

## ***Interactive comment on “Retrievals of chlorine chemistry kinetic parameters from Antarctic ClO microwave radiometer measurements” by S. Kremser et al.***

**S. Kremser et al.**

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Reply to Anonymous Referee #2

**(1) I have a couple comments on taking the day-night differences. First, I assume that "day" and "night" are defined as they were in Solomon et al. [2000] or Connor et al. [2007], but this should be explicitly mentioned.**

We agree that the description of the ClO measurements was not sufficient. We included now the definition of day-time and night-time. Furthermore, we included more information on how the subtraction of day minus night time measurements was performed. We rewrote the paragraph line 4 to 11 pg. 26051 (see comment of reviewer

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1).

**Second, the statement is made "While the day/night subtraction is essential to retrieve the daily ClO profile, the ClO concentrations themselves are unaffected by this step in the retrieval." I don't believe that this is entirely true. Under certain conditions during polar winter when ClO is strongly enhanced, nighttime ClO is non-negligible. Thus subtracting the nighttime spectrum from the daytime one could remove some real atmospheric signatures and cause the daytime ClO enhancement to be underestimated. The authors should comment on any effects this might have on their results. It may be that their sensitivity tests on the prescribed ClOx cover this point, but that should be discussed.**

We agree with the reviewer that the wording is not entirely true. Depending of the day of the year the subtraction of night-time measurements could cause an underestimation of day-time ClO concentrations. However, several examinations of the ClO spectra were performed in the past and the definition of day-time and night-time were chosen so that rapid changes in ClO, i.e. at sunrise and sunset are excluded.

We included more information on that and changed the wording in the manuscript to: The day minus night subtraction is essential for the analysis of the measured spectra to remove the ozone line and artefacts. The day minus night definitions were determined by detailed examination of spectra intensity relative to sunrise and sunset and the definition for day and night was chosen so that periods where ClO changes rapidly were avoided (Solomon 2002).

In the result section of the revised manuscript we now discuss the effect the day minus night subtraction can have on our results. (see also comment of reviewer #1)

**(2) I think it would be appropriate to note here the vertical resolution of the groundbased measurements. The authors discuss retrieving ClO concentrations on 20 altitude levels from 11 to 30 km, but my understanding of their averaging kernels is that they have relatively coarse vertical resolution, so clearly not all of**

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**these levels contain independent information.**

We added the following sentences: CIO profiles from 10 to 56 km are derived from the CIO day minus night spectra. It should be noted that although the vertical resolution of the retrieved CIO profile is about 10 km, the location of the peak in the CIO mixing ratio can be determined to an accuracy of 1 to 2 km (Solomon et al., 2000, 2006).

**(3) Temperatures are discussed, but neither the text in this section nor the caption to Fig. 1 indicate how the temperature information is obtained. On p26054, it is stated that the temperature profiles come from NCEP, but that information should be provided here.**

We are now providing the information in Section 2.1:

The atmospheric temperatures shown in Fig. 1 were extracted for the location of Scott Base from the National Centers for Environmental Prediction, NCEP (Kalnay et al., 1996) reanalyses using bilinear interpolation.

Later on pg. 26054 we changed the sentence to:

Similar to the temperature profiles (Section 2.1), the pressure profiles for the analysis period were extracted from the NCEP reanalyses.

**p26055, L19-20: In the sentence "... to estimate the dependence of the kinetic parameters on changes in the prescribed CIO<sub>x</sub> profile", it would be better to say "retrieved kinetic parameters" or "estimated kinetic parameters".**

We agree with the reviewer and changed the sentences accordingly: ... to estimate the dependence of the retrieved kinetic parameters on changes in the prescribed CIO<sub>x</sub> profile, the CIO<sub>x</sub> profile was scaled between 0.5 and 1.0 times the a priori CIO<sub>x</sub> profile used in the OE approach. . .

**p26056, L24-26: I am a little confused by the statements: "The kr values associated with the prescribed Keq scale shown in Fig. 2 decrease with increasing**

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Keq scale, as does Jscale / kf scale. However, the decrease in kr is small such that kf scale needs to increase to cover the large range prescribed for Keq scale (0.2-2.0)." Surely in the first sentence the decrease in kr with increasing Keq is for a fixed value of kf? I also don't quite get the second sentence. Perhaps just some rewording would help to clarify these statements.

We rewrote that paragraph in the revised manuscript to clarify the interpretation of the results found in this study. (see comment of reviewer #1)

**p26057, L25-26: "The measurements they used were taken from a different period (1996-2000) when stratospheric temperatures were, on average, 4K lower than in 2005." As written, this sounds like a very general statement; it would be better to be a bit more precise in the wording here, reminding readers that you are specifically analyzing the August-September late winter period in this study.**

We agree with the reviewer and included additional information for clarification:

The measurements they used were taken from a different period (late winter/early spring 1996-2000) when stratospheric temperatures were, on average, 4 K lower than in the analysis period our study focuses on i.e. the period from 21 August to 20 September 2005.

**p26058, L7: Rather than "Antarctic measurements of ClO made in 2005", I suggest that you specify "Scott Base", since other ClO datasets from that winter have been published previously.**

We changed that sentence to:

The results suggest that to explain the ClO measurements from Scott Base, Antarctica, made from August to September in 2005, J/kf is unlikely to be. . .

**Also, in L23, it would be good to provide the day of year as well as the calendar dates to help orient readers in Fig. 1.**

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We agree with the reviewer and additional information are now provided in the manuscript. Furthermore, we corrected a typing mistake:

Between 7 September (day 250) and 8 September 2005 (day 251), ClO dropped from 2.2 ppbv to 0.8 ppbv before increasing back to 2 ppbv two days later (see Fig. 1).

**p26059-26060, section 4.2: (1) The authors note that "the ClOx values obtained from SLIMCAT may be uncertain". Indeed, it has been shown previously that SLIMCAT typically overestimates chlorine activation, and a citation or two would be appropriate here.**

We included one reference here: The study by Santee et al. (2010) reported that SLIMCAT overestimates the ClOx concentration by about 25

**(2) "An upper bound of  $K_{eq\ scale}=1.6$  was used since JPL09 and most other studies ... suggest  $K_{eq\ scale} < 0.7$ ." The value of 1.6 seems somewhat arbitrary to me relative to 0.7, and other values might have been just as justifiable.**

We chose the upper limit of  $K_{eq\ scale}$  so that the laboratory and field studies recently published are included. We had to choose a limit below the JPL06 upper limit as sampling the whole parameter space is computational very demanding and we had to reduce the computing time. The value of 1.6 represents the value that includes all previous studies on  $K_{eq}$  but also the maximum value that could have been used in this study so that the computational burden was not too high.

**Also, why is the Ferraci Rowley value not depicted in Fig. 2?**

Thank you for pointing out the missing value. The  $K_{eq}$  value derived by Ferraci Rowley scaled to JPL06 is now included in Fig. 2.

**p26061, L14-15: "The results presented above show that OE is a reliable method for investigating the kinetics of the ClO-dimer cycle." Didn't the study of Schofield et al. [2008] in particular and also Santee et al. [2010] already prove that OE is a useful approach to investigating the kinetics of the ClO dimer cycle?**

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We changed the wording of that sentence.

The results presented above confirm, as shown in Schofield et al. (2008), that OE is a reliable method for investigating the kinetics of the ClO dimer cycle.

**p26063, L20-21: "Day-time and night-time measurements of ClO are required to determine a reliable value of  $K_{eq}$ ." It is not true that both daytime and night-time measurements of ClO are required to reliably determine  $K_{eq}$ ; as the authors themselves state in L25-26, other studies have used nighttime measurements of ClO alone to derive an estimate of  $K_{eq}$  based on atmospheric observations.**

Thank you for pointing out this mistake. We corrected that mistake in the revised manuscript.

**(By the way, the references provided in L25-26 do not represent an exhaustive list, so "e.g." should be added.)**

Done.

**p26064, L12-15: "stratospheric temperatures above Scott Base during the period of ClO measurements, and over the altitude range where ClO concentrations maximize, varied from 183.7K to 217.6K. In contrast, most of the earlier studies took place in conditions with temperatures above 190K." While it is true that this study encompasses a broader temperature range than some of the other analyses, I'm not sure that "differences in the underlying temperature fields" really provide a plausible explanation, especially considering that some of their data were taken in conditions with temperatures as high as 217 K.**

We were simply arguing that the higher  $K_{eq}$  values are at least in part associated with the temperatures below 190 K, since it seems from studies that were conducted at higher temperatures much lower values of  $K_{eq}$  were required compared to those made around 190 K. We fully acknowledge that this cannot be the whole story, and our reduced sensitivity to  $K_{eq}$  through the day-night spectra subtraction is also a likely

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source of uncertainty. We reworded that sentence for clarification.

**p26061-26064, discussion and conclusion section: Although I leave the choice to the authors, I am not convinced that having a combined discussion and conclusion section is the best approach for this paper. The authors should bear in mind that many readers will want to hit just the highlights and will read only the abstract and conclusions. The lengthy discussion of how the various previously published values of J, Kf, and Keq map into the new results from this study is useful and interesting for a discussion section, but seems less appropriate for a conclusions section to me. Moreover, by doing things this way, they have not reminded readers of some key aspects of their analysis. Although somewhat repetitive, it would probably be good to re-state certain points, such as the exact time period of their analysis; the fact that the day-night differences provide information only on J/kf, not on these parameters individually; that they are retrieving scale factors, etc., etc. They mention that there are 19 OE runs, but a sentence summarizing the point behind them would be good. Again, the decision is theirs, but the authors should be aware that the current formulation of the final section of the paper both assumes that readers have thoroughly read the rest of the paper and does not provide a succinct summary of the main conclusions.**

We partly agree with the reviewer and considered his suggestion in the revised manuscript. We included a brief summary at the beginning of the discussion section to remind the reader what we have done.

**Minor wording comments:**

**p26047, L4: delete hyphen in "late-winter"**

Done.

**p26048, L5: add comma after "stratosphere"**

Done.

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**p26049, L25: delete hyphen in "ClO-dimer"; L27: "were" -> "was"**

Done.

**p26050, L8: delete hyphen in "late-winter"; L16: "occur" -> "occurs"**

Done.

**p26052, L16: add "was" before "started"**

Done.

**p26053, L16-17: delete "performed", delete the comma after "study", "are" -> "is"**

Done.

**p26055, L4: "kf sale" -> "kf scale"**

Done.

**p26056, L22: delete "either"**

Done.

**p26058, L20-21: "measurements of ClO to make a robust evaluation of  $K_{eq}$ " -> "measurements of ClO and thus a robust evaluation of  $K_{eq}$  is not possible"**

We changed that to: '... measurements of ClO and therefore a robust evaluation of  $K_{eq}$  is difficult'

**p26058, L27-29: "the reduction is not commensurate with the observed reduction in ClO apparent in the disagreement between measured and SLIMCAT modelled ClO profiles on these days." -> "the reduction is not commensurate with the observed reduction in ClO, as is apparent in the disagreement between measured and SLIMCAT modelled ClO profiles on these days (not shown)."**

Done.

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**p26059, L1: "As such" -> "Therefore";**

Done.

**L19: "these two days in questions" -> "the two days in question"**

Done.

**p26062, L4: "corresponds" -> "correspond"**

Done.

**p26066, L3-4: the Ferraci Rowley reference has some formatting issues.**

Done.

**p26071: panel (a) should be Keq scale = 0.4, not 0.2 (or the text of the manuscript is wrong in multiple places)**

Yes, it should be 0.4. Thank you for pointing out this error. We corrected this mistake in the manuscript.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 26045, 2010.

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