

We would like to thank the reviewers for their detailed and constructive comments. We have revised the manuscript accordingly and our responses appear below.

Reviewer #1

This manuscript presents a valuable and carefully compiled dataset of high-precision in situ aircraft measurements of ClO and ClONO₂ from 29 research flights during the two-year NASA DCOTSS mission. The precision achieved by the HAL instrument is unprecedented for this altitude range and enables analyses that satellite observations alone cannot support. This study indicates that no significant chlorine activation was observed despite targeted sampling of both convectively influenced and biomass-burning-influenced air masses, which is scientifically important and provides a valuable observational constraint on previous modeling studies. The agreement between measured and steady-state calculated ClONO₂ also provides an important quantitative test of stratospheric chlorine photochemistry. Overall, the manuscript is well written, and the conclusions are generally well supported by the observations. The comments below concern clarification, interpretation, or additional discussion rather than substantial new analyses. I support publication in Atmospheric Chemistry and Physics subject to minor revisions.

We sincerely thank the reviewer for this positive feedback on the manuscript.

Major Comments

1. In Section 3.3, it would be helpful to report more explicitly whether the sampled convective events actually reached the temperature, aerosol conditions, and water vapor levels under which the Anderson et al. (2012, 2017) mechanism predicts chlorine activation, and to compare these conditions directly with those assumed in the cited modeling studies. This would help clarify whether the absence of observed activation reflects a genuine absence of the proposed mechanism, insufficiently extreme sampled conditions, or differences in reaction timescales relative to those assumed in the models.

We completely agree that a detailed analysis to compare with prior modeling studies is important, and we have already done exactly that. We published this work last year in JGR: Howar et al. (2025), which is cited in the present manuscript.

2. In Section 3.4, Figure 5b is fitted using ordinary least-squares regression, which assumes negligible uncertainty in the x-axis. However, both measured and steady-state calculated ClONO₂ carry substantial uncertainties (approximately 20% and 45%, respectively), making an errors-in-variables regression (e.g., York or Deming regression) more appropriate. I recommend repeating this fit using such a method before suggesting that the recommended value of $k_{\text{ClO}+\text{NO}_2}$ may be biased high, and briefly discussing whether uncertainties in the NO₂ measurement or the JClONO₂ calculation could also contribute to the observed discrepancy.

The reviewer is correct that there is significant uncertainty in both the x- and y-axes of Figure 5b, but this is a point we already highlight in the manuscript. Moreover, we also state (lines 392–393

in the original submission) that “the discrepancy between steady-state calculated and measured ClONO_2 is not statistically significant”. Doing a different fit would show the same result. When the possible high bias in $k_{\text{ClO}+\text{NO}_2}$ is mentioned (lines 395–396 in the original submission), we use the word “suggesting”, i.e., there is no definitive claim. We have added a new sentence to the Conclusions to further clarify this point.

3. In Section 3.5, the HCl values are derived from a regional-mean MLS $\text{HCl}:\text{O}_3$ relationship and applied to all DCOTSS observations. Please discuss whether this relationship remains valid for the convectively influenced air masses that are central to this study, where chlorine partitioning may differ from the regional background. As the same calculated HCl is subsequently used in the Cl_y budget analysis (Fig. 7b), please clarify the extent to which this budget closure represents an independent validation of the ClO and ClONO_2 measurements rather than a self-consistency check. This concern is amplified by the fact that HCl accounts for over 95% of total inorganic chlorine, and both the calculated HCl and the independently derived Cl_y are expected to correlate strongly with O_3 through their shared dependence on air mass age.

The reviewer is correct that if inorganic chlorine chemistry had been perturbed following convection, the calculation of HCl in this study would be impacted. But there was no evidence of chlorine partitioning being impacted during DCOTSS sampling. In particular, we know from modeling studies that ClONO_2 would initially increase in concert with any HCl decrease due to heterogeneous chlorine reactions, but such an increase in ClONO_2 was never observed, which provides confidence that HCl was also not perturbed.

As for the second question about whether the budget calculation represents an independent validation, it definitely does. What is derived from the satellite data is the $\text{HCl}:\text{O}_3$ relationship as a function of pressure. This relationship is then applied to the DCOTSS O_3 dataset to determine relevant HCl mixing ratios used in the budget calculation. Importantly, the Cl_y values we compare with for the budget determination are completely independent values determined from organic chlorine species. If calculated HCl were incorrectly determined, the inorganic chlorine budget would not agree despite the shared dependence with Cl_y on air mass age.

4. In Section 3.6, the negative correlations shown in Fig. 8 may largely reflect the common dependence of both chlorine species and aerosol composition on potential temperature (i.e., age of air), as the authors note. I recommend accounting for this confounding effect, for example by examining residuals after removing the θ dependence or by presenting the Cl_y -normalized comparison currently shown in Supplement Fig. S5 as the primary analysis in the main text. Such analyses would provide a more rigorous test of whether biomass-burning aerosol independently influences chlorine partitioning.

Thank you for this suggestion. We moved Figure S5 to replace Figure 8 in the manuscript and edited the text in the manuscript and supplement accordingly.

5. Also in Section 3.6, the Solomon et al. (2023) mechanism specifically concerns aged organic-rich biomass-burning aerosol. Where available please provide additional information on the transport history or processing state of the sampled biomass-burning air masses and discuss how representative these air masses are of the aged smoke plumes for which the mechanism was originally proposed. This would help clarify how broadly the reported null result can be generalized.

We thank the reviewer for this comment. We have updated the manuscript with additional information framed around the text below.

A DCOTSS study by Shen et al. (2025) showed that: (1) All stratospheric biomass burning (BB) particles observed during DCOTSS contained sulfate, which is an indicator of atmospherically aged particles (Hudson et al., 2004), in contrast to fresh BB particles commonly observed in the troposphere (Reid et al., 2005). (2) These stratospheric BB particles were also organic-rich, with the presence of organic acids and chlorine-containing compounds providing further evidence for chemical modification during atmospheric processing. (3) Their volume-weighted diameter peaked at $\sim 0.4\ \mu\text{m}$, which is larger than the $\sim 0.25\ \mu\text{m}$ peak reported for fresh BB particles (McClure et al., 2020). Thus, the stratospheric BB particles sampled during DCOTSS clearly displayed evidence of having been chemically aged in the atmosphere.

New References:

McClure, C. D., Lim, C. Y., Hagan, D. H., Kroll, J. H., and Cappa, C. D.: Biomass-burning-derived particles from a wide variety of fuels – Part 1: Properties of primary particles, *Atmos. Chem. Phys.*, 20, 1531–1547, doi:10.5194/acp-20-1531-2020, 2020.

Reid, J. S., Koppmann, R., Eck, T. F., and Eleuterio, D. P.: A review of biomass burning emissions part II: intensive physical properties of biomass burning particles, *Atmos. Chem. Phys.*, 5, 799–825, doi:10.5194/acp-5-799-2005, 2005.

Minor Comments

1. The anomalously high ClONO₂ values from three May 2022 flights (lines 241–247) are attributed to "large-scale dynamics" rather than convection, but no trajectory or potential vorticity analysis is presented to support this attribution. Please provide supporting evidence or soften the claim.

The text states “suggesting” with regards to large-scale dynamics being responsible, but to be clearer, we have softened this further by stating “likely responsible”.

2. The aerosol composition analysis (Fig. 8) uses only the 16 flights from 2022 with PALMS-NG data. This limitation should be stated earlier and more prominently in the main text rather than only in the figure caption.

The reviewer appears to have missed that this limitation is already discussed in the main text on lines 533–534 in the original submission.

3. Please clarify the specific division of analysis and conclusions between this manuscript and the companion paper (Howar et al., 2025), as the latter is cited repeatedly to explain the absence of observed chlorine activation. Readers would benefit from a clearer statement of the distinct contribution of each paper.

As with all citations in this work, everything presented here without citation is a result from this paper. The reviewer's confusion is difficult to understand, as the Howar et al. (2025) paper is only cited once (not repeatedly) in the present paper with regards to the absence of observed chlorine activation in DCOTSS, and that occurrence in context is a clear statement differentiating the Howar study from this work (lines 337–338 in the original submission): “Further explanation for the absence of observed chlorine activation is provided in an extensive modeling study of DCOTSS data (Howar et al., 2025).”

Reviewer #2

General comments

The manuscript by Wilmouth et al. presents unprecedented airborne data of the inorganic chlorine species chlorine monoxide and chlorine nitrate from the DCOTSS mission covering two stratospheric summer periods over Northern America. No chlorine activation was observed in the surrounding of convective injections and also no inorganic chlorine activation in wildfire influenced air masses. Steady-state calculated ClONO₂ agreed well with measured ClONO₂. Further, HCl was calculated along the flight track using satellite data. The sum of ClO, HCl and ClONO₂ showed good agreement with the total inorganic chlorine, calculated by independently measured organic chlorine species. By covering the different aspects of the inorganic chlorine species, the manuscript adds relevant knowledge to the research community. I support publication in Atmospheric Chemistry and Physics after minor revisions.

We sincerely thank the reviewer for this positive feedback on the manuscript.

Specific comments

L429: “interpolating between the three available MLS pressure levels” Do you mean linear interpolation or exponential decay or something else?

Linear interpolation. We now specify this in the text.

L487/488: “... and expected differences between the studies due to different latitudes being sampled,” Would also different seasons and years play into the differences?

While latitude is the primary cause, the reviewer is correct that other factors can contribute. We edited the sentence to present latitude as an example reason for the difference.

L490: “Cly determined from organics might be biased low at low mixing ratios.” Could detection limits play a role in here?

Thank you for this suggestion. The detection limits are quite low for the relevant measured species, so that alone could not explain a discrepancy of the magnitude considered here.

L588-594: How severe had been the fire seasons in 2021 and 2022 in Northern America? The ANY fires had for example strong overshooting convection? Do you mean this with “significant interannual variability in stratospheric conditions” (L590)?

There were no fires of the significance of the ANY fires in 2021 and 2022, but there were fires that impacted stratospheric aerosols. We have added new text to discuss the evidence for aged biomass burning aerosols sampled in DCOTSS. Please see our response #5 to Reviewer #1.

Technical corrections

L187: suggestion for easier reading and understanding for people outside US: “southern IL” to “southern Illinois”

We made this change.

Figure 5: in 5a the x-axes range from 50° to >110° SZA, in the caption and the text (L365) you state filtered for SZA >= 60°. Please unify

The text is correct as written. The data selection for Figure 5a was that only flights were included that had measurements at high solar zenith angles, i.e., at some point during the flight the solar zenith angle was greater than or equal to 60 degrees. Once the flight selections were made, the plot shows all the data for those flights with solar zenith angles from 50–115 degrees.

Figure 6b: please enlarge the dots in the legend, that different colours are easier to identify per molecule. Additionally, cross check also other Figures. Additionally, I would recommend to not use red and green in one plot, where possible, to make it more readable for people with colour-blindness.

Good point regarding the dot sizes. We have edited not just Figure 6, but also Figures 2, 4, 5, 7, S3, and S4 to make the dots in the legends larger and more visible. We certainly appreciate the color-blindness concern, but we ran all the figures through a Color Blindness Simulator, and they all checked out fine. There are no overlapping red and green points in the figure panels, so the points can be easily distinguished.