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Interactive comment on "Stratospheric lifetime ratio of CFC-11 and CFC-12 from satellite and model climatologies" *by* L. Hoffmann et al.

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We thank the referees for the time and effort spent on the manuscript. We carefully considered all comments and hope that the revised draft properly addresses all concerns and issues raised. Below please find our point-by-point replies. A revised manuscript with 'tracked changes' is made available as an electronic supplement.

Anonymous Referee #1

This is a timely revisit and application of the formalism from Volk et al. I have one technical question and several suggestions for presentation.

Technical question: I would like the authors to say a few more words to justify the

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Interactive Discussion
Discussion Paper

assumption that C is linear in time (Figure 2). The values for 2003 and 2006 are used in the calculation. I feel comfortable with the 2006 values since it corresponds to the value calculated by Brown et al. The 1994 value is from Volk et al and the effective linear growth rates for CFC-11 and CFC-12 are both positive. (This is a little surprising in that Figure 1 shows that the tropospheric burden was just about to turn over in 1994.) Between 1994 and 2006, the linear growth rates change sign, but not at the same time. Is it OK to assume that C is linear? I would prefer you just extrapolate the Brown et al results to 2003.

Reply: The transience correction factor (C) may indeed not vary linearly during the time period from 1994 to 2010. We followed the advice of the referee and recalculated the fit based only on the data of Brown et al. This caused minor changes of C (-1.2% in 2003 and -0.4% in 2006) and in the CFC-12 lifetimes (about 1-2 yr) compared to the previous version of the paper. We revised Fig. 2 and the paragraph describing the estimation of C (p16875, l3-14), where we removed the data and the references to the work of Volk et al.

Suggestions

p. 16868, line 3: The use of the term "stratospheric lifetimes", even in quotation marks, should be avoided. The use of the term should be restricted to refer to the proper definition (partial lifetime due to stratospheric loss) as was used at the bottom of the page.

Reply: We replaced "global loss rates" by "stratospheric loss rates" to refer to the correct definition in this place. In general, we think that the term "stratospheric lifetimes" may be applicable here even though a minor limitation is posed by the fact that CFC-11 has a small sink in the tropical upper troposphere. However, the term "stratospheric lifetimes" was also used in other studies of this kind, e.g., by Brown et al. (2013).

p. 16870, line 8 "The slope of the correlation curve equals the ratio of the net global fluxes of the two species through the corresponding surface of constant volume mixing ratio, if that surface lies below all sinks." The sentence should be fixed. The first part is always true. The qualifier applies when you try to relate flux to partial lifetime.

Reply: We reworded: "The slope of the correlation curve equals the ratio of the net global fluxes of the two species through the corresponding surface of constant volume mixing ratios. If this surface is chosen to lie below all sinks, the slope of the correlation curve can be related to the ratio of the tracer lifetimes [...] For stratospheric tracers such as CFCs Eq. (2) holds at the tropopause."

p. 16882 I would like to suggest adding a table or use a table to replace the text. The rows of the table will be: data range, reference year, alpha factor for burden, sigma ratio, gradient, C, lifetime ratio; the columns will be the different data set.

Reply: We agree that a table summarizing the input data for the lifetime calculations would be helpful and we added it in the revised draft. Unfortunately, we realized that not all of the important details can be included, otherwise the table gets overcrowded and confusing. We decided to include the ratio of burdens (B_1/B_2), the tracer-tracer slope (dchi_2/dchi_1), and the transience correction (C_2/C_1), which are the three factors used in Eq. (2) to calculate the lifetime ratio (tau_1/tau_2). We also included the range of years covered by the four data sets. The reader may find the exact time periods in Sect. 2 or in Fig. 3. The alpha factor is the same for all data sets and discussed in Sect. 2.1. The new Table 1 is referenced at the beginning of Sect. 3.

Anonymous Referee #2

The paper describes the application of the standard 'tracer-tracer correlation' technique to three different satellite datasets and a model to update assessments of the ratio of CFC-12/CFC-12 lifetimes or, if a standard value for the CFC-11 lifetime is assumed, the absolute lifetime of CFC-12.

General Comments

1. I assume all three satellites derive CFC concentrations from the same spectral

region (850cm-1 for CFC-11, 925cm-1 for CFC-12) and use the same cross-section data available from the HITRAN web-site? Perhaps there should be some mention of this and its consequence (ie if there any significant spectroscopic errors they will be common to all 3 datasets).

Reply: We agree that spectroscopic errors are an important error source for CFC retrievals. For instance, Hoffmann et al. (2008, Fig. 5) showed that in the MIPAS CFC-11 retrieval the retrieval errors due to uncertainties of the spectroscopic data are about 3-4%. The leading error sources (5-10%, depending on altitude) are the radiometric calibration and the noise. Validation activities showed that the accuracy of the CFC vertical profiles is typically about 10-20%. It is true that the retrievals are based on the same spectroscopic bands of CFC-11 and CFC-12. However, the individual spectral ranges used for the retrievals are different. Therefore the systematic retrieval errors due to the spectroscopy likely differ to some extent as well. Nevertheless, we agree that this issue should be mentioned in the paper. We added on p16872, l13: "Forward model parameters errors such as uncertainties of spectroscopic data are another important error source in the CFC retrievals." We rewrote on p16869, l13-15: "The high degree of consistency of the results for the different and, except for use of the same lists of spectral lines, independent data sets analyzed here provides confidence in the validity of our approach."

2. The satellite gradient data are extrapolated to derive the slope at the ’tropopause’ defined by the independently derived (and more accurate) CFC-11 surface value. (I assume there is upper tropospheric data in the satellite measurements and that this extrapolation is not intended just to cover the gap in vertical coverage). Now, one could argue that the slope should be taken from the maximum of the satellite CFC-11 & CFC-12 values, or that surface measurements should be used to provide bias corrections for both CFC-11 and CFC-12 values, but by extrapolating to the surface CFC-11 measurement aren’t you effectively providing a (positive) bias correction for satellite CFC-11 without any similar correction for CFC-12?

Reply: Our assumption is that the data quality of the CFC satellite measurements is much better in the stratosphere than in the troposphere, because systematic measurement errors are smaller and data coverage is not limited by clouds. The tracer-tracer slope at the tropopause is obtained by extrapolating the slopes from the analysis windows, which are mostly based on data points in the mid and lower stratosphere (where satellite data quality is good), to the tropopause (where satellite data quality is worse). The tropopause vmr is assumed to correspond to the surface vmr, which is best determined by the in-situ measurements. Our approach tries to combine satellite data (from the stratosphere) and in-situ data (from the troposphere) in a way that only the data with good quality are used in the lifetime analysis. Systematic biases of the CFC profiles typically vary with altitude, therefore we decided to not apply any corrections to the entire profiles based on the tropospheric values. These issues are discussed in several places in the paper (e.g., p16869, l9-15; p16871, l26-p16872, l5; p16874, l13-p16875, l2; p16883, l13-18; appendix A).

3. Perhaps I am missing some subtlety here, but taking a simple model of photochemical decay with a constant lifetime T would suggest stratospheric concentrations given by x = x0 exp(-t/T), and hence that an alternative estimate of the ratio of lifetimes of different species is obtained from the gradient of the ln[VMR]s of the species, ie T_12/T_11 = ln[CFC-11/x0_11] / ln[CFC-12/x0_12] (where x0 are the tropospheric values). If true, this gradient in ln[VMR] would be constant throughout the stratosphere, and this seems a simpler analysis than having to extrapolate (linearly in this study) the fundamentally curved line of the gradient in [VMR] to some tropopause value.

It would have been helpful to see a plot of ln[CFC-11] v ln[CFC-12] to verify this (as well as provide alternative estimates of the lifetime ratio) but what is surprising to me (although apparently not the authors since they don't comment on it) is that the [VMR] (rather than ln[VMR]) gradient of the ACE-FTS data is almost constant with altitude (Fig 4, lower right) and the lower left panel of Fig4 seems to show CFC-12 at an almost constant 250 pptv higher than the CFC-11 concentration. This does not seem physi-

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cally reasonable considering the factor 5 variations in CFC-11 values. Perhaps the a priori is having undue influence here?

Reply: This is an interesting thought, but what seems to be missing is that the stratospheric distributions of the CFCs are not only determined by photolytic loss, which varies in strength with altitude, but also by diabatic advection and quasi-isentropic mixing of different air masses. Therefore the CFC vertical profiles are generally not expected to follow an exponential scaling law. The tracer-tracer concept of Plumb et al. and Volk et al. is taking the different atmospheric processes (photochemistry, transport, and mixing) into account.

Specific comments

p16873: I didn’t understand the ’analysis’ window width of 100ppt. If you assign the derived gradient to the mid-point of the analysis window I would not expect the gradients plotted in the lower right plots in Figs 3,4,5 to exceed (satellite maximum-50pptv), yet the points seem to be plotted right up to the satellite maximum. Did you use narrower windows as you approached the end of the range?

Reply: We rewrote (p16873, l26-p16874, l1): "As the data points are unevenly distributed within the windows, we also calculated the mean CFC-11 volume mixing ratio, to which the corresponding slope from the linear fit was assigned." This means that the slopes are not assigned to the mid-point of the window, but to the mean of the CFC-11 volume mixing ratios within the analysis window. As there are usually a lot of data points with vmrs close to the tropospheric value (from all the tropospheric tangent heights), the mean of the CFC-11 vmrs approaches the tropospheric vmr, as the nominal center of the analysis windows is shifted towards the tropospheric vmr.

p16876/77: HIRDLS had a major issue with absolute calibration and, in the past, I believe that they have used MIPAS fields to provide an indirect calibration. I don’t know if this is still true for the data version that you have used, but if so it removes some independence between the two results.

Full Screen / Esc
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Interactive Discussion
Discussion Paper

Reply: A detailed description of the HIRDLS calibration procedure is provided by Gille et al. (2008), which is referenced in our paper. According to that paper the radiance calibration involves an one-time adjustment of absolute values, which is based on radiance calculations for Goddard Modeling and Assimilation Office (GMAO) Earth Observing System version 5 (GEOS-5.01) meteorological data. MIPAS data are used for validation of the HIRDLS data, but not for calibration.

p16877: MIPAS operated from 2002-2014 yet you only use the 2002-2004 data. I presume this is the limit the Hoffmann et al dataset but data for the full mission are available (eg the ESA L2 products) and it seems a pity not to have used years which overlap the ACE climatology (2004-2009) which might have provide some insight into whether the differences between the two satellites could be explained by interannual atmospheric variability.

Reply: Based on this comment we performed additional analyses of the ESA MIPAS data for 2005-2008 (to compare with HIRDLS) and 2004-2009 (to compare with ACE-FTS). Both analyses provided global CFC-12 lifetimes of about 130 yr, i.e., about 15% larger than the results for the other data sets. These differences are important, but they are still within the error bars of our other lifetime estimates. A closer inspection revealed that the differences of the additional ESA data sets are related to non-linear behaviour of the tracer-tracer slopes near the tropopause. In particular, we found that a linear fit does not provide a good way to extrapolate the slopes towards the tropopause. In contrast, the ESA data for 2002 to 2004, which we had already discussed in the paper, show a more linear behaviour towards the tropopause and provide a lifetime estimate that is consistent with the ACE-FTS and HIRDLS data. It should be noted that the MIPAS experiment had significant technical problems in March and April 2004. According to the MIPAS group at Oxford (http://www.atm.ox.ac.uk/group/mipas), MIPAS operated at full spectral resolution (0.025/cm) with nominal 3 km steps in the lower atmosphere from July 2002 to March 2004 (known as "FR mode"). During August and September 2004 MIPAS operated at reduced spectral resolution (0.0625/cm), but keeping the original 3 km scan pattern. From January 2005 to April 2012 MIPAS was still at reduced spectral resolution, but with a nominal scan pattern with 1.5 km spacing in the lower atmosphere ("OR mode"). A significant amount of time was also spent in other measurement modes with different altitude ranges and scan patterns. Our analysis seems to indicate that the results of the FR and OR modes are not fully consistent with each other. However, we feel that further analyses of this issue would be beyond the scope of our study (none of us was directly involved in the ESA operational data processing). We therefore decided to not include these additional analyses in our paper.

Minor/Technical corrections:

Just a superfluous comma after 'account' on p16881, line 17.

Reply: Fixed.

Anonymous Referee #3

General: This paper presents an analysis of satellite data and model simulations of CFC-11 and CFC-12, and applies a tracer-tracer correlation method to assess the ratio of steady-state atmospheric lifetimes. It is an important topic - and one has been the focus of several recent papers and a SPARC evaluation. The paper is generally clear and concise and the figures and tables are all useful and complete. There is one major recommendation for the Discussion and Conclusion section, along with minor comments for revision below

Major: Most of the discussion centers on Table 1, which is an excellent summary and comparison of results. More clarification and discussion is needed, however, for a complete comparison.

1. Differences with Brown et al. are much larger (16%) than one might expect given that the same satellite data set was used. Three possibilities are mentioned (different time period, linear vs. quadratic fit, satellite vs. surface burdens). It would be most useful to other researchers if this paper quantified the impact of each effect. For example, it

would be helpful to know whether using 2005-2010 vs. 2004-2009 really makes that much of a difference, or whether the method is really that sensitive to using a linear vs. quadratic function to extrapolate the slope.

Reply: We expanded the discussion regarding the comparison with the results of Brown et al. in the following way (p16884, l2-10): "Compared to the study of Brown et al. (2013), who applied the method of Volk et al. (1997) on ACE-FTS data, we found a 17% larger CFC-11/CFC-12 lifetime ratio for measurements from the same instrument. Part of the difference is due to the fact that we applied a linear fit to extrapolate the tracer-tracer slope at the tropopause, whereas Brown et al. (2013) applied a quadratic fit. If we replace the linear fit by a quadratic fit in our analysis, the differences to the results of Brown et al. (2013) are reduced to 10%. However, we also found that the quadratic fit significantly increases the error of the extrapolated tracer-tracer slope and thus decided to keep the linear fit in our analysis. The ratio of burdens from our analysis is in good agreement (within 0.7%) with the data reported by Brown et al. (2013). The data for the transience correction are directly obtained from Brown et al. (2013) and therefore can not explain any significant differences. We think that the remaining differences may be due to different data sets used for the lifetime analysis. The study of Brown et al. (2013) covers ACE-FTS data (version 3.0) for the years 2005 to 2010, whereas in our study the Jones et al. (2012) climatology based on version 2.2 was used, covering the years 2004 to 2009. In addition, the median average deviation filtering for each data set was applied using different altitude, spatial and temporal bins." A more detailed comparison of the different time periods (2004-2009 vs 2005-2010) is not possible at this point because the filtered data set used by Brown et al. are not available to us (e.g. supplementary data was not posted with the article).

2. There is no discussion for the large (∼25%) disagreement with Laube et al (2013). That study used aircraft and balloon data. Can all of the difference be attributed to different data sets, or are there large differences in the analysis techniques?

Reply: We think that the disagreement is mostly due to the different data sets rather than differences in the analysis techniques. We expanded the paragraph discussing the variability of the lifetimes (p16886, l8-15): "These issues are of practical relevance for the analysis of temporally and spatially limited data sets from aircraft campaigns, for instance. One example is the recent study of Laube et al. (2013) that closely followed the approach of Volk et al. (1997) to estimate the CFC-11/CFC-12 lifetime ratio from measurements of two aircraft campaigns in late 2009 and early 2010 in northern Europe. Laube et al. (2013) found a CFC-11/CFC-12 lifetime ratio which is 30% larger than our combined result from the satellite data and 18% larger than the new SPARC recommendation. This larger lifetime ratio corresponds to model results (Douglass et al., 2008; Chipperfield et al., 2014), but further study would be helpful to assess possible impacts of the limited sampling characteristics of aircraft measurements. Long-term satellite data sets and model simulations bear the potential to study variability of lifetimes in detail. Brown et al. (2013) studied the hemispheric and seasonal differences based on ACE-FTS data from 2005 to 2010 and found substantial variations of the CFC-12 lifetime estimates (from 94 to 173 yr), but no clear correlations with either hemisphere or season. We also analyzed the hemispheric differences [...]"

3. There is no discussion of the large difference between the EMAC/CLaMS model and the Chipperfield et al (2013) model results. The latter was based on a multi-model analysis. Does this imply that the EMAC/CLaMS model is doing something significantly different than most of the other models used in CCMVal? It will be important to identify the reason or reasons for the difference.

Reply: Indeed, the EMAC/CLaMS model does something different from the other CCMVal models, namely it uses a Lagrangian transport core (Hoppe et al., 2014). We expanded the discussion (p16885, l10-25): "We found that after a spin-up phase of 5 yr the EMAC/CLaMS results are in excellent agreement (<=3%) with the satellite observations. However, the CFC-11/CFC-12 lifetime ratio found here is about 17% smaller than the result of the recent multi-model study of Chipperfield et al. (2014). One the one hand, it should be noted that our simulations are based on a simplified chemistry

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scheme that neglects CFC loss due to reaction with exited state atomic oxygen (Sect. 2.3). However, this is only a minor loss mechanism. On the other hand, we put forward that the Lagrangian transport scheme of EMAC/CLaMS provides an improved representation of advection and mixing in the stratosphere (Hoppe et al., 2014). The Lagrangian transport scheme used by EMAC/CLaMS is fundamentally different from the other schemes used by the models discussed by Chipperfield et al. (2014). We conclude that the new EMAC/CLaMS model will likely become a useful tool to assess the impact of advective transport, mixing, and photochemistry as well as climatological variability on the stratospheric lifetimes of long-lived tracers."

Minor: p. 5, line 22: The tropopause is not entirely below the sink region. Up to 2-4% of CFC-11 loss occurs in the tropical upper troposphere (e.g. Chap 5 of SPARC Lifetimes Report). It would be useful to note this and to quantify the impact of neglecting this loss on the tracer-tracer slope method.

Reply: We agree and added additional information to the introduction (p16868, l2-4): "For CFC-11 it was recently recognized that there is a minor sink in the tropical upper troposphere (SPARC, 2014), which is neglected in our analysis, though." To our knowledge, this tropospheric sink of CFC-11 was not specifically dealt with in other studies based on the tracer-tracer approach for lifetime analysis. Moreover, there is no direct impact of a tropospheric loss on the validity of the tracer-tracer method for the stratosphere (see e.g. the derivation of a stratospheric lifetime of CH4 by this method by Brown et al. (2013)). Owing to the small tropospheric loss rate of CFC-11, however, the impact on the results reported here will be negligible.

p. 7, line 23: The given value for alpha depends on B_1 as representing CFC-11 and B_2 as CFC-12, I think. However, this is not explicitly stated (or it was not obvious to me).

Reply: This is correct. We clarified: "To take into account the stratospheric distributions, we apply a scaling factor alpha=0.97+/-0.01 to convert the ratio of surface values to the ratio of total atmospheric burdens. This value of alpha specifically applies to the ratio of CFC-11 and CFC-12. It was estimated from data reported by [...]"

p. 8: It is made clear that the analyses are based only on midlatitude data, but not so clear whether annual means are used until pp. 11-12. It might be useful to point this out early on p. 8, but more importantly in connection with the tracer-tracer slope technique, it should be discussed why the analysis is not restricted to the fall-winter-spring season. In Volk et al (1997) it was pointed out that for this method, vertical gradients should be derived from data taken during the winter half-year that dominates net transport.

Reply: On p16869, l5 and p16873, l10 we replaced "zonal means" by "multi-annual zonal means" to point out more early that multi-annual means were used. The recommendation to use data from the winter half-year from Volk et al. (1997) refers back to Plumb (1996). In that paper it is argued: "Assuming that little transport is occurring, concentrations may be ’frozen in’ for the summer, but chemistry will cause changes [...], thus leading to a spreading of the compact correlations until they can be reestablished with the onset of wave activity in fall." However, Plumb (1996) and Volk et al. (1997) also argued: "Finally, if the correlation slopes in both hemisphere do not differ much from each other, (3) [i.e., the equation for the lifetime ratio] applied at the tropopause using an average correlation slope is likely to be a good approximation for the ratio of the global stratospheric lifetimes." Our analysis did not show any large differences between the hemispheres for the different data sets (see section 3 and 4) and we conclude that the use of annual mean data is justified in this case.

p. 14, lines 10-11: A more complete description is needed for the CLaMS simplified chemistry scheme and its treatment of photolysis rates and O(1D) (and thus, ozone) chemistry since these are the main loss reactions for CFC-11 and CFC-12. For example: the input UV solar spectral irradiances, the treatment and parametrization of oxygen and ozone absorption, and whether the modeled ozone distribution is realistic in comparison to observations.

Reply: We rewrote "Here, we employed a simplified chemistry scheme that is efficient for long-term simulations (Pommrich et al., 2014). The simplified scheme uses daily-mean photolysis rates and describes the first order loss of long-lived tracers, such as CFC-11 and CFC-12. The photolysis rates were calculated as diurnal averages using the CLaMS photolysis code (Becker et al., 2000). The simplified chemistry scheme does not simulate chemical loss due to the reaction with exited state atomic oxygen, O(1D). However, the contribution to global CFC loss due to the reaction with O(1D) is below 10% (Minschwaner et al., 2013)." At the end of Sect. 2.3 we added "Further validation of the EMAC/CLaMS simulation results is provided by Hoppe et al. (2014)."

Figs 4-7: Suggest terminating the red line at CFC-11 = 100 ppt, since the linear fit to the slope is restricted to values of CFC-11>100 ppt.

Reply: We changed the plots as suggested.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C8098/2014/acpd-14-C8098-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 16865, 2014.