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Interactive Comment

Interactive comment on "Global stratospheric chlorine inventories for 2004–2009 from Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) measurements" *by* A. T. Brown et al.

Anonymous Referee #2

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This paper combines measurements of nine chlorine-containing species from ACE-FTS with simulated results for another nine species from the SLIMCAT model to produce a global stratospheric chlorine inventory. Trends are calculated over the period 2004–2009 to demonstrate the effectiveness of the Montreal Protocol. Although this work is essentially an extension of two previous studies that developed stratospheric chlorine budgets from ACE-FTS data (Nassar et al., 2006; Brown et al., 2011), it incorporates some new elements and is therefore potentially of interest to the ACP readership. Unfortunately, the manuscript is sloppy and not well written. In my opinion, the

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Interactive Discussion

Discussion Paper

care with which this paper was put together calls into question the rigor of the analysis. The specific comments detailed below need to be adequately addressed before this manuscript can be considered for publication.

Specific substantive comments:

Title: Since the chlorine budget derived here is really a measurement/model hybrid (with model results representing half of the species contributing to the budget, as well as all of the information at the top and bottom of the altitude range), it is not quite fair to characterize it as “from ACE-FTS measurements”. SLIMCAT should be mentioned along with ACE in the title.

P23493, L5 and L7–8: I find the pseudo-citations of the Molina & Rowland and Farman et al. papers very odd. Why haven’t these papers been included in the reference list?

P23493–23494: Waugh et al., GRL 28, 1187, 2001 (“Is upper stratospheric chlorine decreasing as expected?”) should be included in the review of previous studies using satellite measurements to investigate the evolution of stratospheric chlorine.

P23494, L23–25: The sentence “Since . . . layer” is highly redundant with the previous paragraph and is out of place here.

P23494, L27–28: More background explanation of the concepts of GWP and ODP would be helpful here. These terms are used with no definition of what is meant by them and no references to previous work.

P23495, L1: This is the first reference to Brown et al. [2013], which is cited several times throughout the text. But this paper does not appear in the reference list.

P23495, L15–16: It is stated that ACE “gives almost global coverage from the Antarctic to the Arctic”, but this is somewhat misleading. ACE actually has quite poor coverage in the tropics, as Brown et al. [2011] acknowledged and as is shown in Table 2 of this manuscript.

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P23495, L25: It is stated that ACE currently measures 9 chlorine-containing species, but in actuality at least 12 are "standard products" in v3 and a couple others are "research products" (e.g., ClO). The authors may be choosing not to use the other species in this work, but the data exist, so they should be more precise in their language.

P23496, L2–3: I understand that ACE data are problematic after September 2010. But it is not clear why only data through 2009 have been shown here. It is stated that "the work presented in this paper was carried out when only data between 2004 and 2009 had been fully processed", which is a rather poor excuse, especially given that the Brown et al. [2011] study did make use of some v3 ACE data from 2010. Of course, having data only through September precludes calculation of a yearly mean, on which the trend estimates in this paper are based. If that is the reason that 2010 data are omitted, then that should be stated.

Section 2.1: The subsections discussing ACE measurements of the individual species contributing to the chlorine inventory are not very useful. For one thing, almost no information is conveyed about the quality (accuracy, precision, resolution) of any of the data. For example, one of the two sentences that make up the paragraph on CH3Cl cites a study of "biomass plumes", which is of no consequence at all for this work. Just because an extreme event such as a major biomass burning plume can be discerned in the ACE data does not mean that their quality is adequate for trend detection. Brown et al. [2011] found a slight increase in ACE CH3Cl measurements over the 2004–2010 period that is not mentioned in this manuscript, an omission that I find curious. Although the authors cite Velazco et al. [2011] for other species (CFC-11, -12), they neglect to mention that Velazco et al. also validated ACE v2 measurements of CH3Cl against those from MkIV, finding that ACE data were consistently biased high in the lower stratosphere. Another paper has recently become available that discusses the quality of the v3 ACE CH3Cl data: Santee et al., JGR 10.1002/2013JD020235. Although the authors could not have known about this paper when they submitted their original manuscript, it may be relevant. Even where some validation information has

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been provided, for example for CFC-11 and -12, the authors fail to note that the cited papers examined v2 ACE data, not v3 as used here, and thus the quality information may no longer be applicable. Finally, they have included a new retrieval of HCFC-22 in the chlorine inventory. They state that a paper discussing this new retrieval is currently in preparation, but that is insufficient. Without some indication that these new data are reliable, any budget based on them is practically useless.

P23499, L23: Bins of 30-70 degrees latitude strike me as very large. These bins will inevitably include some profiles inside the vortex or in the collar region, especially in the southern hemisphere. These profiles could exhibit substantially different morphology than extra-vortex profiles for some species, such as HCl, ClONO2, or ClO. Although measures to screen out vortex profiles are discussed later in the manuscript (P23500, L21–22), I am not convinced that the MAD-based approach successfully eliminates all vortex profiles. That should be demonstrated.

P23500, L24–26: It is stated that "Profiles were extended by using the SLIMCAT profiles of the corresponding species scaled to match the ACE-FTS data at its highest and lowest retrieved altitude point". I don't quite get this. Since the measured and modeled profiles may not have the exact same shape, it seems to me that this approach could result in unphysical profiles.

P23501, L4–8: It seems arbitrary to replace the VMRs of the anomalous HOCl and ClO profiles from 2004 with values from 2005, especially for calculating trends (but then I find it somewhat problematic to calculate trends from purely modeled results in the first place). In addition, the apparent justification for doing so is that "small atmospheric anomalies had a large effect on these profiles". How is this possible – that is, what mechanism caused SLIMCAT to produce atypically high values for these species? What "atmospheric anomalies" induced these problems in the modeled HOCl and ClO, and why did they not affect other species? The implication is that if such anomalies occurred in the other years, they were smeared out when larger numbers of occultations were averaged together, but it is hard to evaluate the plausibility of that

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idea without knowing what may have given rise to the anomalous behavior.

P23501, L8–10: “All profiles were extended up to 54.5 km corresponding to the maximum altitude of the corresponding fluorine budget produced from ACE-FTS data”. First, which profiles are we talking about here? Does this sentence refer just to HOCl and ClO (the subject of the previous few sentences), or to all species? If the latter, then is this consistent with the statement in P23500, L24–26 commented on above? If so, then it would be much less confusing for the reader if all of this information were provided at the same time. Second, why is the altitude range of the fluorine budget relevant here? I don't see why it is necessary or even desirable to match the altitude ranges of the two inventories, since they are not being analyzed together.

P23501, L11–20: I found the discussion of the calculation of local solar time somewhat puzzling. For one thing, although the bit about adding 24 h for an occultation whose local time is the day before the universal time makes general sense, the idea of subtracting 24 h for occultations with positive local time seems odd (at least for $0<t<24$; I suppose rare occasions with $t>24$ may crop up near the date line or something) – doesn't this imply that there is never a situation in which the local time is on the same day as the universal time, since 24 h is always being either added or subtracted? More fundamentally, however, it seems to me that this level of detail is not only potentially confusing but also unnecessary to include in the text. I believe that most readers will trust that the authors have correctly segregated the occultations into “morning” and “evening” categories, which is all that this is used for, without going into all of the detail.

P23501, L23–24: “The total chlorine volume mixing ratio was calculated at 54 levels between 0.5 km and 53.5 km.” It was just stated above that all profiles were extended up to 54.5 km. More importantly, as Table 1 indicates, ACE does not provide any measurements below 5 km, so I suppose that all of the information between 0.5 and 5–10 km (depending on the species) comes from the model. If the total chlorine profile is really calculated over this entire domain, then why is it being represented as a “stratospheric inventory” in this paper?

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P23503, L1–2: I find it hard to believe that a flat 5% error in the SLIMCAT VMRs is an overestimate of the uncertainty of the ground-based measurements (plus this value also accounts for transport errors). Some references are needed to back up this statement.

P23503, L4–9: "The percentage of the total chlorine which comes from ACE-FTS measurements varies between 80% and 96%. At lower altitudes ACE-FTS measurements account for around 90% of the total chlorine VMR. This percentage contribution rises until it peaks at between 23 and 28 km . . .. Above this altitude the percentage contribution from ACE-FTS decreases slightly to around 80% . . .. the percentage contribution to the total chlorine from ACE-FTS increases to around 96% at 53 km." This passage is written in a very confusing manner. Exactly what is meant by "lower altitudes" in the second sentence should be specified. The first sentence states that the maximum contribution from ACE is 96%. Thus when it is stated in the third sentence that the contribution "peaks" between 23 and 28 km, the reader naturally assumes that that is where the value of 96% comes in. But then the fifth sentence indicates that the value of 96% pertains to the 53-km level. This discussion should be clarified.

P23503, L12–18: I have several comments about these lines: (1) These sentences should be made into a new paragraph, as they are not strongly connected to the preceding sentences. (2) It should be made clear whether the "mean" morning profiles shown in Figure 5 are multi-year averages or represent a particular year. (3) "The total chlorine profiles follow a straight line with slight deviations around 40 km. . . . It appears that this decrease in the VMR of HCl . . . is not compensated for by an increase in the VMR of ClO". What decrease in HCl? Figure 5 shows that HCl increases more or less steadily from 25 to 55 km. If there is a dip in the HCl at 40 km (which might be what these sentences are trying to indicate), then it is extremely difficult to see in the plots; moreover, ClO is increasing at 40 km. This discussion needs to be clarified. (4) The dips are attributed to a peak in stratospheric OH at this altitude, but is there in fact a peak in the OH profile at 40 km (I thought that the peak in the OH profile was slightly

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higher than that)? In any case, a reference is necessary for this point.

P23504, L6: It is not appropriate to say "the results of these plots can be seen in Table 5" when no plots are shown.

P23504, L10–21: I read through this entire paragraph wondering whether it was describing results from this paper or summarizing conclusions from previous studies (and I am quite sure that some previous studies have addressed these same points). It is not until the last sentence that the reader learns that the results on which these statements are based are tabulated in the Appendix. This sentence needs to be moved from the end of the paragraph to the beginning. In addition, it would be appropriate to put the results of this analysis in context by discussing and including references to previous work.

P23504, L23–24: Over what altitude range are the mean stratospheric total chlorine values shown in Figure 6 calculated? This is essential information that I do not believe is given anywhere in this manuscript. Brown et al. [2011] constructed similar plots for individual species; in that study, averages were calculated over different altitude ranges for different species, but presumably some uniform subset of levels was used to produce the results shown in Figure 6 and Table 6. The lack of information about the altitude range considered is made all the more confusing when the results of Table 7, which were calculated over the range from 48.5 to 53.5 km, are presented (P23505, L11–18).

Section 5.4: In my opinion, this entire section is very confusingly written. Apparently contradictory statements are made in several places. The reader has to wade through a lot of detail about morning, evening, and combined trends in various latitude bands, all of which are nearly impossible to gauge "by eye" from looking at Figure 6. Only towards the very end of the section is it stated that the trend information is compiled in Table 6. The reference to Table 6 should come at the beginning of the section since cross-checking with the Table would make the discussion of the differences in the trends in the various regions/periods much easier to follow. Even then, however, the discussion is challenging because the values stated in the text do not always match those in the Table. Specific examples for all of these points are given in the following comments.

P23504, L24–25: The statement that “there does not seem to be significant latitudinal dependence to these time series” is belied by the sentences that follow it. If indeed the differences between the various latitude bins are not significant (and I agree that in most, but not all, cases the differences do fall within the range of uncertainties), then why do the authors go on to discuss them in some detail? Why not simply focus on comparing overall Northern and Southern Hemisphere differences, which do lie outside the combined errors, at least for the morning occultations?

P23505, L1: The statement that the difference between morning and evening means is not statistically significant appears to be contradicted a few lines later (L7–10) when the difference in the rate of change between morning and evening occultations is discussed. It seems to me that the presence of substantial differences in the inventories and trends compiled from morning and evening occultations would have had significant implications (e.g., possible missing species, etc). Although the partitioning between the diurnally varying species might change between the morning and the evening measurements, the total chlorine mixing ratio should be constant. The authors might consider elaborating on this point in the manuscript.

P23505, L3: “This rate is similar in the Northern Hemisphere and the southern tropics.” This is true only for morning occultations; for evening measurements, the value for the southern tropics is much larger while that for the southern extratropics is similar to the one for the Northern Hemisphere. In fact, I wonder whether the rows for the southern tropics and extratropics for the evening occultations have been swapped in Table 6. Several sentences in the text would make more sense if that were the case.

P23505, L10: The values of 0.40 +/- 0.05% and 0.30 +/- 0.22% do not agree with those

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in Table 6 (0.40 +/- 0.09% and 0.33 +/- 0.20%, respectively).

P23505, L18–22: “The rate of decrease appears to be slightly higher in the southern mid-latitude stratosphere. . . . This increased rate of change is due to a slightly higher mean total chlorine value for 2004 (yellow and purple points in Fig. 6). If this value is removed then the rate of change becomes . . .”. The removal of the 2004 values seems somewhat arbitrary, as though the authors summarily rejected data points because the resulting trend values were inconsistent with those in the other latitude bands. Elimination of the 2004 data points in the calculation of the southern extratropical rates and the global trends in Table 6 needs to be better justified.

P23507, L13: The text says 0.27 +/- 0.13%, whereas Table 8 says 0.27 +/- 0.12%.

P23508, L5: I think this should be “chlorine”, not “fluorine”.

P23508, L14–15: “These results show that the Montreal Protocol has had great success in reducing the emissions of ozone-depleting substances.” Certainly the fact that the trends are all negative indicates that the Montreal Protocol is working. But how do the authors quantify “great” success? If the rates had been only, say, half as large, would that still have constituted “great” success?

P23508, L17–19: “the latitude bands of 70N–30N, 30N–0N, 0N–30S, and 30S–70S, which represent the extra-tropical and tropical latitudes in the stratosphere”. Actually these bands represent the extratropics and tropics everywhere, not just in the stratosphere.

P23509, L20–21: This sentence is confusing, because both decreases in chlorine and increases in HCFCs were discussed in the preceding sentence. However, I believe that in L20 “the fastest rate of increase” should be “the fastest rate of decrease”. In addition, it’s not clear where the quoted value of 0.35 +/- 0.01% for the Northern Hemisphere extratropics comes from. According to Table 8 this value should be 0.37 +/- 0.09.

Figures 1–4: These figures are not well formulated and in addition are mislabeled in the caption. First, are all of these 48 panels really necessary? None are discussed individually in the text. In fact, most of the figures in this entire manuscript are essentially superfluous, as all of the detailed discussion centers around tables, not figures. Second, these plots are basically useless because the x-axis conveys no information whatsoever. The only tick mark denotes "0" in the middle of each panel, with no indication of the axis range given. More labeled tick marks are necessary for these plots to be meaningful. Third, the caption states that inorganic chlorine is plotted in blue and organic chlorine is plotted in red, but that must be backwards.

Figure 6: It would make much more sense to swap the order in which these panels are arranged on the page, so that all of the Northern Hemisphere panels are shown on one side and all of the Southern Hemisphere panels on the other. In addition, the different colored symbols in the Southern Hemisphere extratropical panel need to be described in the figure caption. These are discussed in the main text, but this kind of information belongs in the figure caption as well.

Figures 7 & 8: I am not convinced that either of these figures is necessary. Figure 8 is not even mentioned in the text, so clearly it is not important.

Minor wording and/or grammar comments:

Throughout the text: The equator should not be characterized as 0 degrees N (just 0 degrees).

P23495, L6: CTM has already been defined on P23494.

P23498, L23–24: MLS has already been defined on P23494.

P23499, L9: CTM has already been defined (twice).

P23499, L19: "volume mixing ratio" should be "volume mixing ratios".

P23500, L14: "distribution . . . is shown".

P23501, L25–26: VMR has already been defined on P23493.

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P23502, L10–11: “impact . . . is presented”.

P23503, L9–10: “contributions . . . increase”. Also, the semicolon here should be a comma.

P23503, L26 and P23505, L9: it would be better to refer to the 30–70 degree latitude band as “extratropical” rather than “subtropical”.

P23504, L7: “slopes are greater than 1.01 and smaller than 1.11” – actually, the slopes are equal to or greater (smaller) than 1.01 (1.11).

P23506, L11: “a similar means” should be “similar means”.

P23509, L6–7: VMR has already been defined (twice).

P23512, L23: “aura Satellite” should be “Aura satellite”.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 23491, 2013.

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