

Authors' Reply

The authors appreciate the helpful and constructive comments. In the following, the comments are printed in *italic face* while our replies are printed in normal roman face.

Reviewer Comment 1 by Chris Boone:

This article presents a comprehensive look at a molecule with an important role in atmospheric chlorine processing. I have no major concerns, but there are a few typos and wording issues (described below)

We are happy about this encouraging general statement and we appreciate the help to improve the language and the clarity of the paper. Thanks a lot, Chris!

page 2, line 25: Remote sensing of ClONO₂ from ground > from the ground
Corrected.

page 2, line 27: because the ray-path avoided to cross the humid boundary layer which has lead to a much clearer spectral signature of ClONO₂. > Awkward wording. Suggest “: :because the measured light does not pass through the humid boundary layer, yielding a much clearer spectral signature from ClONO₂.”
Corrected.

page 2, line 31: Summaries of stratospheric chlorine chemistry and its history is given > are given
Corrected.

page 3, line 2: in atmospheric sciences it is relevant as a stratospheric trace gas > Awkward wording. Suggest “in the stratosphere it is a trace gas with a significant role in chlorine-related chemistry.”
Corrected.

page 4: Why did Equation 3 end up on two lines? It would look better on one line.

You are right for the discussion paper which is type-set in a one-column format. In order to avoid additional type-setting errors when transforming the paper from the 1-column discussion format to the 2-column ACP journal format, we have typeset all equations in a way that nothing has to be changed for the final 2-column format.

page 6, line 1: Along with photodissociation, also these sinks depend on sunlight > Awkward wording. Suggest “Although no photons are explicitly involved in the above reactions, these sinks have an implicit dependence on sunlight”

We have changed the wording as suggested except from “above” which we have replaced with the equation numbers.

page 7, line 12: *The product Cl is involved in catalytic ozone destruction > I believe you mean BrCl, not Cl*

No, we mean the atomic Cl resulting from the photolysis of Cl₂. We have rewritten the sentence for clarity: "... is photolyzed by sunlight in polar spring to give atomic Cl which is..."

page 7, line 20: *The variable k is used for both rate constant and the Boltzmann constant. Perhaps you should use a different label for the Boltzmann constant (k_B ?)*

Done.

page 9, line 17: *The net reaction R25 indicates a photon (hv) was involved, but no photon appears in any of the reactions involved (R21-R24)*

Corrected

page 9, line 23: *but also allow that chlorine is transported over long distances without reaction. > Awkward wording. Suggest "...but also allow chlorine to be transported over long distances without reaction."*

Corrected

page 10, line 14 (R31): *The net reaction R31 does not indicate any photons (hv), but the reactions indicate that there were two photons involved*

Corrected

page 11, line 5: *which is only available in seizable amounts > sizeable amounts*

Corrected

page 11, line 16: *sedimentation of HNO₃-laden particles > HNO₃-laden*

Corrected

page 11, line 21: *This in tendency counter-balances > Awkward wording ("in tendency"). Either delete this phrase or change the wording to something like "...tends to counterbalance..."*

Corrected

page 12, line 5: *formation of seizable amounts > sizeable amounts*

Corrected

page 13, line 1: *if temperatures are below 190 K a lot of aerosol is available. > Suggest "...if temperatures are below 190 K and a lot of aerosol particles are available."*

Corrected

page 14, line 11: *de-accelerate > decelerate*

Corrected (also in l. 13)

page 15, line 4: An example of these cross sections are > An example of these cross sections is...

Corrected

page 15, lines 6-8: The recent version of the HITRAN (high resolution transmission) spectra database (Gordon et al., 2017) recommends the usage of these absorption cross sections for atmospheric research. The spectra are part of the HITRAN recommendations since the version of 2004 (Rothman et al., 2005). > Suggest “These absorption cross sections are recommended for use in atmospheric research by the most recent version of the HITRAN (high resolution transmission) spectral database (Gordon et al., 2017) and have been the recommendation since the 2004 version of HITRAN (Rothman et al., 2005).”

Corrected

page 15, line 15: In their paper these authors also summarize > Perhaps “The paper also summarizes...”

Corrected

page 17, line 18: Table Mountain Observatory, California Gunson and Irion (1991) > Brackets misplaced in reference: “(Gunson and Irion, 1991)”

Corrected

page 19, line 26: reported by von Clarmann et al. (1997); Wetzel et al. (2006, 2008, 2010, 2013), Many of these flights... > the “;” should technically be replaced by “and”, and there is a comma at the end of the sentence instead of a period

Corrected.

page 20, line 15: periods of particularly sparse measurements in 2006 and 2006. > 2006 is repeated (2005 and 2006?)

Corrected.

page 20, line 16: While not part in the original MIPAS ESA data product > While not part of the...

Corrected.

page 21, line 30: A similar technique has been applied by Von Hobe et al. (2003); Stroh et al. (2011) with the HALOX instrument. > Again the “;” should be “and”

Corrected.

page 21, line 30: A maximum of ClONO₂ with 1.5 ppbv at 27 km altitude before sunrise is observed, which is decreasing one hour after sunrise down to 1.3 ppbv until two hours after sunrise > Suggest (if I interpret this correctly) “The maximum volume mixing ratio for ClONO₂ was 1.5 ppbv, observed at an altitude of 27 km one hour before sunrise. During the time period of one to two hours

after sunrise, ClONO₂ levels decreased to 1.3 ppbv.”
Corrected.

page 21, line 31: They explain this decrease > They explained this decrease...
Corrected.

page 23, line 3: Rinsland et al. (2010) found that ClONO₂ stopped to increase.
> stopped increasing
Corrected.

Thanks again, Chris!

Review RC2:

The paper gives a very nice and detailed overview on atmospheric ClONO₂. The authors have spent a lot of time on collecting all the different pieces of information to give a complete picture on atmospheric ClONO₂. The paper is very well written, and the reference list is very good.

The authors are thankful for the appreciation of their work and for the advice how to make the paper more complete and clearer.

I have only one major comment. Since ClONO₂ shows a high variability in the atmosphere, and its concentration in the stratosphere is directly linked to HCl and the CFCs, the authors might think about showing the long-term trend of HCl and may be one of the CFCs. Otherwise Fig. 3 gives the impression as if the long-term trend of ClONO₂ is small.

We have included a figure from DeMaziere et al., 2018, which shows trends of ClONO₂ and HCl. This figure is now part of the “Trends of ClONO₂” section.

Minor comments: Page 2, line 30: It would make sense to give here already the NDACC reference (deMaziere et al., 2018).

Yes, indeed. Done.

The two papers mentioned by M. J. Tang in his review should be included.
These papers have been included.

The authors might think about including the paper by Rex et al (Prolonged stratospheric ozone loss in the 1995/96 Arctic winter, Nature, 389, p. 835-838, 1997), where ClONO₂ is also shown.

Done.

Figure 1, Table 1, Table 2: It would make sense to give here a reference.

Figure 1 was not copied from elsewhere but drawn in LaTeX by the 1st author:

```
\begin{figure}
  \chemfig{N^{+}(-#(0pt,5pt)[: -30](0(-[:30] Cl)))=([:90]O)}
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(-[:210]{^-}0)}
\hspace{2mm}$\longleftarrow$\hspace{2mm}
\chemfig{N^+(-#(0pt,5pt)[:30](0(-[:30] Cl)))
(([:90]0)([:180]{-\quad}))([:210]0)}
\caption{\label{fig_structure}The chemical structure of
chlorine nitrate.}
\end{figure}

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There exist similar figures in the internet we have used for “inspiration” but these are in the public domain. For the values in the tables, a reference has been added.

Regarding the stratospheric ozone chemistry, the most important trace gas resulting from reactions of ClONO₂ is ClO. The authors might think about writing a bit more on the ClO molecule, and not only give the important reactions.

We have checked the manuscript with respect to this and we have found that the role of ClO in the context of polar stratospheric ozone chemistry is discussed at some length in Section 6.2. We are somewhat reluctant to include too much information on chlorine monoxide besides what is relevant in a direct context of ClONO₂ because we hope that not too far in the future there will be a dedicated article on ClO in the Encyclopedia of Geosciences.

Page 9, line 18: I do not fully understand the sentence: The reason is that there is typically much less reactive chlorine available than released from the chlorine source gases. May be rewording it a bit?

Slightly reworded: “The reason is that there is typically not all of the reactive chlorine released from the chlorine source gases is available for ozone destruction. Instead, reaction ...”

Page 15, line 3: Instead of: a spectrally highly resolving Fourier transform spectrometer. better: a high resolution Fourier transform spectrometer
Corrected.

Comment SC1:

The authors provided a nice overview of heterogeneous reactions of ClONO₂ in Section 5.2. May I draw their attentions to my work in which heterogeneous reactions of ClONO₂ with TiO₂ and SiO₂ aerosol particles were studied (Tang et al., 2016)?

Tang, M. J., Keeble, J., Telford, P. J., Pope, F. D., Braesicke, P., Griffiths, P. T., Abraham, N. L., McGregor, J., Watson, I. M., Cox, R. A., Pyle, J. A., and Kalberer, M.: Heterogeneous reaction of ClONO₂ with TiO₂ and SiO₂ aerosol particles: implications for stratospheric particle injection for climate engineering, Atmos. Chem. Phys., 16, 15397-15412, 2016.

This reference has been included

In addition, a previous study (Molina et al., 1997) explored heterogeneous reaction of ClONO₂ with aluminium oxide. Molina, M. J., Molina, L. T., Zhang, R. Y., Meads, R. F., and Spencer, D. D.: The reaction of ClONO₂ with HCl on aluminium oxide, Geophys. Res. Lett., 24, 16191622, 1997.

This reference has been included

The authors thank Dr Tang for helping us to make the paper more comprehensive.

Further Errors Detected by the Authors:

Eq. 3: In the denominator of the exponent, 1, inf should have been a subscript. This has been corrected.

p20 l16: “Initially” inserted, because otherwise this sentence makes no sense.

Table with links to original data: The ILAS and ILAS-II links have been updated. Also the CRISTA-NF footnote has become obsolete and has thus been removed.