

Interactive comment on “First remote sensing measurements of ClOOCl along with ClO and ClONO₂ in activated and deactivated Arctic vortex conditions using new ClOOCl IR absorption cross sections” by G. Wetzel et al.

Anonymous Referee #2

Received and published: 23 November 2009

This study represents a timely re-analysis of Arctic vortex observations of chlorine radicals taken during January 2001 and March 2003 using the MIPAS-B balloon instrument. The focus of this work is to ascertain levels of ClOOCl, ClO, and ClONO₂ in the polar vortex during activated and deactivated conditions and to test their retrievals by comparison with model results from the EMAC atmospheric chemistry model. Overall, the paper is well written and the material presented is appropriate for this journal. The results of this work will be very useful to the scientific community provided some issues are addressed, however.

C7378

More details of the EMAC model are needed:

The authors should mention how large their model time steps are and how well the model handles twilight conditions. The chemistry of the chlorine system in an activated vortex is non-linear and highly dependent upon solar zenith angle. A concern is how well the EMAC model is able to reproduce the fast chemistry that governs Cl during sunrise/sunset transitions.

The authors do not mention how the model handles the timing of the chemistry of the Cl system. Does the model assume instantaneous steady state, 24 hour steady state, etc.? This assumption may have profound ramifications on the interpretation of the observations reported in this paper.

The range of solar zenith angles associated with the times of observation should be provided as this information is important for other groups who wish to refer to this work.

The chemical kinetics used in the EMAC model for this paper is very narrow when compared to the amount of discussion in the literature regarding the main chemical reactions that control chlorine chemistry in the vortex.

The authors reference the previous measurements of ClOOCl reported by Stimpfle et al., 2004 and that there is good agreement between the two studies. Stimpfle et al., also did a sensitivity study of the kinetics that control chlorine chemistry in the polar vortex. While Wetzel et al., report good agreement between model and observations using JPL02 chemical kinetics, they fail to address that Stimpfle et al., found best agreement between model and measurements when using a faster photolysis rate based on the larger ClOOCl cross sections published by Burkholder et al., 1990. In fact, Figure 11 of Stimpfle et al., 2007 show that, when using the JPL02 recommendation for JCIOOCl, agreement between model and observations only occurs when the forward (ClO+ClO) reaction is based on the fast rate reported by Tropier et al., 1990. Some discussion as to these differences is warranted if the authors wish to claim good agreement with the Stimpfle et al., observations.

C7379

The authors do not mention whether OCIO was present in the atmosphere during the 11 January observations. If the authors are unable to retrieve a profile of this species, an estimate of OCIO from their model could be used to understand how this species may affect the amount of active chlorine available in the vortex region where the observation took place. This is not a straight forward calculation as nighttime OCIO is highly dependent upon air mass history. So, while the polar vortex may be activated, depending on when the last time the air mass saw daylight, OCIO may or may not be present. A back trajectory analysis may be needed to fully explore this.

The relationship that the authors are using for K_{eq} , equation 1 on page 20105, is appropriate for nighttime conditions, which the authors do not mention. During daytime, photolysis of ClOOCl is the main pathway to reformation of ClO so the ratio $[\text{ClOOCl}]/[\text{ClO}]^2 = k_{\text{rec}}/(k_{\text{diss}} + k_{\text{ClOOCl}})$. The authors need to clarify this as it may lead to some confusion. A further complication, if the authors wish to use equation 1 to determine K_{eq} from the model, is that depending on how well their model handles the non-linear chlorine chemistry, the model results at the time of the observations may be influenced by the history of the air parcel. To overcome this, Stimpfle et al., 2004 only looked at data taken at solar zenith angle > 95 degrees for their analysis of the nighttime observations. They report that a value of K_{eq} based on the Cox and Hayman, 1988 study gives best agreement between model and observations. The authors should comment on this discrepancy.

While the authors motivate their study by referring to the questions raised by the Pope et al., 2007 study which reported very low ClOOCl cross sections. This study has since been called into question. Several recently published papers have reported ClOOCl cross sections much larger than Pope et al., in better agreement with studies published prior to the Pope study. The authors may wish to comment on these recent findings.

Page 20106, Line 26: change "...1999/2000 aboard a NASA ER-2..." to "... 1999/2000 aboard the NASA ER-2..."

C7380

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 20103, 2009.

C7381