

Comment: Soni et al. report an updated mechanism for the community atmospheric chemistry box model CAABA/MECCA, adding some 35 gas-phase reactions, 15 aqueous-phase reactions, and 4 reactions governing the partitioning of gases between gas and aerosol phase. The focus is on chemistry of chlorine compounds (Cl_2 , ClNO_2 , etc.). Reactive intermediates such as the nitronium ion (NO_2^+) are treated explicitly. The revised model's was tested using two recent urban data sets collected in New Delhi (India) and Leicester (UK).

The paper is written well. I have a few concerns that the authors will hopefully be able to address in revision.

Response: We thank the reviewer for the comments and suggestions, which have improved our manuscript. Please find our responses to the comments below in blue fonts. The discussion added/updated in the manuscript is presented by red color font.

General comments.

1. More explanation is needed to justify the chlorine nitrite chemistry in the mechanism, considering this molecule has not been unambiguously observed in ambient air. The authors are correct that chlorine nitrite may form from $\text{Cl} + \text{NO}_2$ (e.g., Golden, J. Phys. Chem. A 2007, 111(29), 6772–6780, <https://doi.org/10.1021/jp069000x> and Niki et al., Chem. Phys. Lett. 1978, 59(1), 78–79, [https://doi.org/10.1016/0009-2614\(78\)85618-8](https://doi.org/10.1016/0009-2614(78)85618-8)) - these papers should be cited. However, its chemistry is incomplete. ClONO is metastable and converts to ClNO_2 (Janowski et al., Berichte der Bunsengesellschaft für physikalische Chemie 1977, 81(12), 1262-1270, <https://doi.org/10.1002/bbpc.19770811212>; Niki et al. Chem. Phys. Lett. 1978, 59(1), 78-79, [https://doi.org/10.1016/0009-2614\(78\)85618-8](https://doi.org/10.1016/0009-2614(78)85618-8)) - a reaction that should be added to the mechanism. Note that Niki et al. report a ClONO lifetime of ~ 150 s.

Response: We thank the reviewer for pointing out the important references to improve the understanding of ClONO to ClNO_2 mechanism. We have incorporated the suggested reaction of the metastable state ClONO converting it into ClNO_2 as proposed by Janowski et al., 1977. According to their work, the conversion time between ClONO and ClNO_2 ranges from 4 to 20 hours. In our manuscript, we have adopted a conversion time of 12 hours (average of 4 and 20 hours) and consequently, the corresponding rate constant is calculated to be $2.3\text{E-}5 \text{ s}^{-1}$. This discussion is added in the manuscript citing the suggested references.

Lines 83-86 : “ ClONO is formed through reaction of Cl with NO_2 (G2), and exists as a metastable intermediate (Janowski et al., 1977, Niki et al., 1978, Golden, 2007). This intermediate subsequently transforms into ClNO_2 (G10), with an average conversion time of ≈ 12 h (ranging from 4 to 20 h), and the corresponding rate constant is $2.3 \text{ E-}5 \text{ s}^{-1}$ (Janowski et al., 1977).”

Table 1: “(G10) $\text{ClONO} \rightarrow \text{ClNO}_2$; $2.3\text{E-}5 \text{ s}^{-1}$; Janowski et al. (1977)”

Be it as it may, the reaction between Cl and NO_2 is generally thought to be negligible compared to reaction of N_2O_5 on chloride containing aerosol, except for unusual environments such as Delhi in winter. This paper thus seems to be tailored towards specific data sets, which should be mentioned in the introduction, and the relevant measurement papers (e.g., Haslett et al., Atmos. Chem. Phys. Disc., <https://egusphere.copernicus.org/preprints/2023/egusphere-2023-497/>) should be cited.

Response: Yes, generally Cl + NO₂ reaction is negligible or much smaller compared to N₂O₅ reaction on aerosols. However, inclusion of this chemistry makes the model more comprehensive and our results highlight the implications of such different reactions in two distinct urban environments (Delhi as well as Leicester). For example, gas phase reaction of Cl with NO₂ contributes significantly to the ClNO₂ formation in Delhi, while aqueous phase reaction of Cl⁻ + NO₂⁺ is dominant in Leicester. Therefore, incorporating all these reactions into the model is essential for better and more complete understanding of the Cl chemistry. As recommended by the reviewer, we have included a discussion of the relevant paper (Haslett et al., 2023) addressing the unusual chemistry observed in Delhi in the revised version of the manuscript.

Lines 177-179: “Similar unusual daytime high levels of N₂O₅ (≈21.9±29.3 pptv) during wintertime were recently measured over Delhi using a high-resolution iodide adduct chemical ionization mass spectrometer (Haslett et al., 2023)”

2. More discussion as to the applicability of this model is needed.

For example, a limitation of this study is that all species are assumed to be well-mixed. In reality, there will be vertical gradients for most species evaluated here, in particular radical reservoir species such as HONO and ClNO₂ (e.g., Young et al., Environm. Sci. Technol. 2012, 46(20), 10965-10973, <https://doi.org/10.1021/es302206a>). This limitation should be discussed.

Response: As suggested, we have added discussions in the applicability of this model including the suggested references. The discussion regarding the generic limitations of the box model (vertical gradients, transport, etc.) and recommendation for future study is mentioned in toward the end of manuscript.

Lines 361-365: “It is important to note that box models, despite their general limitation of neglecting transport phenomena and assuming species to be well mixed, do include highly detailed chemical mechanisms. Furthermore, because the model is initialized with measurements of chemical species at both locations and the modeled levels align with observed data, significant discrepancies in model estimates would be unexpected. Future studies focussing on modeling vertical gradients, in particular for radical reservoir species such as HONO, and ClNO₂ (Young et al., 2012) are recommended.”

Transport phenomena should also be acknowledged (since the model does not include them) and assumptions should be clearly stated. For example, it is well established that ClNO₂ formation occurs in the nocturnal residual layer (which contains less NO than the surface layer), and ClNO₂ then mixes downward in the morning when the convective mixed layer forms (e.g., Bannan et al., J. Geophys. Res. 2015, 120(11), 5638-5657, <https://doi.org/10.1002/2014jd022629>; Tham et al. Atmos. Chem. Phys. 2016, 16(23), 14959-14977, <https://doi.org/10.5194/acp-16-14959-2016>).

Response: We agree with the reviewer that absence of transport phenomena would cause deviations in variability of species when compared with actual observations. In the revised version of the manuscript we have acknowledged the previous studies (Bannan et al., 2015, Tham et al., 2016) showing the formation of ClNO₂ in the nocturnal residual layer, which contains lower levels of ClNO₂ and then it mixes downward during the morning when mixed

layer forms. We have also added the limitation of box model which does not include the effects of transport. The following discussion is added to the manuscript:

Lines 219-222: “Previous studies have demonstrated that the formation of ClNO₂ occurs within the nocturnal residual layer, which contains lower levels of NO compared to the surface layer. Subsequently, ClNO₂ mixes downward during the morning when the convective mixed layer develops (Bannan et al., 2015; Tham et al., 2016). However, the present study does not account the the effect of transport processes due to the limitations of the box model.”

Specific comments

1. Title - specify season of study in title of paper (winter)

Response: Although we have presented model results from a newly developed chlorine chemistry mechanism for the winter season, this mechanism also holds during other seasons, possibly improving the estimation of the oxidation capacity of the atmosphere across various photochemical states. In light of this perspective, our title, without specifying the season of the study, would effectively emphasize the wide-ranging implications of the developed chlorine chemistry module. Therefore, we wish to retain the title of the manuscript.

2. line 27 - The authors differentiate between nitryl chloride (ClNO₂) and chlorine nitrite (ClONO), citing a the MCM modeling study by Riedel et al (2014). More explanation is needed here since Riedel et al. do not mention chlorine nitrite in their paper.

Response: Thanks for pointing this out. We have added the correct reference Atkinson et al., 2007 which shows that photolysis of ClONO produce Cl radicals (Line: 28).

Chlorine nitrite may form from Cl+NO₂ (e.g., Golden, J. Phys. Chem. A 2007, 111, 29, 6772–6780, <https://doi.org/10.1021/jp069000x> and Niki et al., Chemical Physics Letters 1978, 59(1), 78-79, [https://doi.org/10.1016/0009-2614\(78\)85618-8](https://doi.org/10.1016/0009-2614(78)85618-8)); however, the reaction between Cl and NO₂ is generally thought to be negligible compared to reaction of N₂O₅ on chloride containing aerosol. It would thus be informative to add the relative contributions of ClONO and ClNO₂ to the bottom trace of Figure 2.

Response: As suggested by the reviewer, the individual concentrations of ClNO₂ and ClONO are now shown in Figs. 3b, h and 3c, i, respectively.

3. line 3. Please define the abbreviation CAABA/MECCA.

Response: It is already defined, in the first sentence in mechanism development section.

4. line 80. Please state here that the full mechanism is shown in the SI.

Response: Now we have mentioned in the revised manuscript (Lines: 77-78).

5. Page 4 - Table 1. Please state the units for the reaction rate constants.

Response: The rate constants mentioned in Table 1 are mostly in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is now mentioned in the table's caption. Unit of reaction G10 and photolysis reactions (s^{-1}) is mentioned in the table. The updated table caption:

“Gas-phase chlorine reactions and corresponding rate constants added to MECCA. The rate constants are expressed in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ unless otherwise specified. Model-simulated maximum noontime J-values for Delhi are provided.”

6. Page 4 - Table 1. For the photolysis reactions, please state the maximum (noon) j values.

Response: Model simulated maximum J-values for Delhi are now added to the Table 1, and table's caption is updated accordingly.

7. Page 6, Table 2 - reaction A13 - please subscript the 3 in CH_3COO .

Response: The typographical error is now corrected in the revised manuscript.

8. Line 100 - The Sander et al. (2014) reference is inappropriate. Cite Ghosh et al., J. Phys. Chem. A 2012, 116, 5796-5805, <https://doi.org/10.1021/jp207389y>, please.

Response: We agree that Ghosh et al. 2012 should be added as the reference for the UV/VIS absorption spectrum of nitryl chloride. The paper by Sander et al. (2014) is cited because it explains how cross sections are converted to photolysis rate constants (j-values) in the model. Now, Ghosh et al., 2012 is also cited along with Sander et al., 2014 in the revised manuscript **(Line: 104)**.

9. pg 7 - Figure 1 - The nitronium ion (NO_2^+) is a potent nitrating agent, and there are many more organic molecules in the aerosol-phase than shown here. Please discuss the limitations of the abridged mechanism.

Response: We thank referee to emphasize on this point. We agree that NO_2^+ is a potent nitrating agent which could participate in with many more aqueous phase reactions with organic molecules than shown here. However, the chemical kinetics for nitration reactions of other alcohols (e.g. catechol and polyphenols) are not available in literature, and the rate constant for nitration of methoxyphenol is ~ 10000 times smaller than nitration of phenol. Coombes et al., 1979 reports that rate constant for nitration of phenol and cresol is similar, based on which NO_2^+ reaction of cresol is also added to the model and simulations are updated accordingly. The manuscript is updated as follows:

Figure 1, Table 2 are updated and above discussion is added to the revised manuscript as:

Lines 111-112: “ cresol (A11-A16) (Staudt et al., 2019; Ryder et al., 2015; Heal et al., 2007; Iraci et al., 2007; Coombes et al., 1979).”

Lines 116-120: “The rate constant for NO_2^+ reaction with methoxyphenol is about ≈ 10000 times smaller than NO_2^+ + phenol reaction (Kroflič et al., 2015), so it is not considered in this study. In addition, nitration reactions of other alcohols (e.g. catechol and polyphenols) could be potentially important, however due to unavailability of corresponding rate constants, these reactions are not considered in this study, nonetheless future studies calculating the kinetics of these reactions are recommended.”

10. pg 10 - Figure 2: It would be informative to add the relative contributions of ClONO and ClNO_2 to the bottom trace of Figure 2.

Response: The concentrations of ClONO and ClNO_2 are now added separately to the figure 3.

pg 10 - Figure 2: The NO_3 and N_2O_5 peaks at noon local time are highly unusual. Consider adding a brief explanatory note to the caption.

Response: The diurnal pattern of NO_3 and N_2O_5 is really unusual in Delhi. The main reasons for negligible NO_3 at night is because of zero O_3 , which is due to its titration by the high NO concentrations. Although mixing ratios of NO_3 and N_2O_5 peak during daytime, their levels remain quite low. As suggested by reviewer, following brief explanatory note is added regarding the noticeable unusual levels to the figure’s caption:

“.....The unusual and negligible nighttime NO_3 in Delhi is attributed to the nearly non-existent O_3 , due to titration by higher concentrations of NO . This leads to the negligible nighttime N_2O_5 in this region. Although mixing ratios of NO_3 and N_2O_5 peak during the daytime, their levels remain quite low.....”

11. pg 10 - Figure 3. The left-hand side graphs suggest that there is no nitryl chloride formation from heterogeneous uptake of N_2O_5 in Delhi. This seems unlikely considering non-zero mixing ratios of N_2O_5 are shown in Figure 2 (see also the next comment).

Response: $\text{P}(\text{ClNO}_2)$ is small but not zero, it is not visible in the plot due to large scale of y-axis. However, the plot on log-scale depicts its production through $\text{Cl}^- + \text{NO}_2^+$ in order’s of about $10^3 \text{ molec cm}^{-3} \text{ s}^{-1}$. This point is clarified in the revised manuscript.

Lines 251-252: “In contrast, there is lesser contribution of $\text{Cl}^- + \text{NO}_2^+$ reaction (rate $\approx 1 \times 10^3 \text{ molec cm}^{-3} \text{ s}^{-1}$) in ClNO_2 production in Delhi.”

12. pg 10 line 201. Morning ClNO_2 peaks are generally due to vertical transport of ClNO_2 produced in the residual layer to the surface. Please cite relevant literature here and discuss.

Response: The relevant literature is discussed in following lines in the manuscript (similar to response of general comment 2; Lines: 219-222).