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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stratospheric lifetimes of CFC-12, CCl_4, CH_4, CH_3Cl and N_2O from measurements made by the Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS)" *by* A. T. Brown et al.

Anonymous Referee #1

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General Remarks:

This paper presents calculations for the stratospheric lifetimes of CFC-12, CCl4, CH4, CH3Cl and N2O. The calculations based on measurements made by the ACE-FTS satellite instrument. Beside the estimation of the lifetimes itself, the aim of this paper is also to test the "universality" of long-lived tracer-tracer correlations in the lower extratropical stratosphere which are a fundamental theoretical prerequisite for the estimation of the lifetimes based on tracer-tracer correlation. The terminus "universality" is meant here in the sense described by Volk et al. (1997) (for details see comment

“Page 10, Line 318-321”). This is an important issue and a satellite instrument has the advantage over in-situ measurements of much better temporal and spatial coverage and therefore it is ideally suited for this problem. The paper is very well written, coherent and comprehensive and the topic is of high relevance. However, there is one thing that necessitates a major revision. The error estimates have to be revised. The authors have not accounted for systematic errors. As outlined in the comments the systematic error(s) are essential for this kind of study – they cannot be ignored.

Comments:

Page 6ff Please update the reference for the Laube et al. Paper: Laube, J. C., Keil, A., Bönisch, H., Engel, A., Röckmann, T., Volk, C. M., and Sturges, W. T.: Observation-based assessment of stratospheric fractional release, lifetimes, and ozone depletion potentials of ten important source gases, Atmos. Chem. Phys., 13, 2779-2791, doi:10.5194/acp-13-2779-2013, 2013.

Page 6, Line 171 “This value has been scaled by the effective linear growth rate ($\gamma 0$) of CFC-11 during this time (the values for which can be seen in table 2).” What does this means exactly? Looking at table 1 the gradient dCFC-11/dAOA (AoA: mean age of air) is monotonically increasing from 2005 to 2010 while the effective linear growth rate of CFC-11 does not show the same behaviour. Why?

Page 6, Line 171 For the sake of traceability and because it is an important part of this kind of lifetime calculation, it would help, if you can specify precisely, how you calculate the effective linear growth rate. I assume that you use equation (A13) of Volk et al. (1997) – further on V97. If so, it will still be interesting over which time interval and how you fit the tropospheric time series (probably eq. (A12) in V97). Especially, this is true for tracers which could not well be characterised by a quadratic function.

Page 6ff Why you are using only 2 seasons? If the seasonality has a significant impact on the lifetime estimation then it will be better to calculate gradients and subsequently lifetimes for all 4 seasons. It is a fact that temporal (and also spatial) coverage is the big advantage of the satellite remote sensors in comparison to high-resolution/precision but sparse in-situ measurements. Therefore you should fully resolve the seasonality - if possible with the given amount of ACE satellite occultations during each season. This would help to interpret the seasonal influence for specific localised in-situ measurements.

Page 7, Line 203ff “In addition measurements made within the vortex were filtered out when the outliers of the data were removed.” How you filtered out vortex data? Is the criterion of 2.5 times the median absolute deviation sufficient enough to remove vortex data – especially in the northern hemisphere where the elongation of the vortex to lower latitudes is much more prominent than in the southern hemisphere?

Page 7, Line 195-197 “Tropical correlations thus reflect local rather global sources and sinks and are thus unrelated to stratospheric lifetimes (Plumb, 1996).” This is only true for the tropical pipe model (Plumb, 1996), but not for the global diffuser model (Plumb, 1992) and not for the more up to date and realistic tropical leaky pipe model (Neu and Plumb, 1999). However, it is not the scope of this paper to discuss the nature of tropical tracer-tracer correlations, but it is definitely not true or at least misleading to say that tropical correlations are unrelated to stratospheric lifetimes. The tropical tracer-tracer correlations are at minimum related to the photochemical decay in the tropical stratosphere and therefore these correlations are related to the overall stratospheric lifetime even though they do not reflect and cannot be used to calculate the overall stratospheric lifetime. My suggestion would be to change the sentence to: “Tropical correlations thus reflect more local rather than global sources and sinks (Neu and Plumb, 1999; Plumb, 2007) and are therefore not suited to derive global stratospheric lifetimes.”

Neu, J. L., and Plumb, R. A.: Age of air in a "leaky pipe" model of stratospheric transport, J. Geophys. Res., 104, 19243-19255, 1999.

Page 7-8, Line 224f and 244f You stated out that CFC-11 is on the y- and the other

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correlating species is on the x-axis. In all of your Figures (1,4-24) it is the other way round.

Page 7-8, Line 224-245 For the slope estimation at the mid-latitude tropopause only statistical errors were assumed. Due to the fact that the absolute value of the slope at the tropopause is of interest also systematic errors of the satellite measurements (retrievals) are not negligible – just think of a possible systematic offset in the lower stratosphere for one of the tracers. This would shift the whole correlation including the slope at the tropopause. To my opinion the statistical error alone is not sufficient to describe the uncertainty of the slope at the tropopause which is essential for a tracer's lifetime. This may not be of importance for high-accuracy in-situ data (with little systematic uncertainties) but it is a problem when using satellite data.

Page 8, Line 228-234 It is not clear to me why the derived slopes are irregularly spaced – fewer points for all correlated species in the range of 140 to 200 ppt CFC-11 (see left side of Figure 1). Following your description how you calculate the slopes, the yielded data points should be evenly spaced when using an 80 ppt CFC-11 window and a regular step size of 5 ppt. If it is true that the density of points (each representing a tracer-tracer slope over the range of 80 ppt CFC-11) is distributed like it is shown in Figure 1 and all other appended correlations (Figures B1 to B21) then the the polynomial fit to this data is biased towards the higher (>200 ppt CFC-11) and the lower (<140 ppt) mixing ratios. Especially the latter is problematic because one must ask why this part of the correlation far away from the tropopause has a higher weight the data closer to the tropopause on the estimation (extrapolation) of the slope at the tropopause.

Page 8, Line 247-249 Page 29 and 38-42 Figure 1 and Figure B6-B10 You are arguing that the curvature of the correlation closer to the tropopause in the range below 210 ppt CFC-11 is caused by the non-steady state flux of chemical species into the stratosphere – or in other words by tropospheric trend of the tracers. That means the observed curvature would be indicative for the tropospheric trends of the specific tracers. As an example, I looked at the CFC-11/CFC-12 correlations during northern

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hemisphere winter. Both tracers are fairly well mixed in the troposphere and they show neither a significant interhemispheric gradient nor a strong tropospheric trend (i.e. decrease) during the last decade. For these tracers the specific correlation seems to tilt towards smaller slopes closer to the tropopause. This behaviour is completely different compared to the in-situ observations of the CFC-11/CFC-12 correlation shown by Laube et al. (2013) (see Figure 5 in the supplementary). These data show late 2009 and early 2010 correlations. This behaviour is essential for the slope extrapolation. Therefore it is essential to understand what causes this discrepancy. Again, there are systematic errors for satellite retrieval products that could not be ignored for the data interpretation if the accuracy of the data matters.

Page 9, Line 277-281 Page 25 Table A4 The mean VMRs at the tropopause ($\sigma 0$) were calculated solely from ACE retrievals. It is conspicuous that the mean VMRs at the tropopause are significantly lower than the global tropospheric background from the observation networks (AGAGE, NOAA) for tracers like CFC-11 (e.g. $\sim$241 ppt in 2010), CFC-12 (e.g. $\sim$530 ppt in 2010) and N2O (e.g. $\sim$323 ppb in 2010), which are all homogeneously distributed in the troposphere and do not have a vertical gradient because they have no significant sinks in the troposphere. One can argue that $\sigma 0$ is only needed for the steady-state correction of the slopes, which is rather small for all three tracers mentioned above. Nevertheless, there is another impact of $\sigma 0$ – it defines the tropopause and therefore the endpoint of the polynomial fit extrapolation. However, this is obviously true only for CFC-11. It looks even worse for CCl4. The global tropospheric background is about 90 ppt in 2007-2008. Your estimation is about 105 ppt during this time, more than 15% above the expected upper tropospheric VMR. In the case of the other three one might argue that the mean VMR at the tropopause might be biased by some stratospheric data due to the limited resolution of the satellite product in the tropopause region, but this argument doesn't work for CCl4. Looking at such big differences between satellite data and observations - and we are talking here about the comparison of statistical significant mean values and not single profiles - the question arises again: Do systematic uncertainties play a role for this lifetime

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calculation? To my opinion, if the tropospheric VMR is systematically wrong then there is a high probability and certain risk that the correlation itself is biased in this region, at least in case of CCl4.

Page 9, Line 284-295 If taking into account that more than 80 % of the atmospheric mass is located in the troposphere then it is obvious that the uncertainty of the mean VMRs at the tropopause (σ0) directly affects the uncertainty of the mean atmospheric VMR, especially if you are expanding these values down to the ground. As outlined above the given error bars for the mean VMRs at the tropopause are of only statistical nature and therefore seems to be significantly too small. The consequence is that the error bars for the mean atmospheric VMR are also much too small, even if the systematic errors of the whole stratospheric part of the tracer profiles are completely ignored. The fact is most obvious for CCl4. The mean atmospheric VMR is higher than the observed global tropospheric background and the discrepancy is by far not covered by the given error bars.

Page 10, Line 318-321 "Since neither the season or the hemisphere appears to have a significant effect on our results it is possible to calculate a total weighted mean." This finding is beside the calculated lifetimes itself the core of this paper. However, the conclusion is questionable. First, the error analysis has to be revised (see comments above), because realistic error estimation is the basis for such a conclusion. Second, it is not correct to draw the conclusion from the seasonal and/or hemispheric averaged lifetimes shown in Table 4. The universality of the tracer-tracer correlation must hold for each hemisphere and season separately. That means the non-averaged values shown in Table 3 must be the basis for the analysis. Inside the given error bars the specific correlations are definitely not universal. As an example, N2O has a lifetime of 66 (+12) years for SHS and 185 (-35) years for NHS in 2009. This is more than twice of the estimated lifetime in SHS and clearly outside the given error bars.

As stated by V97 (and references within), the universality for the correlation of long-lived tracers in the lower extratropical stratosphere is a fundamental theoretical prereq-

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uisite for the estimation of the lifetimes using tracer-tracer correlation. The terminus "universality" is meant here in the sense how it is described in V97: "Universality shall indicate compactness on a wide temporal and spatial scale, meaning little scatter in a correlation diagram containing data from all seasons and from a large spatial region (here generally the extratropical lower stratosphere)." V97 showed that for tracers with lifetimes greater than the lifetime of H1211 or at least greater than CFC-11 the correlation in the extratropics is universal below a potential temperature of 475 K.

Page 24ff, Appendix A The references in the text referring to the Tables and Figures in the Appendix are often incorrect. Also the nomenclature and numbering of the Tables and Figures in the Appendix A is inconsistent. Further, I would suggest moving the Table A4 (Mean VMRs at the tropopause) and Table A6 (Mean atmospheric VMRs) to the main section and discussing the results – see remarks above.

Page 29 and 41, Figure 1 and Figure B9 There is missing northern hemisphere winter 2009 correlations in the supplementary. Instead Figure 1 and supplementary Figure B9 both showing the same data - northern hemisphere winter 2008. The latter should show 2009 winter correlations.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 4221, 2013.

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