

1 Answers for comments from Referee II,

2 We thank you very much such careful, detail, and encourage comments to lead us toward right directions.
3 All the comments are very valuable for us to improve the quality of this study. We would like to address
4 your comments as follows. Page numbers and line numbers of the text denote these of the revised
5 manuscript.

6 We use following notations about rate constant:

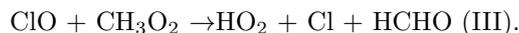
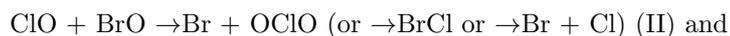
- 7 1. ${}^c k_1$: Rate constants calculated from HOCl production. The symbol of c means calculated.
- 8 2. ${}^c k'_1$: Rate constants calculated from ClO loss. The symbol of c means calculated.
- 9 3. k_1 : Rate constant of Reaction (R1) estimated from ${}^c k_1$ and ${}^c k'_1$ using the threshold of $\Delta k =$
10 $|{}^c k_1 - {}^c k'_1|$.

11 General comments

12 'Purity' of the Reaction (1)

13 Your first question is about the 'purity' of the Reaction (1) as follows:

14 **Q1** Maybe I am wrong but I am very skeptical if the assumed pure conditions in the mentioned region
15 of 0.28 hPa and 20° S–40° S during night exist at any time. I think that HOCl is only involved
16 in Reaction (R1) but for ClO this is probably not the case. At least in our chemistry climate
17 model EMAC (Joeckel et al., 2006) we have for the mentioned altitude and time interval besides
18 the reaction (R1) for ClO loss also the reactions $\text{ClO} + \text{NO}_2 \rightarrow \text{ClONO}_2$ (I);



21 Also the production of ClO through the reaction

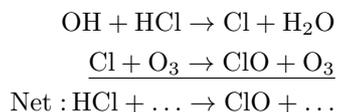


23 takes place during the night. Maybe this is wrong in our model but I am very skeptical.

24 **A1:** This is the crucial question that is why we also very carefully confirmed both from the model
25 study and the SMILES observation as bellow. I will follow the reactions you mentioned one by one.

26 First three reactions, (I), (II), and (III) should occur in parallel, but the reaction rates of them are
27 quite small in the nighttime at 0.28 hPa. From our model calculation result, the effects of these reactions
28 are less than 1% for ClO loss.

29 We confirmed the Reaction (IV), $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$, by model study as bellow. The Reaction
30 (IV) requires a more detailed discussion, because most of its rate is balanced by the reaction $\text{ClO} +$
31 $\text{NO} \rightarrow \text{Cl} + \text{NO}_2$ (both reactions together form a ClO zero cycle). However, some Cl comes from HCl
32 via $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$. Together with the above-mentioned reaction it forms a ClO production
33 pathways:



34 Our model results suggested that there is a significant ClOx production by $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$
35 which together with $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ leads to a ClO production (cf. manuscript, p.XX, YY). Until

1 after the sunset, this reaction is so strong that it even leads to modify the sum of [ClO] + [HOCl]. The
2 effect of the Reaction (IV) is about 10% of the sum of [ClO] + [HOCl] in Fig.1 of the manuscript.

3 We confirmed the contributions of the four reactions you mentioned on the SMILES observation
4 during the night time. The sum of [ClO] + [HOCl] should be modified if the effect of these reactions is
5 large enough. But our extracted SMILES dataset suggests the sum of [ClO] + [HOCl] become constant
6 in variabilities of the SMILES observation after MLT18:30 as shown in Figs. 2 and 6 of the manuscript.

7 We further confirmed the reaction (IV) for the difference between the model and SMILES observation
8 during LT18:30 and LT19:30 as follows: We used the modified local time to reduce effects of variabilities
9 from latitude and season, but still some variabilities are left from the temperature and the precision of
10 the amount of ClO, HO₂, and HOCl. The reaction (IV) may still remain between LT18:30 and LT19:30,
11 but the reaction (IV) did not appear on the SMILES observation.

12 As a conclusion, our model results suggested that the effects of first reactions, (I), (II), and (III)
13 are less than 1% for ClO loss, but the reaction (IV) may affect on the sum of [ClO] + [HOCl] between
14 LT18:30 and LT19:30. But our extracted SMILES dataset suggests the sum of [ClO] + [HOCl] become
15 constant in variabilities of the SMILES observation after MLT18:30 as shown in Figs. 2 and 6 of the
16 manuscript. We consider the Reaction (IV) may happen between MLT18:30 and MLT19:30, but did
17 not appear on the SMILES observation. One reason why we did not see on the SMILES observation is
18 because the HCl-to-ClO conversion may be masked by variabilities of the temperature and the precision
19 of the amount of ClO, HO₂, and HOCl. That is why we took the pure reaction period as MLT18:30–
20 MLT04:00. We added the detail explanation on the manuscript (page 7, line 24–43).

21 The variation of HOCl

22 Your second question is about the variation of HOCl in Eq. (XX) of the manuscript as follows:

23 **Q2** I am also not convinced from the evaluation of the pure conditions by equations 6 and 9. Why
24 you use in both equations the variation of the observed ClO and HO₂ (in $k/2^*(t_{m+1} - t_m)$) and
25 not in one of the equation the variation of HOCl? Please use also the HOCl observation in one of
26 these equations.

27 **A2:** We used the variation of HOCl in Eq. (8) of the manuscript to optimize the calculation function
28 of Eq. (7) of the manuscript. This calculation function was obtained from following second-order rate
29 equation of the Reaction (R1):

$$\frac{d[\text{HOCl}]}{dt} = k[\text{ClO}][\text{HO}_2] \quad (1)$$

30 This equation means that HOCl is produced by ClO and HO₂. To simplify the derivation of the
31 calculation function, the integration of this equation is performed as follows:

$$[\text{HOCl}](t) = [\text{HOCl}](t_0) + k_1 \cdot \int_{t_0}^t [\text{ClO}(\tau)][\text{HO}_2(\tau)]d\tau \quad (2)$$

32 The variations of the observed ClO and HO₂ are used to calculate an approximation to the integral in
33 Eq. (2) for discrete times, $t = t_m$. The variation of HOCl was not needed in Eq. (7) of the manuscript but
34 was used to optimize k_1 and $[\text{HOCl}](t_0)$ in Eq. (8) of the manuscript. We added the detail explanation
35 on the manuscript (page 4, line 34).

36 Our model calculation

37 Your third question is about our model calculation as follows:

1 **Q3** Another question for me is the use of a box model for the definition of the relevant area with pure
2 conditions (defined i the altitude 0.28 hPa). Does this box model reproduce the atmospheric condi-
3 tions regarding temperature or transport? How is the photolysis integrated? Why you don't use
4 here a Chemistry Transport Model with (for example) the meteorology of ERA-Interim? I mean
5 the definition of the relevant area with pure conditions is very essential for the subsequent calcu-
6 lations. At least you could mention which assumption regarding the temperature and transport
7 you have made for the box model calculations.

8 **A3:**

9 Temperature: For the analysis in the manuscript observations at a temperature of 245 ± 1.4 K are
10 used (Page 12803, Line 14). That is why a temperature of 245 K is used in the box model.

11 Transport: We analyse the variation of the mixing ratios of species during less than 1 day (from
12 sunset to before sunrise). During this time transport does not play a significant systematic role. That
13 is why the box model is run at a fixed altitude and latitude, representative of the mean conditions of
14 the observations used.

15 Photolysis: Photolysis rate constants are calculated by the program TUV (Madronich and Flocke,
16 1999).

17 As mentioned above, transport during the time of the analysis does not play a significant systematic
18 role. One advantage of a chemical box model is that it provides mixing ratios and reaction rates with
19 a high temporal resolution (CTM output is usually available only once or twice per day). However,
20 the output from a CTM might be useful for providing the species mixing ratios at the beginning of the
21 box model run. In the present study we use SMILES data for the initialization of species observed by
22 SMILES and values from Brasseur et al. (1999) for the remaining species.

23 Temperature dependence

24 Your next question is about the temperature dependence as follows:

25 **Q4** I don't see any explanations for the calculation of the temperature dependency of the rate constants
26 (Figure 7). How do you calculate the rate constants for different temperatures? Do you have
27 observed the total temperature range from 200–300K at 0.28/hPa (that cannot be) or do you use
28 other altitudes? If so, do you have than the same 'purity' conditions in these altitudes? Please
29 explain this in more detail in the paper.

30 **A4:** The rate constant of the Reaction (R1) was calculated only at 245 ± 1.4 K. We discussed the
31 temperature dependence in data from 'previous studies' and did not discuss the temperature dependence
32 from the SMILES k_1 . To avoid the misreading, we delete the discussion of the temperature dependence.
33 We changed the manuscript (Section 5.3).

34 Threshold and Systematic error

35 Your last questions are about the threshold and the systematic error as follows:

36 **Q5** A last point is your error analysis. If I understand this correct you choose your region with the best
37 agreement of Δk (only results with $\Delta k < 0.1$), skipping all other values, assume that the variation
38 in k is due to the measurements errors of SMILES and calculate the standard deviation for this
39 measurements error. I think this is much too simple. First it is very critical to narrow first your
40 results and then to calculate the standard deviation (I mean you can also determine $\Delta k \leq 0.01$
41 and then your error is probably even smaller) and second there are much more uncertainties in
42 your calculation as only the measurement errors (see also comments of Review 1 by D.G. Johnson).

1 **A5:** I will follow questions you mentioned one by one.

2 Threshold

3 We used the threshold $\Delta k \leq 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to estimate the rate constant of Reaction
4 (R1), and the deviation of ${}^c k_1$ and ${}^c k'_1$ under this threshold was considered as the 1σ precision of the
5 derived rate constant in the manuscript. We agree that the values of the rate constant of Reaction (1)
6 and the 1σ depend on the value of the threshold (See Fig. 3). The usage of this threshold is essential to
7 derive a reliable rate constant in our analysis.

8 As described in the manuscript, we focused to the modified local time range of $19.0 \pm 0.7 - 3.6 \pm 0.7$
9 hr at which we consider that the purity of Reaction (1). This time range was roughly determined for
10 convenience sake, therefore there exist many data which ${}^c k_1$ and ${}^c k'_1$ are not identical (see Fig. 1).
11 In fact, the probability distributions of ${}^c k_1$ and ${}^c k'_1$ within this time range show quite (without any
12 data selection with respect to Δk) inhomogeneous distribution (Fig. 2): values of $7.2 \times 10^{-12} \text{ cm}^3$
13 $\text{molecule}^{-1} \text{ s}^{-1}$ or less are only composed of ${}^c k_1$, and values of $8.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or more
14 are only composed of ${}^c k'_1$.

15 The mean value of all the ${}^c k_1$ and ${}^c k'_1$ collected from this modified local time range (without any
16 data selection with respect to Δk) is $7.80 \pm 0.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. However, we consider
17 that this standard deviation $0.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ certainly overestimates the precision of
18 the derived reaction rate because of the contamination of such inconsistent ${}^c k_1$ and ${}^c k'_1$.

19 What we consider is that the reasonable estimate for the precision of the derived reaction rate can
20 be obtained from the uncertainty of "each" ${}^c k_1$ and ${}^c k'_1$ derivation. This uncertainty is calculated via
21 the chi square functions of Eq (8) and (12) of the manuscript. The σ_{HOCl_m} at Eq (8) and σ_{ClO_m} at Eq
22 (12) yield the uncertainty of the derived σ_{HOCl_m} , respectively (hereinafter denoted as $\sigma_{c_{k_1}}$ and $\sigma_{c_{k'_1}}$).
23 The mean values of $\sigma_{c_{k_1}}$ and $\sigma_{c_{k'_1}}$ for the local time range of $19.0 \pm 0.7 - 3.6 \pm 0.7$ hr are:

$$\sigma_{c_{k_1}} = 1.15 \pm 0.09(1\sigma)[\times 10^{-12} \text{ cm}^3 / \text{molecule}^{-1} \text{ s}^{-1}] \quad (3)$$

$$\sigma_{c_{k'_1}} = 0.26 \pm 0.03(1\sigma)[\times 10^{-12} \text{ cm}^3 / \text{molecule}^{-1} \text{ s}^{-1}] \quad (4)$$

24 $\sigma_{c_{k_1}}$ becomes larger than $\sigma_{c_{k'_1}}$ because SMILES has less sensitivity to HOCl compared to ClO. In order
25 to take full advantage of SMILES high sensitivity, we considered using $\sigma_{c_{k'_1}}$ for the precision of the
26 reaction rate estimation instead of using $\sigma_{c_{k_1}}$. Then the Δk threshold was determined with the value
27 that gives the " variation " of ${}^c k_1$ and ${}^c k'_1$ equal to the mean uncertainty of individual ${}^c k'_1$ derivation
28 ($\sigma_{c_{k'_1}}$).

29 Figure 3 shows the threshold dependence of the mean value and variation of ${}^c k_1$ and ${}^c k'_1$ in the
30 modified local time range of $19.0 \pm 0.7 - 3.6 \pm 0.7$ hr. The value of Δk threshold was to be 0.1×10^{-12}
31 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from Fig. 3.

32 In summary, the criteria on Δ is required to evaluate a more reliable reaction rate in our analysis,
33 and its threshold is determined to have a reasonable extent of ${}^c k_1$ and ${}^c k'_1$ variation. We added the
34 detail explanation on the manuscript (page 7, line 62 - 8, 2).

35 Systematic error

36 We agree that the discussion about the accuracy of the analysis is very important. We updated the
37 manuscript with including new paragraphs (at page 3, line 70–78) to clarify our thought about the
38 accuracy. The systematic error (bias uncertainty) of SMILES NICT ClO data for the single measurement
39 has been estimated by Sagawa et al. (2013). It is about 3% at 0.28 hPa for the mid-latitude nighttime
40 condition by the maximum. Using the same method with the ClO error analysis, we newly estimated
41 the systematic errors for HOCl and HO₂: 10% and 9%, respectively, at 0.28 hPa for the mid-latitude
42 nighttime condition by the maximum. It should be noted here that this systematic error estimation is
43 carried out based on forward model simulations without taking the SMILES actual instrumental noise
44 into account. For the real SMILES measurements, the individual retrieval of HOCl and HO₂ contains
1 random errors (such as σ_{HOCl_m}) much larger than these estimated systematic errors. It is considered

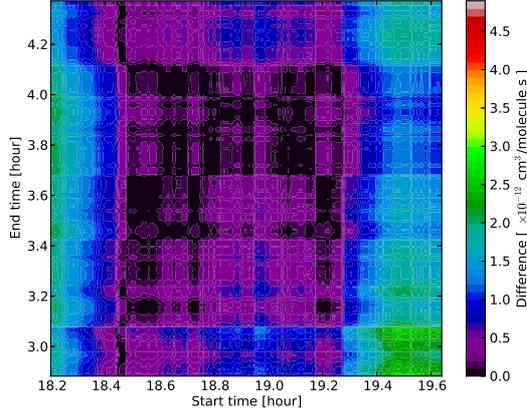


Figure 1: The contour plot of Δk calculated in from the SMILES observation data set between MLT 18:10 - 19:40 and MLT 02:50 - 04:20.

2 that the way how systematic errors appears in our reaction rate derivation is not that simple. If we
 3 mechanically consider the systematic errors of ClO, HOCl, and HO₂ of 3%, 10%, and 9%, then it turned
 4 out that there are no dataset which satisfy ${}^c k_1 \simeq {}^c k'_1$: this breaks the premise of our analysis, and we
 5 consider it is not appropriate to employ such a case for the accuracy evaluation. Contrary to HOCl and
 6 HO₂, ClO has been measured by SMILES with a relatively high signal to noise ratio ($S/N \sim 4$) and is
 7 more sensitive to the systematic error. In this study, we consider that the systematic errors of HOCl
 8 and HO₂ are sufficiently smaller than the systematic error of the ClO.

9 The impact of the systematic errors of ClO, HOCl, and HO₂ is evaluated as follows:

$${}^b[\text{ClO}] = [\text{ClO}]^{\text{obs}} \times (1 + a) \quad (5)$$

$${}^b[\text{HO}_2] = [\text{HO}_2]^{\text{obs}} \times (1 + b) \quad (6)$$

$${}^b[\text{HOCl}] = [\text{HOCl}]^{\text{obs}} \times (1 + c) \quad (7)$$

10 In these equation, a , b , and c are the systematic errors of ClO, HO₂, and HOCl, respectively. We
 11 denoted ${}^b[\text{ClO}]$, ${}^b[\text{HO}_2]$, and ${}^b[\text{HOCl}]$ as values including the systematic errors, respectively.

12 The numerical solution for the calculation of the rate constant based on the HOCl production using
 13 Eq. (7) is given as;

$${}^b[\text{HOCl}]_0^{\text{calc}} = [\text{HOCl}](0) \quad (8)$$

$${}^b[\text{HOCl}]_{m+1}^{\text{calc}} = {}^b[\text{HOCl}]_m^{\text{calc}} + \frac{{}^b k_1}{2} \left(({}^b[\text{ClO}]_m \cdot {}^b[\text{HO}_2]_m) + ({}^b[\text{ClO}]_{m+1} \cdot {}^b[\text{HO}_2]_{m+1}) \right) \times (t_{m+1}^{\text{obs}} - t_m^{\text{obs}}) \quad (9)$$

14 In this equation, we denote the rate constant of HOCl increase using Eq. (7) as ${}^b k_1$. ${}^b k_1$ and $[\text{HOCl}](0)$
 1 are determined by minimizing the following function χ^2 :

$$\chi^2 = \frac{1}{N} \sum_{m=1}^N \left(\frac{({}^b[\text{HOCl}]_m - {}^b[\text{HOCl}]_m^{\text{calc}})^2}{(\sigma_m^{\text{HOCl}})^2} \right) \quad (10)$$

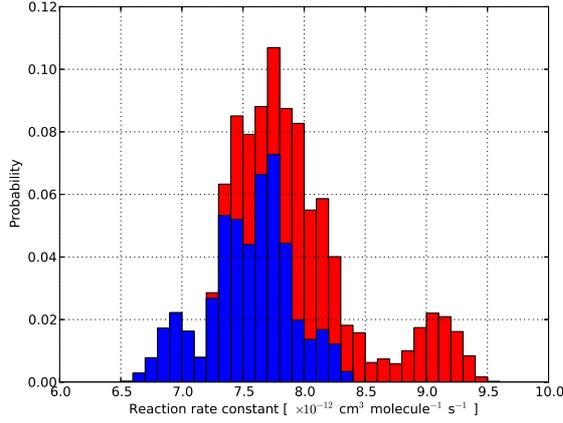


Figure 2: The probability plot of k_1 (blue) and k'_1 (red) in the modified local time range of $19.0 \pm 0.7 - 3.6 \pm 0.7$ hr.

2 Also the calculation function of the ClO decrease and evaluation function are performed using Eq.
3 (7) as following equations;

$${}^b[\text{ClO}]_0^{\text{calc}} = Y_0 \quad (11)$$

$${}^b[\text{ClO}]_{m+1}^{\text{calc}} = [{}^b[\text{ClO}]_m^{\text{calc}} - \frac{{}^b k'_1}{2} \left(({}^b[\text{ClO}]_m \cdot {}^b[\text{HO}_2]_m) + ({}^b[\text{ClO}]_{m+1} \cdot {}^b[\text{HO}_2]_{m+1}) \right) \times (t_{m+1}^{\text{obs}} - t_m^{\text{obs}})] \quad (12)$$

$$\chi^2 = \frac{1}{N} \sum_{m=1}^N \left(\frac{({}^b[\text{ClO}]_m^{\text{calc}} - {}^b[\text{ClO}]_m)^2}{(\sigma_m^{\text{ClO}})^2} \right) \quad (13)$$

4 In this equation, we denote the rate constant of ClO decrease using Eq. (7) as ${}^b k'_1$.

5 We calculated two rate constants, ${}^b k_1$ and ${}^b k'_1$, using following value as the systematic error;

$$a = 3\% \quad (14)$$

$$b = 1\% \quad (15)$$

$$c = 1\% \quad (16)$$

$$(17)$$

6 The value of the systematic error of ClO is the maximum value obtained from the error analysis. Also
7 the values of the systematic errors of HO₂ and HOCl are determined by the reason that we consider
8 that the systematic errors of HOCl and HO₂ are sufficiently smaller than the systematic error of the
9 ClO.

10 The difference between ${}^b k_1$ and ${}^b k'_1$, ${}^b \Delta k = |{}^b k_1 - {}^b k'_1|$, is shown in Fig. 4. The horizontal and
11 vertical axes are the start and end time of the considered time intervals, respectively. The blank area
1 represents the time intervals where the data numbers are less than our threshold.

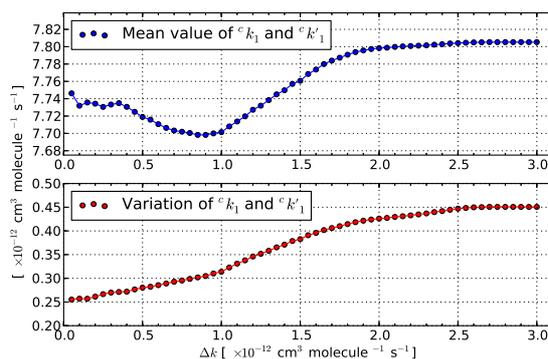


Figure 3: The threshold dependence of the mean value of ${}^c k_1$ and ${}^c k'_1$ (top) and the variation of ${}^c k_1$ and ${}^c k'_1$ (bottom) in the modified local time range of $19.0 \pm 0.7 - 3.6 \pm 0.7$ hr.

2 We estimated the rate constant of the Reaction (R1) from Fig. 4 obtained using values of Eq. (17).
 3 To estimate the rate constant of the Reaction (R1), we used following conditions:

- 4 1. Time range of 18.5 - 4.0 (same with our estimated pure reaction period)
- 5 2. Threshold of $\Delta k = |{}^b k_1 - {}^b k'_1| \leq 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (same with our estimated
- 6 threshold)

7 The rate constant of the Reaction (R1) was obtained to be $\bar{k}_1 = 7.49 \pm 0.73(1\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$
 8 s^{-1} at 245 K. To distinguish the rate constant of the Reaction (R1) including the systematic errors,
 9 we denoted \bar{k}_1 . Also the SMILES k_1 was obtained to be $k_1 = 7.73 \pm 0.26(1\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$
 10 s^{-1} . The value of \bar{k}_1 is consistent with one of k_1 within the 1σ error of k_1 . There is the effect of the
 11 systematic errors in Eq. (17) within the range of σ_k of k_1 .

12 The conclusion of this section is as follows: The maximum systematic error from the single scan
 13 spectrum of SMILES was estimated to be 3%, 10%, and 9% for ClO, HO₂, and HOCl, respectively
 14 in the night time at 0.28 hPa by using theoretical error analysis based on forward model simulations
 15 without taking account the actual random noise component. On the other hand, the signal to noise ratio
 16 of the single scan spectrum of SMILES was about 4, 1, and 1 for ClO, HO₂, and HOCl, respectively
 17 in the night time at 0.28 hPa. We consider that the systematic error estimated is sufficiently apparent
 18 only for ClO but HOCl and HO₂, since ClO has been measured by SMILES with a relatively high signal
 19 to noise ratio. The impact of the systematic errors of ClO, HOCl, and HO₂ is estimated using values of
 20 3% of ClO, 1% of HO₂, and 1% of HOCl as the systematic errors with taking account the signal to noise
 21 ratio. The estimated rate constant of the Reaction (R1) including the systematic errors is consistent
 1 with k_1 within 1σ . We added the detail explanation on the manuscript (page 8, line 11–28).

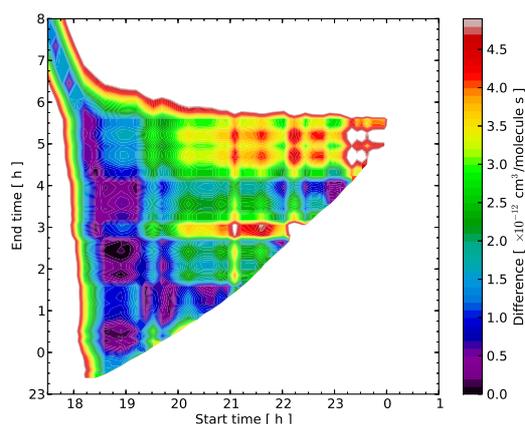


Figure 4: The contour plot of the difference between $^b k_1$ and $^b k'_1$, $\Delta k = |^b k_1 - ^b k'_1|$ in each local time interval.

2 Minor comments

3 **Page 12798, line 6–7: This is very general, why do you use than only the**
 4 **altitude 0.28 hPa?**

5 We checked other altitudes, 0.10 hPa and 0.54 hPa, but these altitudes were not suitable for the analysis.
 6 In higher altitudes than 0.28 hPa, there were not enough HOCl and ClO. And in lower altitudes than
 7 0.28 hPa, there were the effect of ClONO₂ production reaction, $\text{ClO} + \text{NO}_2 + M \rightarrow \text{ClONO}_2 + M$, in
 8 the nighttime. The altitude 0.28 hPa was the only condition for the direct estimation of k_1 and the
 9 evaluation of the purity of the Reaction (R1).

10 **12798, 9: I would write ‘between the HOCl production rate and ClO loss rate’.**

11 We rewrote as you had pointed out (at Abstract).

12 **12799, 13: Why extra polar region?**

13 We delete ‘in polar regions’ (Page 1, Line 35). And we add the reference of Chipperfield et al. (1994) in
 14 Page XX, Line YY. They reported the ClO-HO₂ cycle contributed 10% of the ozone loss in the region
 15 of maximum loss in the Arctic winter 1991-1992.

16 **12800, 8–9: Which laboratory experiment do you have performed?**

17 We did not performed the laboratory experiment. To avoid misunderstanding, we add the citation of
 1 references for the laboratory experiments (of other groups) in the total of the manuscript.

2 **12800, 21: I would say depletion instead of destruction and calculated instead**
3 **exploited.**

4 We changed the manuscript as depletion instead of destruction (Page 2, Line 49). We would like to keep
5 'exploited' instead of 'calculated' because we feel 'calculation' is only for the numbers and 'exploitation'
6 is for the derivation of the equation. But we are not native English speakers and we may be wrong. If
7 we were wrong, we will correct it.

8 **12801, 1: Again Calculation instead of Exploitation**

9 We would like to keep 'Exploitation' instead of 'Calculation'. By saying Exploitation, we mean 'Uti-
10 lization of the information contained in the observed temporal evolution of ...'. We consider that
11 Calculation does not express this properly. But we are not native English speakers and we may be
12 wrong. If we were wrong, we will correct it.

13 **12801, 10: Is there a reference for the box model? What temperatures you**
14 **use for the levels? What transport is assumed?**

15 The box model is based on a module for stratospheric and mesospheric chemistry provided by Guy
16 Brasseur. The list of reactions is similar to that given by Brasseur et al. (1997) Reaction rate constants
17 were updated to the data in the JPL 2011 recommendation (Sander et al., 2011). Photolysis rate
18 constants are calculated according to Madronich and Flocke (1999). The automatic generation and
19 numerical solution of the differential equations corresponding to the chemical system is done by the
20 kinetic preprocessor KPP (Damian et al., 2000). Temperature and transport: cf. above.

21 **12802, 5: Please skip 'due to the lower air pressure'**

22 We changed the manuscript as you mentioned (Page 3, Line 12).

23 **12804, 8: Is 18:30 not relative? I mean, the sunset changes from February to**
24 **April in 20 °S to 40 °S at least one hour.**

25 The modified local time is used to reduce the error for merging data of different latitudes and seasons.
26 We explained in the paragraph (Page3, Line 52–61). In order to make clear that a modified local time
27 is used, we rewrote the sentence.

28 **12805, 8: Do a reference exist for the midpoint method scheme?**

29 We explained that we used the midpoint method scheme for approximating the integral but exactly
30 used the trapezoidal rule (Press et al., 1992). We changed the manuscript (Page 4, Line 35).

31 **12808, 23: This formulation please change in the total paper: Instead [x 10-12**
32 **cm/molecule s] write x 10-12 cm³ molecule⁻¹ s⁻¹ (without brackets)**

33 We changed the manuscript as you mentioned in the total of the manuscript.

34 **12809, 6-7: This is in my opinion only a too simple assumption.**

35 As discussed in above section about the threshold of Δk , the 1σ precision of the SMILES k_1 is consistent
1 with the average value of calculated error of k'_1 .

2 **12810, 2-3: That is true, but I also think it is also very difficult to find such**
3 **a condition in the atmosphere. Currently I am not sure if you have found**
4 **this condition.**

5 We found the pure reaction period from SMILES observations. Of course, there is a possibility that
6 other competitive reactions for Cly chemistry exist. But, these competitive reactions are not detected
7 in SMILES observations.

8 **12810, 20-22 and 12811, 20-25: You don ' t explain these measurements in**
9 **high pressure conditions (1,5 Torr) in the manuscript. If you have made these**
10 **calculations than please explain these in more detail.**

11 The high pressure conditions are previous laboratory experiments. To avoid misunderstanding, we add
1 the citation of references for the laboratory experiments (of other groups).

2 References

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