**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Observation-based assessment of stratospheric fractional release, lifetimes, and Ozone Depletion Potentials of ten important source gases" *by* J. C. Laube et al.

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Referee comment

1. Age of air. There is a very good discussion of the overall data analysis, quality checks, and specific numbers for the amount of useful measurements, number of excluded measurements, etc., but the fraction of measurements with insufficient precision for SF6 was not clear (I estimated about half based on all of UFra data plus all 2011 data). If it is a significant fraction of the data, then the use of a 2010 high-latitude correlation between age of air and CFC-12 could be explained further. Although a similar methodology was used in a previous paper, the correlation from that paper was based

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on tropical measurements and it was used for deriving tropical FRFs, whereas the correlation in the present paper is for high latitudes and it is used for mid latitude FRFs. Clearly the age-CFC-12 correlation is different between the tropics and extra-tropics but it is not so clear that it would be the same for mid and high latitudes. Since there is a discussion on pp. 9-10 about FRF differences between mid and high latitudes, one might wonder whether eq (1) would be appropriate to use for mid-latitude data. It would be desirable to show the age-CFC-12 correlation plot in the Supplement and include more discussion of the possible impact on FRFs in the text. One reason why this is important is because eq (1) could play a large role in the FRF vs. age relationship for CFC-12. For those data where CFC-12 is used to infer age, the CFC-12 FRF is based entirely on measured CFC-12 since the same measurement is used directly for X(x,y,z,t) and indirectly for Xentry . When the CFC-12 FRF is plotted vs. Γ, those data points using CFC-12 for age appear to be just expressing some form of the relationship set by eq (1).

Author response

As an initial remark we would like to acknowledge the work of the anonymous reviewer which has further improved this publication. As for the age-CFC-12 correlation: The flights with insufficient SF6 precision were exclusively high latitudinal. To make this clearer to the reader we modified the statement in section 3.1 to "For those flights with insufficient SF6 precision (exclusively high-latitudinal, see above) we used the 2010 high-latitudinal correlation between SF6 and CFC-12 mixing ratios...". For the calculation of the CFC-12 lifetime and FRFs we had already excluded all mean ages derived from this correlation to avoid any of the influences pointed out by the referee. This is now stated in the revised manuscript ("Moreover, mean ages derived via Eq. (1) can not be used to infer FRFs of CFC-12.").

Referee comment

There seems to be an inconsistency between equation (1), the slope in Figure 1, and

the correlation slope in Figure S5. It may not be that significant to the overall results, though it should be looked into. If eq (1) is used to evaluate $d\Gamma/dX12$ at $X12 = 540$ ppt, it would be -0.03482 yr/ppt. Combined with the result $dX11/d\Gamma = -20.7$ ppt/yr at $X11=241$ ppt from Figure 1, one would find 1.387. The value of $dX12/dX11$ based on the correlation slope in Figure S5 is 1.339, so it is only a few percent smaller. Perhaps is this because eq (1) is based on a subset of the data whereas Figure S5 includes all of the data, but it would be worth checking to make sure that eq (1) is consistent with the rest of the analysis.

Author response

These slope differences are indeed related to the fact that only high-latitudinal data was used to infer Eq. (1) (see discussion on above comment).

Referee comment

2. Figure 1, showing the correlation of CFC-11 mixing ratios and mean age of air, shows an interesting pattern. It is not immediately obvious from the raw data that the slope is changing by all that much, in order to extrapolate a slope at age=0 yr. The linear relationship between age and slope as shown in the figure (intercept=-20.7 ppt/yr, slope=-6.9 ppt/yr2) implies a quadratic polynomial between X11 and Γ, and it might be useful to overplot such a curve on the figure, in order to show that there is sufficient curvature to justify a linear change in slope. There is a question of why there is such a sharp break where the slope is approximately constant for $\Gamma > 2.5$ yr. If there is a physical explanation then it would be desirable to include a discussion of this behavior. Otherwise, how can one be sure that there is not another sharp break where the slope is constant for $\Gamma<0.7$ yr, so that the intercept should be -25 ppt/yr rather than -20.7 ppt/yr?

Author response

As noted by the referee no curvature in the correlation of CFC-11 with mean age would

result in no correlation of slope with average mean age. The observed slope changes thus already demonstrate a curvature of the original correlation below mean ages of 3.3 years (which are equivalent to average mean ages of 2.5 years). The respective polynomial was added to the figure as requested. The break in slope changes is likely due to a) increased uncertainties in higher mean ages and b) decreased data density at higher mean ages due to the exclusion of polar vortex data. We can not rule out another break in slope at younger ages but this is accounted for in the derived uncertainties (displayed are 1 sigma uncertainties, so within 2 sigma the intercept could be between -11.4 and -29.8).

Referee comment

3. The correlation slopes of the mixing ratios versus CFC-11 that are presented in the Supplement, which are fit to polynomials and extrapolated to the slope at the tropopause, also show interesting behavior. Most (but not all) show an upward concavity. If there a physical explanation for why some gases have this curvature, then it might be useful to include a discussion since this curvature does seem to be important for extrapolating the slope at the tropopause. For example, Volk et al 1994 identified two key factors contributing to curvature: tropospheric growth and fluxes across the tropical/mid-latitude barrier (the "leaky pipe"). Can anything be updated from that discussion using this newer data? The curvature here for CFC-12 vs. CFC-11 appears to be a little larger than seen in the 1994 data from the Volk et al paper, even though effective linear growth rates for the 2010 data are negative as opposite to positive for 1994, and the growth magnitude for CFC-12 is now much smaller than what is was in 1994. This might imply that the leaky pipe has more of an influence on curvature than growth, or is there another conclusion that could be drawn?

Author response

The following sentence was added to the relevant section in the supplement: "As has been noted by Volk et al. (1997) tropospheric growth and fluxes across the tropical/mid-

latitude barrier are the major contributors to the curvature of the slope evolution of these correlations." A further discussion of the influences of tropospheric trends and stratospheric transport on the curvature of these correlations is beyond the scope of this work.

Referee comment

Finally, it seems that the extrapolation will be sensitive to the behavior of the correlation slope for CFC-11 mixing ratios less than 170 ppt, and yet this region is not considered when assessing the slope of CFC-11 vs. age in Figure 1 (see comment 2 above). For example if data for CFC-11<170 ppt were excluded from the fit in Figures S4 and S5, then the extrapolated slopes and lifetimes for CFC-113 and CFC-12 could be different. On the other hand, if data for CFC-11<170 were included in a quadratic fit to the slope in Figure 1, consistent with the way the other correlations are treated, then the derived CFC-11 vs. age slope, which is important for all lifetimes, would probably be different. Either way there should be a consistent treatment of fitting and data ranges, or sound reasons given for changing things up.

Author response

Different ranges and fitting algorithms have indeed been used to infer the slopes of CFC-11 versus mean age as compared to CFC-11 versus other tracers. This distinction has been made for the following reasons:

1) The use of a smaller range: Our data set has a gap between average mean ages of 2.5 and 2.8 years. It also shows higher uncertainties and a break up of the mean age-CFC-11 correlation at ages greater than 2.8 years. As a result we refrained from the inclusion of such data. This has already been stated in the manuscript: "We... choose a smaller age range as compared to Volk et al. (1997) (0.8 to 3.5 years) as we observe higher variability of the slopes at larger mean ages.

2) The use of a linear fit function: Mean age is different to all other tracers here as it is

a chronological tracer and therefore has a source constant in space and time. We find no significant curvature of this particular slope evolution and thus consider a linear fit more appropriate. This is in agreement with the data presented in Volk et al. (1997) where also very little curvature was observed for the slopes of the CFC-11-mean age correlation. The following statement was added to the caption of Figure S4: "Finally, in contrast to the slope evolution of the correlation of CFC-11 with mean age (linear regression line fitted, see Figure 1 in the main manuscript) a quadratic polynomial was fitted here as we observe more complex curvatures."

Minor suggestions/corrections:

Referee comments

p2 line 3: "we calculate lower ODPs than recommended by WMO". Otherwise the implication is that WMO calculated the ODPs.

p2 line 25 "study" should be "studies"

p3 line 15 "GCMS" (no hyphen)

p4 line 13 Levin and Hesshaimer (1996) is not in the ref list

p5 line 23 I suggest adding mean in this sentence: "We then calculated the mean mixing ratios..." and similarly suggest adding an overbar to Xi,entry in eq (2) to make it clear this is a mean entry mixing ratio

p10 line 11, "differences with Newman et al"

p12 line 7 "differences with the correlations of"

p12 lines 16-17 may be an extra "CFC" in this sentence

p14 line 18 Grammar "for; here: 60"

p. 24 Table 1 header "Differences with NOAA-ESRL"

Author response

All changes were made as requested.

Referee comment

p6 eq (4) It might be useful to remind the reader after this equation that $\Lambda = \Delta 2 / \Gamma$, rather than waiting until halfway down the next page (lines 18-20). Also, it is mentioned that three different values of Λ were used for lifetimes. I could not find where it was discussed how this impacted the lifetime values (I suspect not very much), though it should be noted that the value of 1.25 used for the best estimate lifetime is different from the value of 0.7 that is used for the FRFs. It seems odd to use different values of a supposedly invariant quantity in the same paper.

Author response

The definition of Λ was added to the caption of eq (4). A statement on the sensitivity of fractional release to Λ was already in the manuscript (section 3.1): "Laube et al. (2010a) tested the sensitivity of this parameterisation with different ratios and found the corresponding changes to have little influence on fractional release." Depending on the growth of the tracer the influence on the stratospheric lifetime can be bigger and 1.25 was used for consistency with Volk et al. (1997). The following statement was added to the manuscript: "We generally find that the stratospheric lifetime uncertainties are dominated by the two slope uncertainties with a smaller contribution from the different widths of the age spectrum."

Referee comment

p7 lines 3-10: It was not clear to me why expanding the slope expression into two terms offers an advantage. Even though CFC-11 has one of the best precisions in the dataset and the best-constrained slope against mean age, it would seem that the addition of any random error from CFC-11 should make the expansion of the slope expression less accurate than a direct correlation of that source gas with age. On simple terms, one might expect that if there is a good correlation of any tracer with CFC-11, then

there ought to be a reasonable correlation of that tracer with mean age.

Author response

Equation (5) currently expresses the sought steady-state slope vs F11 (dsigmai/dsigmaF11) as function of the observed slope vs F11 (dXi/dF11) and the F11 slope vs age (dF11/dgamma), which is achieved by the expansion made in the numerator. Not making the expansion, the result would alternatively be derived as function of the two slopes (dXi/dgamma and dF11/dgamma) versus age. In either case, two observable slopes are needed. There are two major advantages in the former formulation:

1) dXi/dF11 can be measured to higher accuracy than dXi/dgamma, both due to the limitations in age precision and the fact that for a number of species (not F11), the correlations with age strongly curve toward the tropopause (cf. Volk et al., 1997).

2) the less precise slope dF11/dgamma appears in both the nominator and denominator partially cancelling out (in fact it would cancel out exactly if neither the species in question nor F11 had tropospheric growth). Overall, in equation (5) in its present form, the principal information always comes from the (well constrained) dXi/dF11, while the more uncertain slope dF11/dgamma enters effectively as a (usually small) correction term that only gains significant influence when tropospheric growth is very large. Not making the expansion would spread the information about evenly between two observables (dXi/dgamma and dF11/dgamma), even in the absence of growth when the result could be delivered from only one (dXi/dF11).

We complemented the explanation in the manuscript with: "The less precise slope dF11/dgamma now appears in both the nominator and denominator resulting in uncertainties partially cancelling out. Overall, in Eq. (5) the principal information always comes from the well constrained dXi/dF11. The more uncertain slope dF11/dgamma is in many cases a small correction term that only gains significant influence when tropospheric growth is very large."

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p10 line10 Is it that the FRFs are too small, or that the uncertainties are too large for a meaningful comparison?

Author response

The relative uncertainties of HCFC-142b FRFs are not particularly higher than those of other HCFCs as is apparent in Figure 4. We therefore feel that the current statement is appropriate ("Moreover for HCFC-142b our data set shows FRFs that are too small to evaluate differences to Newman et al. (2006) within the uncertainties.")

Referee comment

p11 line 10. Statement is unclear. I interpreted Engel et al (2009) to have observed no change in mean age.

Author response

Engel et al. (2009) observed a positive trend but could not confirm its significance. The statement was changed to "possible long-term changes in stratospheric mean age."

Referee comment

p13 lines 1-3 This is a really interesting discussion. There should be some comment on the implications for stratospheric chemistry as well, since presumably there is a larger perturbation to stratospheric OH implied by the CH3CCl3 lifetime. There is a small but caring community that still finds stratospheric OH interesting!

Author response

In our opinion the CH3CCl3 stratospheric lifetime change does not necessarily imply a perturbation in stratospheric OH. CH3CCl3 photolysis is also a major sink reaction in the stratosphere (Sander et al.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies - Evaluation Number 17, 2011) and our method allows no distinc-

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tion between different sinks.

Referee comment

p15 line 1 Why choose mean age of 3 years to evaluate FRF? I thought WMO used 3.5 years as recommend by Schauffler et al 2003. Similarly for lines 25-26 on p. 15

Author response

We refer to a statement in Table 5.1 in Chapter 5 of WMO (2011): "From Newman et al. (2007), values for 3-year-old age of air."

Referee comment

p15 line 21 Suggest adding "as our H-1301 FRF" to make it clear. Also, might add "and our tau(1301)/tau(F11)" since this ratio also is involved in setting the ODP.

Author response

"H-1301" was added as suggested. Our ratio of tau(1301)/tau(F11) is very similar to that in WMO (2011) and has therefore less influence on the difference in ODP.

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