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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global carbon tetrachloride distributions obtained from the Atmospheric Chemistry Experiment (ACE)" *by* N. D. C. Allen et al.

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We thank the reviewer for his/her helpful comments.

General comments The paper reports on the first upper troposphere to mid stratosphere global distribution of carbon tetrachloride from the ACE-FTS. The ACE-FTS observations are compared to balloon measurements (from MkIV instrument) as a kind of validation. The comparison gives satisfactory agreement. The observations are also compared to 3 chemical transport models. The shape and the gradient of the profile are in good agreement but ACE overestimates the simulations. The larger values measured with ACE in the troposphere are attributed by the authors to the difficulties of the

retrieval for the lowest altitudes in limb viewing observations. Finally, they derived the CCl4 lifetime that is in agreement with those reported in literature.

The main comments I have and that need to be addressed before publication in ACP are: 1) Characterization of the errors. The errors are defined and characterized in the section that describes the retrievals. They are only evocated at the end of the paper (p13309, lines 13-16) and discussed briefly only for the troposphere. This needs to be discussed earlier in the manuscript (in section 2 for example) and with additional details for both the troposphere and the stratosphere as the 2 regions are discussed in the paper.

The section on the errors has been moved and expanded to detail the varying importance of errors in both the troposphere and the stratosphere: The statistical errors in the retrieval below 15 km remain low at the typical value of 5%, but the systematic errors can grow to 20-30%. The systematic error in the cross section data (Nemtchinov and Varanasi, 2003) used in our retrievals is estimated to be as large as 10%. In the troposphere the major error is the systematic error in the retrieval with minor contributions from the error in the cross sections and the statistical retrieval error. In the stratosphere, the systematic retrieval error is small, the cross section error remains the same, but the statistical retrieval error now dominates.

2) Comparison with the MkIV measurements. This comparison is presumably used to try to validate the CCl4 profiles retrieved from ACE. I'm aware about the difficulty to find dataset to validate such untypical satellite products. However, I'm reserved on the usefulness of this comparison and on the conclusions one can draw as currently presented in the manuscript. The MkIV measurements are of same nature than the ACE measurements: Fourier transform technique, same band used, same spectroscopic data used (I assume it is not precise in the text), etc. So, if some biases arise from the instrumental technique or from spectroscopic problems, this would not be reveal by the comparison. The authors state that ACE measured larger tropospheric CCl4 in the troposphere than the values reported at the surface but the comparison with

MkIV observations, in good agreement with ACE, would suggest that they are correct. Have the MkIV observations been compared to other measurements performed by other techniques? At p13302, l9-12, references are given to aircraft measurements made by other instrumental techniques. How these measurements compared to MkIV measurements?

For the MkIV balloon profiles Toon et al. employed pseudo-lines that were fitted to the Nemtchinov & Varanasi cross-sections for the carbon tetrachloride retrieval. Toon believes that the pseudolines provide a better means of extrapolating/interpolating the cross-sections in pressure and temperature. For atmospheric conditions in our observations, it shouldn't make much difference to the retrieval whether you use the cross sections or the pseudo-lines. Most of the flights mentioned in the introductory paragraphs were taken over one region or at a significantly different time than the ACE measurements. Measurements taken by Robinson over Bauru in Brazil using a GC were originally considered for comparison, but the number of measurements was small and the values somewhat erratic. I have managed to obtain data from the CARIBIC programme. The airplane takes worldwide measurements of many gases onboard long haul flights, including carbon tetrachloride measurements taken between 2006 and 2008 in the northern hemisphere. An average profile for carbon tetrachloride gave VMRs of 92 ppt at 8-9 km dropping to about 85 ppt at 12 km. These measurements highlight the difference in values obtained by flask measurements and FTS instruments, such as ACE and the MkIV. In contrast with ACE the CARIBIC data showed little latitude dependence.

Specific comments 1) p13300, l26: could you precise the contribution of CCl4 to the atmospheric chlorine budget?

The contribution of carbon tetrachloride to the total chlorine budget in the troposphere (11% using WMO report 2003 for reference) and the stratosphere (3% calculated using the budget derived from ACE by Nassar et al.) has been included.

2) p13301, l11: precise from which lifetime the CCl4 lifetime mentioned is reduced to 26 years.

The loss of carbon tetrachloride caused by ocean uptake and hydrolysis reduced the estimated atmospheric lifetime of carbon tetrachloride from 35 to 26 years.

3) p13301, l27: "reducing anthropogenic radiative forcing": could you quantify?

The anthropogenic radiative forcing is estimated to have been reduced by approximately 1.1x10-5 Wm-2 per year. Foster et al. (2007) calculated that between 1998 and 2005 the radiative forcing caused by carbon tetrachloride was reduced by 7.7x10-5 Wm-2 over this period whilst the carbon tetrachloride concentration dropped 7% to 93 ppt.

4) p13303, l25-27: Is it possible to roughly estimate the effect of neglecting line mixing in CO2 Q-branch?

Taking a small sample of 15 occultations (sr10899-sr10943) line mixing was included (based on parameters determined for a single occultation ss11613) to estimate the effect on the Q-branch. The results showed an average reduction in the residuals, and the VMRs decreased by 3-5% above 10 km and 10% above 20 km where the concentration is lower. It is hoped that line mixing effects will be included in the near future for new data versions from ACE.

5) p13304, l16-17: "improve the precision of the global distribution": this is related to the major comment 1 and need more discussion.

We are not completely sure what the referee has in mind here, but we have improved and extended our discussion on the errors.

6) p13304, l25: how many measurements are included in the average?

The number of measurements that go into each latitude bin average has been included in the supplementary data (Table 3).

7) p13305, l10: the term “upper stratosphere” (also used elsewhere in the text) is not very well appropriate as the measurements are not going higher than 30 km.

This was removed and rephrased to state stratosphere, this was changed elsewhere if necessary.

8) p13305, l14-15: Can the asymmetry be attributed to the smaller emissions in the southern hemisphere?

Yes, this is another way of looking at it. However we also need to take into account interhemispheric transport.

9) p13305, l23-24: First, are the difference significant if the errors in the observations are considered? They should be large in this altitude region for which one are close to the detection limit. Second, the authors attribute the hemispheric difference to the severity of the polar vortex in the southern hemisphere. Are the profiles inside the vortex also discarded of the average in this case as explained in the last paragraph of section 2? If yes, the argument of the severity of the polar vortex fails, doesn't it?

We have not done a detailed statistical analysis, but all of the northern hemisphere lines in figure 4 lie above the corresponding southern hemisphere lines. We did not mean to imply that this hemispheric difference is due to the intensity of the southern polar vortex and this sentence has been removed.

10) p13306, l4: “the concentration at ground level had declined” from what “to approximately. . .”

Sentence now reads: Prinn et al. (2000) reported carbon tetrachloride concentrations at ground level had declined from approximately 102-113 ppt in 1990 to 97-100 ppt by June 1998 at the five global AGAGE sites

11) p13307, l4-6: Are the differences consistent with the decrease of CCl4 emissions from 1997 to 2004-2007?

I think that the difference between the MkIV profiles and ACE retrievals in the troposphere are too large simply to attribute to a decrease in emissions.

12) p13309, l6-10: The authors state that ACE overestimate CCl4 in the troposphere compared to surface measurements and attribute this to the difficulty of the retrieval in the lowest altitudes of the limb viewing measurements. As already mentioned, this overestimation has to be investigated through comparison with other measurements and evaluate and discuss according to the errors. Moreover, the comparison with the models shows not only an overestimate in the troposphere but also in the stratosphere. An evaluation of the implication that this overestimate (if really significant, tbc) would have on chlorine budget would be valuable for the paper.

Using the VMR from the ACE retrievals would increase the contribution of carbon tetrachloride in the tropospheric and stratospheric total chlorine budget by between 0.5 and 1%. The discrepancies observed in the troposphere are due to the imposed surface boundary concentration values used to constrain the models, thus values will be no greater than the ground input value. The models assume a uniform surface boundary condition with no latitudinal or longitudinal variation, due to the longevity of carbon tetrachloride, however, asymmetric emissions could lead to some variations. In all three models the sources and sinks are the same. They include loss of carbon tetrachloride by photolysis and reaction with O(1D) but no other sink mechanisms, such as ocean uptake. Differences in the modelled vertical profiles are due to different rates of stratospheric transport (Brewer-Dobson circulation).

Technical correction P13309, l24: replace Fig 13 by Fig 10?

Well spotted(!), this has been altered.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 13299, 2009.