

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

## **Anonymous Referee #2**

Received and published: 29 December 2010

This paper uses ground-based microwave measurements of ClO from Scott Base to constrain the kinetics parameters governing stratospheric chlorine partitioning. An optimal estimation approach was applied to measurements from August–September 2005 to retrieve the ratio  $J/k_f$  for prescribed  $K_{eq}$  values; exploring the full parameter space of  $J$ ,  $k_f$ ,  $K_{eq}$ , and ClO<sub>x</sub> yielded similar results. The methodology is sound and the results obtained will be of interest to the readership of ACP. For the most part I have only minor comments on the manuscript.

————— Specific substantive comments:

p26051, section 2.1:

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(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. 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.

(2) I think it would be appropriate to note here the vertical resolution of the ground-based 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 these levels contain independent information.

(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.

p26055, L19-20: In the sentence "... to estimate the dependence of the kinetic parameters on changes in the prescribed ClOx profile", it would be better to say "retrieved kinetic parameters" or "estimated kinetic parameters".

p26056, L24-26: I am a little confused by the statements: "The  $k_r$  values associated with the prescribed  $K_{eq}$  scale shown in Fig. 2 decrease with increasing  $K_{eq}$  scale, as does  $J_{scale} / k_f$  scale. However, the decrease in  $k_r$  is small such that  $k_f$  scale needs to increase to cover the large range prescribed for  $K_{eq}$  scale (0.2-2.0)." Surely in the

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first sentence the decrease in  $k_r$  with increasing  $K_{eq}$  is for a fixed value of  $k_f$ ? I also don't quite get the second sentence. Perhaps just some rewording would help to clarify these statements.

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.

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. 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.

p26059-26060, section 4.2: (1) The authors note that "the ClO<sub>x</sub> 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. (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. Also, why is the Ferraci & Rowley value not depicted 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?

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 nighttime 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

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an estimate of  $K_{eq}$  based on atmospheric observations. (By the way, the references provided in L25-26 do not represent an exhaustive list, so "e.g." should be added.)

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.

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  $K_{eq}$  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.

———— Minor wording comments:

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

p26048, L5: add comma after "stratosphere"

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

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

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

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

p26055, L4: "kf sale" → "kf scale"

p26056, L22: delete "either"

p26058, L20-21: "measurements of ClO to make a robust evaluation of Keq" → "measurements of ClO and thus a robust evaluation of Keq is not possible"

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)."

p26059, L1: "As such" → "Therefore"; L19: "these two days in questions" → "the two days in question"

p26062, L4: "corresponds" → "correspond"

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

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

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