between ACE-FTS v2.2 and v3.0 HF datasets, however Duchatelet et al. (2010) state that first comparison exercises involving ACE-FTS v3.0 products indicate a decrease of close to 5% in HF amounts". If the bias is not well known while perhaps non-negligible (5%), the authors have to characterize it, this is certainly not beyond the scope of this study, given its aims. They have at hand all what is needed and my recommendation is to use significant subsets of occultations available for v2.2, v3 and v3.5 to determine their consistency and correct for a possible systematic bias. The next step will require a careful combination with the HALOE set, following e.g. the method developed for the generation of the GOZCARDS data product.
As explained in the responses to Reviewer #1, this paper is not focussed on data and the process of combining datasets. We make use of *existing* HF datasets in order to derive trends and information on HF in the atmosphere.
Note that the merging process does not correct for any systematic bias between HALOE and ACE-FTS datasets, only for the relative bias. As described in the preceding paragraph, we can provide a better estimate of the bias between ACE HF v3.0/v3.5 and v2.2. Knowing this bias then makes it possible to estimate the bias between the current GOZCARDS HF product and a potential GOZCARDS product made using ACE v3.0/v3.5 HF.
Undoubtedly a new GOZCARDS HF dataset will be derived in the future, but not as part of this work. A new version will have very little impact on the outcomes of this work.

In the present version of the manuscript, the GOZCARDS ensemble appears useless or underutilized. Added "for completeness" (section 2.3, page 34370), it is only included in Figure 7 and little is learnt from these comparisons. Indicatively, neither the abstract nor the conclusions mention findings resulting from its use. The statement on page 34380-34381 "Had v3.0/v3.5 ACE data been used instead, the GOZCARDS dataset would have been shifted lower in VMR by several percent" further adds to the confusion, leaving the reader unsure about the consistency of the data sets used for the trend evaluation. Trend evaluations which btw do not consider the GOZCARDS merged data set, while it is covering the 1991-1997, 1998-2005 and nearly the 2004-2012 (2004-2010) time intervals. Therefore, my recommendation would be either to discard the GOZCARDS set (saving one figure), or to keep and exploit a merged set for the trend investigations, i.e. supposedly an asset with this respect.
The inclusion of GOZCARDS HF data was simply to ascertain how well a merged dataset would compare with SLIMCAT. Trends were not calculated using GOZCARDS because a merged dataset, which is related to each of the original datasets by a simple multiplicative factor, should produce trends that are the same or at least very similar. The reviewer has

mentioned that we need to correct the systematic bias, however it must be stressed that a merged HALOE-ACE dataset only corrects for a relative bias. Any future GOZCARDS HF product using the same v19 HALOE but a different ACE dataset version will be very similar to the current product, but with a small relative bias. There is still no information as to which is the more accurate. The statement on lines 34380-34381 will be rewritten, with an estimated bias included, and the text will be modified to reflect some of this discussion.

One of the conclusions of this study is that changes or variability in stratospheric dynamics are responsible of variations in the HF trends with altitude and latitude. Several recent papers have identified and investigated these changes (e.g. Ploeger et al., 2015, doi:10.1002/2014JD022468, a reference to it might be useful to the reader), or their impact on significant stratospheric composition changes with time (e.g. for ozone, hydrogen chloride...). As a possible result, the evolution of HF in the stratosphere might well not always follow a smooth route, as is the case in the troposphere, complicating the interpretation of its trend in the stratosphere (upper or lower, in SH or NH), to e.g. support the Montreal Protocol. Indeed, how are the circulation changes and the reduction/variation in source gases emissions contributing to the derived trends? I believe it is therefore important to provide elements allowing to fully characterize these contributions.
Yes, this is a good point. We are aware of papers which have pointed out recent variations in stratospheric circulation – in addition to the Ploeger paper there is one by Mahieu et al. (doi:10.1038/nature13857), which discussed HCl. The modelling in these studies is based on dynamical variability as diagnosed the ECMWF ERA-Interim reanalyses, which are also used in this study. We will add a discussion of these points and mention the consistency between the observed HF variability and the other sources of information. We will also show more results from the fixed dynamics SLIMCAT run (see next point).

The support of SLIMCAT is key here, and the figure 8 (and similar) provide an important input, showing the net and contrasted effect of stratospheric dynamics on the HF trend over the 2004-2012 time period. But there is no information as to the temporal development of HF with altitude/latitude. I think that adding the "fixed to 2000 dynamics" SLIMCAT time series to Figure 6 would be very useful to identify in the various subsets the most significant departures from a smooth unperturbed HF evolution as driven only by surface emissions of the source gases and their subsequent conversion to inorganic fluorine.
Adding the fixed SLIMCAT data to Figure 6 is a good idea, so we will do this.

Minor comments/corrections
Abstract
P34363-L3: suggest adding "involving" to get "...nature, involving e.g. chlorofluorocarbons (CFCs),..."
We are not convinced that this will improve the text.

Introduction
P34364-L7: "source molecules are CFC-12, CFC-11, CFC-113" instead of "source molecules are CFC-11, CFC-12, CFC-113"
The change will be made.

P34364-L16: suggest changing to "Certainly, in addition of HCl, monitoring the growth..."
We will add "(in addition to monitoring stratospheric HCl)" to the end of this sentence.

P34365-L5: suggest adding a blank line between R2 and R3
This is a type-setting issue. The original submission does have a blank line here.

P34366-L15: suggest changing to "..., based on solar spectra recorded by balloonborne and from the ground at Jungfraujoch,"
This will be changed to "… based on solar spectra recorded from balloon and on the ground at Jungfraujoch,"

Section 2.1
P34368-L22: change to "an atmospheric density of 9E15 or 2E16 molecules cm-3"
The text is correct as is. The upper altitude of the retrieval corresponds with the lower atmospheric density (9E15 molecules cm-3).

Section 2.2
P34369-L19: Change to "For the HF channel, the spectral bandpass..."
Will do.

Section 3.1
P34371: I am questioning the relevance and usefulness of the paragraph between lines 8 and 14, starting at "Recently"
This paragraph explains a source of error in the HF spectroscopic line parameters used in this work. The air-broadening parameters were derived using the Galatry lineshape, but these values were attributed to the Voigt lineshape when added into HITRAN.

Section 4
P34374-L12: Could the switch from ECMWF to ERA-I reanalyses be responsible of a bias/change in quality in the SLIMCAT simulations? With a significant impact on the respective HF trends?
The switch actually occurs on 1/1/1979, not 1/1/1989. We apologise for the typo in the text but the earlier 10 years of ERA-I were produced by ECMWF after the main processing and some earlier SLIMCAT runs did change in 1989. We will correct that date in the text. In any case, even 1/1/1989 is significantly before the start of the analysis period and this provides a long enough spin up. The period analysed is all based on consistent ERA-I winds.

Section 6
P34383-L7: a reference such as Ploeger et al. JGR, 2015 might be relevant/useful here
OK.

Table 1. Wouldn't it be more useful to quote the upper approximate altitudes in the last column, for all cases, and mention the density unit threshold in the foot note for the relevant cases?
This is in keeping with the official ACE-FTS microwindow document.

Figure 7: the GOZCARDS symbol should be "empty" (instead of a black diamond)
We will check whether empty or filled works best for this figure.