Reply letter

General remarks / reviewer 1:

The paper is very well written (English and structure), some of the Figures are of good quality (e.g. Fig. 7), the references present a wide spectrum of analyses related to the diurnal variation of stratospheric constituents. It is obvious that the authors have used a tremendous amount of data from different origins, different wavelengths, different vertical resolutions, different time frames, and have averaged and binned them in a correct way, made a sensitivity study on the different values of the rate coefficient kl ($ClO+HO_2$->$HOCl+O_2$) through a 1-D model to assess that the optimum value was the one from Nickolaisen et al. (2000). I can acknowledge, as it is state in the abstract, that all the data sets considered in the study "generally agree" and that the "gas phase chemistry implying the above mentioned species is well understood based on latest recommendations of reaction rate constants". But it is not clear to me whether this paper can be published in a journal like ACP since the amount of scientific new results is very weak. More than half of the manuscript presents the satellite data base and shows the comparisons within the sensors, lots of them were already published before (e.g. MIPAS), but others are presented as the first validation of HO_2 measurements from ODIN. A journal like AMT would better fit this part. The model results are very interesting regarding the value of k1 (Fig. 7) but the conclusions again were already published elsewhere. Consequently I cannot propose the manuscript to go a step further in the ACP journal but recommend some issues listed below to be carefully treated before sending it to another journal.

General remarks / reviewer 2:

The paper is clearly structured and overall well written. It presents a large data set and a detailed comparison between different observations and model results. The SMILES diurnal variations are used as a transfer standard for comparisons between instruments with different observation times and for offset correction which is a sound approach. To my knowledge, there has never before been such comprehensive comparison. In addition, the kinetic study also gives clear indication for preferences on which value to use for the reaction rate coefficients of HOCl formation. However, the problem with this paper is, that there is only very little new which the reader can learn from it:

- *Most of the satellite data used have already been presented before*
- *The model used is pretty standard*
- *The main part of the paper consists of a lengthy description of the similarities and differences between individual results which a reader could also deduce just from looking at the figures*
- *The comparison between model and measurements is again very descriptive and does not provide any new insights on atmospheric processes or their description*
- *The kinetic study is nice but only confirms a similar result from an earlier study for another altitude*

In summary, in my opinion the main value of the paper lies in the compilation of the large number of observations and their thorough processing and comparison. I think that a good job was done on this aspect of the study and I'm sure that the figures presented will be of interest for people working on stratospheric chlorine and hydrogen chemistry. However, due to the descriptive nature of the paper and the lack of really new results, I'm reluctant to recommend it for publication in ACP and would rather suggest to re-submit to another journal which is more oriented towards presentation of data. Should the authors decide to submit a revised version of the manuscript, they will have to remove much of the text just describing what is in the plots. Instead, they will have to make a convincing point of what one can learn from the data and the comparisons performed in this study.

Since both reviewers had several common points, this single section is going to reply to these general comments. We think that the paper provides important new information on atmospheric composition and chemistry for the following reasons:

1. The diurnal variation of HOCl has not been observed before in the upper stratosphere and lower mesosphere region (above 45 km). New observations by recent satellite instruments are here presented for the first time. This analysis also includes satellite observations of ClO and HO_2 that are the precursors of HOCl. Compared to earlier published studies which were based on balloon-borne observations this is important since in the mesosphere – unlike in the stratosphere - nitrogen chemistry can be neglected. At 55 km for instance, HOCl is destroyed during daytime (both observations and simulations show this) and re-formation of HOCl after sunset is the result of the reaction of HO_2 and ClO only. In addition, the relative impact of uncertainty due to the formation of HOCl (seen in figure 8) is more pronounced in the mesosphere than in the stratosphere. This is stated in section 4.3 (kinetics study) in the manuscript. At 55 km, since HOCl is quickly photo-dissociated, the errors on the photo-dissociation rate constant have also a negligible impact unlike in the stratosphere.

2. Several satellite data sets are for the first time presented in this paper such as the new SMILES observations of the diurnal variation of HOCl, ClO, HO_2 and HCl. We also use the latest version of MLS data (version 3.3). In addition, Odin/SMR operational HO_2 data are presented and compared to other data sets for the first time in this paper. The comparison of the large data sets is important in this analysis to estimate the quality of the new unvalidated SMILES HO_2 HOCl and HCl observations. In particular, the good agreement of the diurnal amplitude of HOCl in the stratospheric found between SMILES and the other instruments which provides a strong confidence in the mesospheric HOCl retrieved from SMILES (altitudes where other instruments have a reduced sensitivity. This is more clearly pointed out in the introduction / motivation section. Note that Sagawa et al. (2013) has just published an analysis that shows a good agreement between SMILES stratospheric ClO and Odin/SMR, Aura/MLS, MIPAS and balloon TELIS measurements.

3. Indeed, a large number of satellite datasets has been used, which is a particularity of this study.

4. Observations of short-lived species from polar sun-synchronous orbiters or solar occultation sounders can normally not be directly compared as the local time of observation varies between sensors. We employed therefore a particularly suited method, based on the diurnal variation calculated by an 1-D model and verified with the new SMILES data, to perform a comprehensive comparison between very recent satellite observations at different solar zenith angles / local times. To our knowledge, this is the first paper which takes the diurnal variation properly into account using the new satellite data sets. We found generally a good agreement of the observations with the model, provided that the model was initialized carefully (using latest available data on Cl_y, NO_y, H_2O, temperature), a result which could not be anticipated beforehand. This is stated in the introduction (the second last paragraph) and Section 3 (Model and simulations, second paragraph) in the manuscript.

5. We have now further investigated the effect of vertical smoothing on the measurement-model comparison. A Gaussian smoother is now used instead of a moving average which represents better the averaging kernels of satellite measurements. We discovered that smoothing was

omitted in Figure 7 of the ACPD version which has now been corrected. At the same time the initialization of the model was further improved by taking into account the temporal decrease of HCl and Cl_y species from year 2004 to 2009 (WMO report 2010, Jones at al, ACP 2011a) and also by using the latest NO_y from ACE-FTS (Jones et. al. 2011b**)**. This changed the conclusions of the kinetics part of the paper. The SMILES observations fit now best to model calculations based on the lower uncertainty limit of JPL-2011 (close to JPL 2006), but not to reaction rates suggested by Stimpfle and Nickolaisen. This contradicts also results suggested by an earlier study of Kovalenko et al which was based on observations at lower altitudes. We have conducted a number of sensitivity tests which corroborate this result. (see changes in Section 4.3).

Major comments - reviewer 1:

a. Too vague. The comparison exercise is in my opinion too vague, whilst the presentation of the data is too lengthy. The comparison exercise needs much more quantification, giving more insights in absolute and relative values. This means reducing/avoiding the too numerous occurrences of "generally agree well", "agree reasonably well", "quite well" in the core of the text, in the abstract and in the conclusion.

We improved the comparison part of the manuscript by adding a table (table 1) providing a more comprehensive quantitative summary of the results. The manuscript text has been reviewed according to the reviewer comments and slightly adapted. We prefer to avoid too many quantitative statements in the text, in order to improve readability of the text.

b. Figures. The Figures 3-6 are the corner stones of the study and would require enlarging the y-axis on each individual plot in order to actually highlight the diurnal cycle of the constituents as measured/modelled by different sensors/model. One of the caveats of using so many data is that it is almost impossible to detect for instance the model curve on these Figures since it is hidden by the noisier satellite curves. Why not only showing the debiased diurnal cycles (Figs. 5-6) and adding a Table listing the biases between all the data sets? In general, showing offsets/biases will give more insights in the presented analysis (see e.g. section 4.1).

The panels in the figures have been enlarged. Two tables have been added summarizing the satellite data comparisons. Overlapping of some satellite and model data is inevitable when there is a good agreement. The de-biased figures (5 and 6) are complementary to figures 3 and 4 since absolute values (observations and model) are typically more uncertain.

c. Vertical Resolution. It is mentioned that "the model results have been smoothed using a 5-km moving average for the 35 km (. . .)." This is difficult to understand since a rigorous comparison can be performed by using the averaging kernels of the different sensors to be applied to the model profiles. Furthermore, a moving average will tend to smear out the measurement sensitivity at a considered altitude although the actual averaging kernels in a limb-viewing geometry are well peaked at the tangent altitude. This may considerably affect some of the diurnal variation cycles, e.g. ClO.

We cannot practically use the averaging kernel of each instrument for degrading the vertical resolution of the model as we compare the model to several satellite instruments simultaneously. However, the satellite instruments used in this study have close vertical resolutions for the different species and well centered Gaussian-like shape. Several tests showed that the impact of using just one common span for each species and altitude is not very large. In addition, the smoothing of the model profiles has been modified and is now based on a Gaussian function with full width at half maximum (FWHM) specified for each species and level as the average vertical resolution of all instruments. It is now stated in section 4.2 (model comparison, first paragraph) in the manuscript.

d. Cl_y trends. Another critical problem of the study that considers chlorine compounds is that the time evolution of Cl_y, as it is stated in the text, is decreasing since 2000. So, the comparisons of ClO, HCl and HOCl, from different sensors averaged over different periods not necessarily overlapping produce a natural bias, independent of the instrumental bias. I have not clearly understood whether the model runs were performed over all the periods under investigation or only over one single period. To me, the model run should be performed over the whole period so that comparisons between model and sensors are not affected by this trend issue.

The Cly profile for the initialization has been modified considering the linear decrease of 0.6%/year reported by Jones et al (ACP-2011). The model simulations have been done for conditions during the SMILES measurement period in 11/2009-4/2010 (6 months, one simulation per month and latitude, 20S, 0, 20N, total of 18 simulations). The gray lines show the range of model results during the period of this study. This has been clarified in section 3 (model and simulation, second paragraph) in the manuscript.

Referee 1 - minor points:

Title. "HCl" does not appear in the title. Why?

HCl does not appear in the title since this species is not the focus of this study which is dedicated to short-lived species. HCl is just shown since it is the main reservoir which allows us to verify that the total chlorine level in the model is correctly set. It also helps to check if the partitioning of chlorine species in the model is correctly done.

Stratosphere. Note that the layer at 55 km is in the mesosphere. So the title (and the content) of the manuscript will need to be modified.

"Mesosphere" was added to the title of the paper and in the manuscript where needed.

21070/2: "have" instead of "has"
21072/8: "altitude grid" no "s"
21073/15: not sure "LT" was defined before and add "10:00 LT"
21076/10: what is a "standard error"? You mean a "standard-deviation error"?
21076/24: "between" is missing after "offset"
21079/26: "well" is missing after "reasonably"

21080/6: "amplitude", "u" is missing
21080/20: "The ACE-FTS (. . .)." What is the actual number of measurements?
21080/21: The sentence "This could cause" is rather difficult to understand. This needs clarifications.
21080/ What are the conclusions of the section 4.1?
21085/ What are the conclusions of the section 4.2?

21070/2: done
21072/8: done
21073/15: done
21076/10: standard error of the mean
21076/24: done
21079/26: done
21080/6: done
21080/20: done
21080/21: done
21080: Conclusions added to section 4.1.
21085: Conclusions added to section 4.2.

Referee 2 - major comments:

However, the problem with this paper is, that there is only very little new which the reader can learn from it:
• Most of the satellite data used have already been presented before

This is replied in the points 1 and 2 of the general remarks in this letter (page 2).

• The model used is pretty standard

The use of a photochemical model for this study may be standard (which is partly intentional as we want to test current knowledge of atmospheric chemistry), but the initialization of the model is very crucial to get a reliable result which matches the observations. Water vapour was taken from MLS and the temperature and pressure profiles are according to ECMWF analyses as it has been stated in the paper. The initialization of the model has now even been improved by taking into account the temporal decrease of HCl and Cl_y species from year 2004 to 2009 (WMO report 2010, Jones at al, ACP 2011a) and also by using the latest NO_y from ACE-FTS (Jones et. al. 2011b**)**. This point is now better explained in the manuscript (section 3. model and simulations). In addition, the diurnal variation of HOCl and the related species ClO and HO_2 has not been presented in this context before.

• The main part of the paper consists of a lengthy description of the similarities and differences between individual results which a reader could also deduce just from looking at the figures
• The comparison between model and measurements is again very descriptive and does not provide any new insights on atmospheric processes or their description

This part has been improved by using a table and reducing the text. We prefer to avoid too many quantitative statements in the manuscript, in order to improve readability of the text. More explanation can be found in general remarks in the second page of this letter.

• *The kinetic study is nice but only confirms a similar result from an earlier study for another altitude*

There was one study using balloon measurements (Kovalenko et. al) which has been applied at about 30-36 km altitude. Our study – also performed at higher altitudes - gives now results which differ from those drawn by Kovalenko et. al. As explained in the general remarks, using mesospheric data offer more favorable conditions to study the production rate of HOCl than stratospheric observations.
There have been many laboratory studies measurements aiming to determine the rate constant of the HOCl formation reaction, however these kinetics studies differ considerably. There are not enough verification studies of the reaction rate of HOCl as all measurements have their uncertainties. Our study attempts to contribute to verify the current state of knowledge. This point is now better clarified in Section 4.3.

Referee 2 - minor points:

P 21068, l5: at the wavelengths => at wavelengths
P 21068, l12: the polar ozone loss => polar ozone loss
P 21068, l15: there have been number => there have been a number
P 21069, l25: otherwise noted => unless otherwise noted
P 21075, l10: to hydrogen => to the hydrogen
P 21079, l8: which the mean => where the mean
P 21079, l22: is the => are the
P 21080, l28: of the model => of model
P 21082, l21, smaller then => smaller than
P 21082, l25, consistently => consistent
P 21083, l7: of the model => as the model
P 21083, l29: in a much lower => at a much lower
P 21084, l27: get a correct => get the correct
P 21085, l11: the model reproduces very close HCl volume mixing ratio to all observations => the model reproduces very closely the HCl volume mixing ratio of all observations
P 21089, l19 the night-day => the model night-day

All minor changes are done.