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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Partitioning between the inorganic chlorine reservoirs HCl and $ClONO_2$ during the Arctic winter 2005 from the ACE-FTS" *by* G. Dufour et al.

G. Dufour et al.

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The authors thank the reviewers for their interest in the article and their suggestions for improvements. The comments made are addressed below.

Reply to Referee #1:

1) The referee stated that a more detailed description of the box model should be provided especially concerning heterogeneous chemistry. The following paragraph will be added in the revised paper (page 1259, line 23): "STS is assumed to grow on sulfate aerosols, which have a fixed climatological distribution. The STS parameterization is based on Carslaw et al. (1995). The STS surface area is related to the volume following

the expression of Massie et al. (1998). Below the ice point the fraction of water vapour above the equilibrium vapor pressure (from the expression of Marti and Mauersberger (1993)), with a supersaturation ratio of 1.4, is assumed to form ice and the associated surface area is determined assuming a mean radius of 10 microns. PSCs in our model are determined at every time step based on ambient conditions but there is no tracking of particle growth or decay. A NAT parameterization is not included since it is felt that a good understanding of NAT formation and NAT "rock" growth is lacking."

2) The authors also want to make clear that ACE-derived PSC information has not been used for modeling since it was not available at the time of the study. However, PSCs have been detected during winter 2005 in ACE-FTS spectra. PSCs events, as measured from ACE-FTS spectra, occurred from 24 January to 2 February and from 17 February to 23 February, corresponding well with the observed ClO activation (paragraph 5). This information has been added in the revised paper. Moreover, the paper is now submitted for publication in GRL.

3) According to referee suggestion, an additional x-axis displaying the calendar dates have been added to Figures 4, 5, 6 and 7.

4) In stratospheric research, people often use the potential temperature (K) of the isentropic surface to indicate the altitude. The use of potential temperature at p1255, line 21 and in figure caption of figures 2 and 3 was not clearly defined. We then clarified this point adding that we use potential temperature and the corresponding altitude range (12-26 km).

Reply to Referee #2

1) Answer to the general comment number 4 and to the specific comment "p1260 The variability of the model data is very large (˜100%), which looks larger than the measured data, although the authors claims it is similar. Quantify the variability."

Answer: The aim of the paper was firstly to show the first simultaneous measurement of

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the evolution of HCl, ClONO2, and ClO inside, on the edge, and outside the vortex and secondly, to test if this evolution was in good agreement with the current understanding of chemistry during polar winter as given by a model already validated. To achieve this last point, chemical evolution of different species has been derived from a box model evolving along trajectories initialized with ACE-FTS measurements (time, location and concentrations) that stay confined to the polar region. This model experiment gives then the "theoretical" chemical evolution of HCl, ClONO2, and ClO for processed and non processed air parcels according to the conditions encountered during Arctic winter 2005. Figure 6 represents the evolution of the mean of these selected trajectories as well as their variance. It is worth noting that the mean corresponds to air parcels in a range of altitudes between 16 and 24.5 km, with values at later stages of the evolution tending to be at lower altitudes. The variability reflects the various situations that could have been measured by ACE-FTS: air masses processed or not, inside or outside the vortex. In this way, the variability reflects also the instability of the vortex, especially after mid February. Variability of model and measurements has to be compared for measurements inside the vortex as well as outside the vortex (Fig. 1) and also for the range of altitudes covered by the model (see Fig. 7 for the vortex case). It is in this sense that the variability of the model and measurements is comparable. We agree that this point needs to be clarified. Variability of measured HCl at 20.5 km is about 1.5 ppmv at the peak of the processing, similar to model variability at least for trajectories starting at 22.5 and 23.5 km. Similar results are observed for ClONO2. However, the variability of the model is slightly larger than those of observations at 20.5 km (Fig. 1) in March because lower altitudes are considered by the model for this period. Figure 7 shows evolution of HCl, ClONO2 and their ratio inside the vortex between 12 and 30 km: variability of HCl is effectively larger for altitudes below 20 km in March. The larger variability of the model values may also result from the loss of identity of air parcels through mixing on a 60 day timescale. Mean modeled values of HCl are about 1.5 ppbv until 25 January 2005 and show less processing than observed at 20.5 km (Fig. 1). This can be explained by the fact that the box model lacks representation of PSC

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types that occur in the first half of January. Modeled and observed HCl processing are similar: values close to zero, reflecting complete processing, are modeled even if the mean would show underestimation of processing in the model. The recovery of HCl during March leads to values (˜1 ppmv) lower to those observed at 20.5 km (Fig. 1). However, for this time period, the model is more representative of lower altitudes and thus to smaller values of HCl. As discussed in section 4, ClONO2 is highly variable during the pre-processing and the processing period. However, ClONO2 tends to be overestimated by the model during these periods. The modeled recovery starts after 20 February, while first signs of recovery were observed almost 10 days before. ClONO2 values reached during March (recovery phase) are in both cases (model and measurements) in good agreement, larger than 2 ppbv. The recovery of modeled HCl and ClONO2 starts simultaneously. On the contrary, a delay of almost 10 days is observed for HCl recovery from ACE measurements. The modeled ClONO2/HCl ratio tends then to be smaller than the observed one until the beginning of March. After then, the ratio corresponds to altitudes lower than 20 km, where it is larger in both model and measurements. However, it is still slightly overestimated by the model.

Answer to the specific comments:

2) The referee wrote: "p1251 It is mentioned that HCl and ClONO2 have not been measured (from any technique) simultaneously prior to ACE-FTS nor has it been possible to follow the winter-spring evolution...The author should make his statement a little clearer."

Answer: We agree that this statement needs wording clarification. The sentence "However, very few of these instruments (Payan et al., 1998; Stimpfle et al., 1999; Bonne et al., 2000) are able to measure HCl and ClONO2 simultaneously and not have been able to follow their evolution through the winter and spring" (p1251, lines 13-16) will be replaced by "However, few instruments are able to measure HCl and ClONO2 simultaneously. Ground-based FTIR spectrometers measure HCl and ClONO2 columns continuously during winter and spring but sample one location (Blumenstock et al.,

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1997). Simultaneous vertical profiles of HCl and ClONO2 have been reported (Payan et al., 1998; Stimpfle et al., 1999; Bonne et al., 2000) but for a limited time span and a limited area. As far as we know, ACE-FTS is the first remote sounding instrument capable of measuring vertical profiles of HCl and ClONO2 (and ClO) simultaneously, of sampling many locations within the vortex and of following chemical evolution of various species during most of the winter and spring."

3) The referee wrote: "p1252 (section 2) The retrieval procedure is described very shortly and then most is referenced to Boone et al. I think some more discussion about the measurements is appropriate, such as an estimated accuracy obtained from some kind of error budget. In the retrieval it is mentioned that line parameters from HITRAN 2004 but what more? For instance is the retrieval algorithm using any a priori data, from where are they taken?"

Answer: The retrieval method uses a modified global fit approach, in which all parameters are determined simultaneously with the Levenberg-Marquardt nonlinear least-squares method. As we do not use the optimal estimation method (Rodgers, 2000) but only a "simple" Levenberg-Marquardt minimization method, the fitting routine does not impose constraints based on a priori information, only profiles as first guesses are used. The retrieval results are then not sensitive to the first guess (or a priori). Moreover, in response to this comment, a sensitivity study to uncertainties of forward model parameters (T, ILS, pointing), spectroscopic data and interfering species has been conducted. A table summarizing the results will be added and discussed in the revised version of the paper. For the altitude range of our study, total error budget of HCl is about 5 %, in agreement with validation results mentioned in the paper (Froidevaux et al, 2005). ClONO2 total error is about 11 % in the altitude range of interest (19-25 km). In the case of activation, ClO total error is about 35 % at the maximum of the profile and reliable from 19 to 22 km. The main contribution to the error budget is measurement noise error. This reflects the statement we did in paragraph 4.4: strong ice contamination of the detector, affecting essentially the spectral range used for ClO

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retrievals, limits the signal-to-noise ratio in this region and averaging ClO profiles is recommended to reduce errors.

4) The referee wrote: "p1255 top sentence; From the data the author claims it can be seen that the recovery occurs first at the vortex edge. I had a problem seeing this and wonder if it can be clarified better."

Answer: we based our remark on HCl and ClONO2 time series (Fig.1). HCl vmrs taken on the vortex edge reach outside vortex values before vortex measurements (˜19 February in contrast to ˜10 March for vortex measurements). Concerning ClONO2, high values occur also early on the edge than inside the vortex (end of January against ˜10 February for vortex measurements) but it's less clear due to the high ClONO2 variability until March. We agree that this has to be interpreted very carefully because it may be due to a sampling effect and uncertainty in the classification of a measurement as on the vortex edge. As we noted in the paper, few measurements are classified as edge measurements with a greater uncertainty in the classification (p1254, lines 24-27). Air masses sounded on the vortex edge may also experienced less processing than some vortex measurements. We will explain these different points in the discussion.

5) The referee wrote: "p1256 (Evolution of ClONO2) Every winter the ClONO2-to-HCl ratio increases due to the fact that the speed of reaction ClO+NO2 increases with colder temperature and the fact that the photodissociation of ClONO2 decreases in the dark. Hence there is a latitudinal gradient in this ratio unrelated to heterogeneous chemical processing. This is not clearly described in the analysis of the data and should be better distinguished from the heterogeneous processing."

Answer: Vortex and extravortex occultations for a day are measured along a circle corresponding approximately to the same latitude. Then, these different types of occultations experience an equivalent increasing sunlight at the beginning of the spring and then a similar "natural" recovery (not due to heterogeneous processing). Compari-

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Interactive Comment

son of ClONO2 evolution during March 2005 inside, on the edge and outside the vortex shows that ClONO2 is much smaller outside the vortex (lower than 1 ppbv versus ˜ 2 ppbv inside the vortex), showing that the reaction ClO+NO2 is mainly ClO-limited and that heterogeneous processing will dominate the recovery of ClONO2 in the vortex.

6) Answer to the technical comment: "is" has been added.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1249, 2006.