**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Vertical transport rates and concentrations of OH and Cl radicals in the Tropical Tropopause Layer from Observations of CO$_2$ and halocarbons: implications for distributions of long- and short-lived chemical species" *by* S. Park et al.

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Reply to review #1

We have made changes to the manuscript to answer the suggestions of the reviewers and clarified a few points raised in review. We respond to the reviewer's comments below and a revised version of the manuscript including most of the changes suggested by the reviewers will be submitted to the editor. We thank the reviewers and the editor

for their time and effort and appreciate the recommendation for publication.

Major points

1. Our previous work (Park et al., 2007) presented in situ CO2 data obtained on board the Proteus aircraft, from the PBL up to 15 km over Darwin (12°S), Australia (part of Tropical Warm Pool International Cloud Experiment, TWP-ICE), during the same flight period as CR-AVE. These data allowed the inter-hemispheric comparison of CO2 composition between the southern and northern parts of the lower TTL. Clear concentration gradients between the southern and northern hemispheres were found from the surface to the upper troposphere and lower TTL (see appended Fig. 1 that is same as Fig. 8 in the original paper). However, interestingly the strong contrasts disappeared near 360K: the CO2 composition at ∼360K in the southern tropics over Australia was very close to that in the northern tropics over Costa Rica, implying that the layers below 360K are subject to convective influence from boundary layer, but a global CO2 signal emerges near 360K in the TTL, evidently the result of inter-hemispheric mixing in the Intertropical Convergence Zone (ITCZ). Although direct inter-hemispheric comparison beyond the emergence of CO2 mixing ratio at 360 K was limited due to the lack of TWP-ICE datasets above the level of 360K, any significant difference is unlikely to occur in CO2 mixing ratio, due to limited impact of input of convective air and to large-scale slow ascent and monotonic aging of air at the altitudes above 360K.

2. We examined WAS measurements taken from two transit flights covering part of subtropical region (<36°N) to discuss possible influence of horizontal mixing with extratropics on the WAS species, and found them nearly identical with tropical data. The comparisons of all 11 species are illustrated in Fig. 2 (data points binned by <11°N, 11–25°N and 25–36°N; the plots for CH3Cl, CHCl3, and CH2Br2 had already been given in Fig. 5(d), (e), and (f)), without showing any significant latitudinal separation.

3. On page 6076, line 3: The factor of 200-300 was given under average tropospheric condition by Rudolph et al. (1996), which is cited in the statement. However, in the

upper troposphere and TTL, the ratios of rate constant for reaction with Cl over with OH were 1.8E3 and 1.2E3 on average for C2Cl4 and ethane, respectively. The ratios are given with altitude in Fig. 3. Thus, the loss reaction with Cl for C2Cl4 and ethane is still more significant by 5 and 4 times, respectively, than reaction with OH, even though OH concentrations are about 3 orders of magnitude higher than Cl concentrations. We modified the statement by including the ratio of 1000-2000 for the altitude level between 14 km and 18.3 km, to avoid any confusion.

4. Uncertainty analysis: 2.2E6 molecule cm-3 in line 10 of page 6075 was an average between 14 km and 18.5 km, and the uncertainty of ±0.3E6 molecule cm-3 was determined based on RMSE of 14%, which was the highest value among the resulting RMSE range of 3% to 14% between the modeled profile and the observations of each species. However, as stated in page 6075, considering OH field-related error range in chemical transport models is ∼±30% (Wang et al., 2008), we represented the uncertainty range of ∼±30% along with our estimated OH profile in Fig. 6 and the following fits in Figs. 7-9 had also shown the uncertainty ranges resulting from ±30% error of [OH]. These uncertainties have been clarified in the revised text.

The RMSEs of the optimal fits to the observations of C2Cl4 and ethane were 9% and 15%, respectively. We have further examined error propagation of nominal uncertainty of OH profile, ±30%, into the average of Cl concentration. When 30% more and less [OH] were incorporated, corresponding results of Cl concentration for an optimal fit were 1.8E3 and 3.0E3 atoms cm-3, respectively. Thus, overall uncertainty of the best-fit result of 2.4E3 atoms cm-3 was ±0.6E3 atoms cm-3. This error analysis has been mentioned in the revised text.

5. The listed papers are now referenced appropriately in the revised manuscript. Kruger et al. (2009) and Ploeger et al. (2010) have been added to Sect. 4.1. and Salawitch et al. (2005), Wamsley et al. (1998), Dorf et al. (2008), Sinnhuber and Folkins (2006), Gettelman et al. (2009), Aschmann et al. (2009), Hossaini et al. (2010), Laube et al. (2008), and Liang et al. (2010) have been discussed in Sect. 4.3.

Minor points

Section 4.1. : Done.

p. 6974, l. 12: Changed

p. 6075, l. 15-19.: The sentences have been rewritten to clarify the description.

p. 6078, l. 22 and following: We had mentioned that "most of VSLS can contribute their halogen payload to the stratosphere, possibly excepting CHBr3" based on their lifetimes at 18-km altitude, and we observe ∼0.1 ppt bromine from CHBr3 near the tropopause (cold point level; ∼17 km). Comments on the difference in photochemical properties between CH2Br2 and CHBr3 don't seem to be necessary for our purpose, but each calculated bromine contribution from these two species near the tropopause has been included in expanded discussion of Sect. 4.3 and their mean lifetimes varying with altitude are also summarized in a newly added table (Table 1).

Figure captions

Figure 1. Vertical profiles of CO2 obtained during CR-AVE and TWP-ICE. TWP-ICE observations were plotted from ∼1-km to 15-km altitude on January 25, 27, and 29, 2006. The measurements were performed over the Western Pacific ocean (12°S, 130°E). All the data were averaged into 1-K intervals for each flight. Empty cycle denotes CR-AVE CO2 and empty diamonds for TWP-ICE CO2. The overall 1-K averages for each mission are also shown in solid lines. (Park et al., ACP, 2007, Fig. 8)

Figure 2. Vertical distributions of (a) CFC-11, (b) Halon-2402, (c) CCl4, (d) CH3CCl3, (e) CH3Cl, (f) CH3Br, (g) CHCl3, (h) CH2Br2, (i) CHBr3, (j) C2Cl4 and (k) ethane. Plotted are individual data points (solid circles) measured by WAS on August 5th in the TTL (<11°N), and are compared with observations both from 11-25°N (green empty squares) and from 25-36°N (blue asterisks) on the 3rd and 9th of August, without showing any significant separation from the extratropical observations.
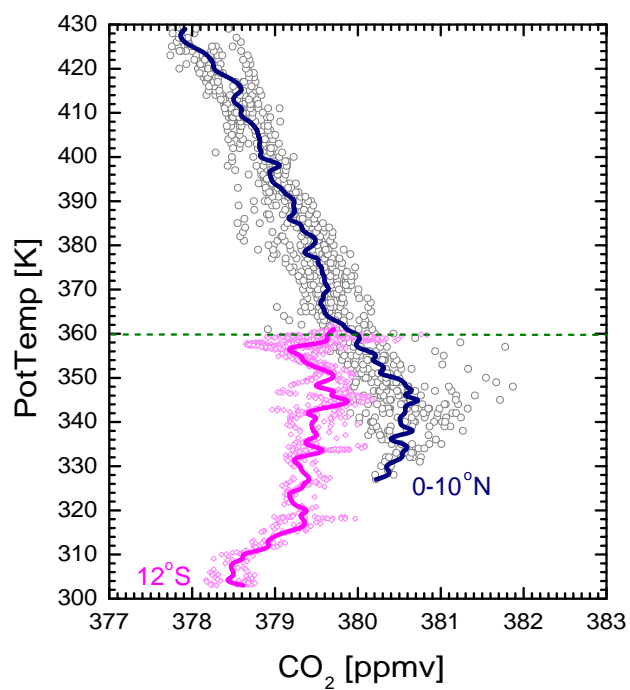
Figure 3. The ratio of rate constant for reaction with Cl against with OH between 14 km

and 18.5 km. C2Cl4 and ethane are represented by black solid line and gray dotted line, respectively.

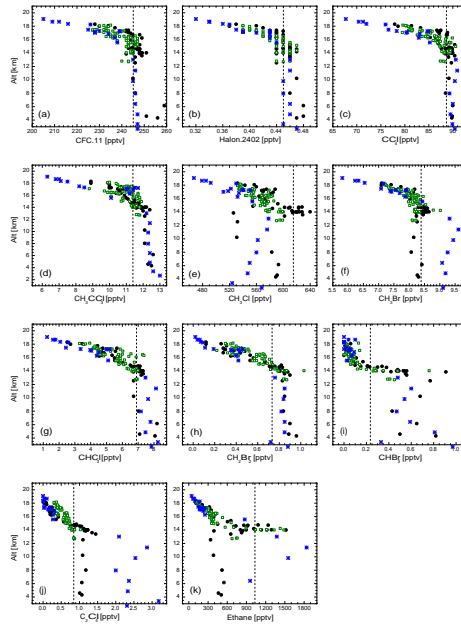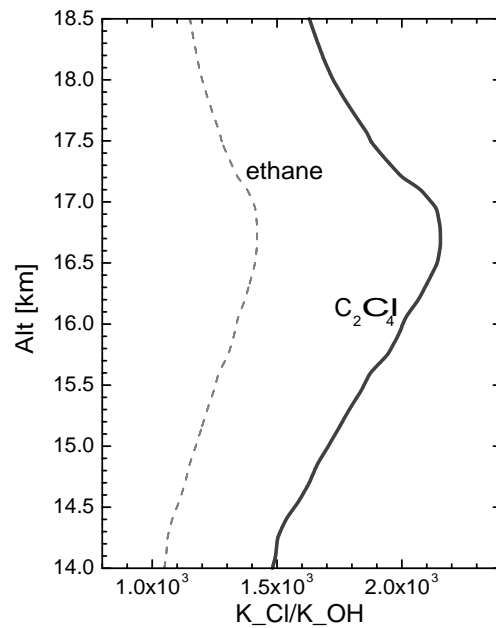———————————————

Fig. 1. Vertical profiles of CO2 obtained during CR-AVE and TWP-ICE. TWP-ICE observations were plotted from ~1-km to 15-km altitude on January 25, 27, and 29, 2006.

Fig. 2. Vertical distributions of WAS species measured on August 5th (<11°N: solid circles), and compared with observations from 11-25°N (green empty squares) and 25-36°N (blue asterisks) on the 3rd and 9th.

Fig. 3. The ratio of rate constant for reaction with Cl against with OH between 14 km and 18.5 km. C2Cl4 and ethane are represented by black solid line and gray dotted line, respectively.