

I appreciate the response from Gaojie Chen et al. to the reviewer responses. However, the main concerns indicated by reviewer 1 are still apparent.

Comment 1:

Referring to the original reviewer 1 comment 4: the authors have responded by providing a traditional analysis of ClNO₂ production. This analysis is very helpful in gauging the potential for formation of ClNO₂ from other mechanisms.

While the analysis seems appropriate the author's conclusion in the reply is not justified :“we believe that the observed daytime ClNO₂ levels, particularly around noon, cannot be adequately explained by heterogeneous N₂O₅ uptake alone, suggesting the presence of additional sources contributing to the formation of daytime ClNO₂.”

The authors provided Figure R2 and argue that Figure R2 shows that observations of ClNO₂ cannot be explained by an upper-limit calculation of N₂O₅ uptake (γ) and ClNO₂ yield (ϕ). In other words, the observed ClNO₂ is greater than what could be produced by traditional chemistry. **Yet, the observation uncertainty is absent from the figure.**

The authors have also mis-quoted their measurement uncertainty. Reviewer 1 requested the authors state their uncertainty in the main text (comment 2) but the reviewer said it is “non-negligible (~20%)”. The authors copied this number to the main text. However, this is incorrect. The SI includes the sensitivities: “The sensitivities of ClNO₂ and N₂O₅ were 0.055 ± 0.018 and 0.11 ± 0.063 ncps·ppb⁻¹” (lines 119-120). This translates to an uncertainty of 33% for ClNO₂ and 57% for N₂O₅.

As such, the author's calculation of ClNO₂ in their response and Figure R2 would have an observed uncertainty which combines both uncertainties of ClNO₂ and N₂O₅ since the calculation of ClNO₂ involves both compounds (equation 3 in author's response). These uncertainties should be added in quadrature as a result.

$$uncertainty = \sqrt{33\%^2 + 57\%^2} = 83\%$$

Remaking Figure R2 (presented below as Figure R2a) shows that the two upper-limit scenarios provided by the authors do indeed fall within the measurement uncertainty.

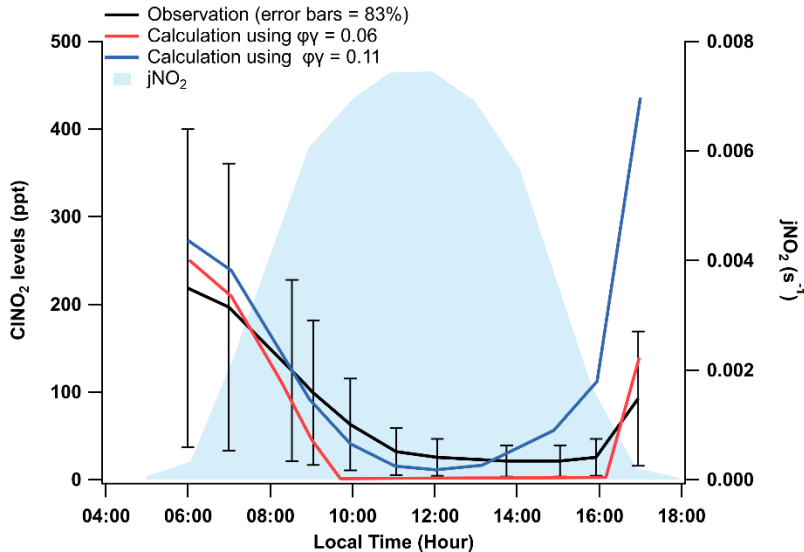


Figure R2a: reproduced from author's response. The data for plotting was acquired by the "Igor Thief" tool in Igor Pro by Wavemetrics. The only addition is the black error bars showing an 83% uncertainty on the observations.

It is understood that the cases presented by the authors represent upper-limit estimations. However, Figure R2a above shows that the $\phi\gamma = 0.06$ case could produce results which match the observations within the uncertainty. I agree that the $\phi\gamma = 0.06$ case is closer to an upper-limit estimation but I argue it is still within the realm of possibility (see references already provided by reviewer 1). Further, additional cases with lower $\phi\gamma$ values will very likely fall within the observational uncertainty.

My interpretation of the author's results is that their observations could be explained by traditional N_2O_5 chemistry. While there is precedent to consider the particulate nitrate mechanism, there is not clear evidence here to say " NO_3^- photolysis promoted the elevation of daytime ClNO_2 concentrations" (line 327). This conclusion and others similar to it should be dampened to say that nitrate photolysis may have contributed but cannot be confirmed. The author's Figure R2 should also be included in the SI with included observational errors.

Comment 2:

The authors did not address concerns regarding the correlation of $\text{NO}_3^- \times \text{jNO}_2 \times \text{Sa}$. I understand that reviewer 1 did not explicitly request a change here. However, the point that panel 7d appears to show little correlation with jNO_2 still remains. This point was never commented on by the authors. Without showing separated correlations between all factors it is impossible to know the drivers of this apparent correlation. As such the author's conclusion ("the photolysis of NO_3^- contributed to the daytime concentrations of ClNO_2 at our study site") cannot be made.