

## **Review of “Night-time NO emissions strongly suppress chlorine and nitrate radical formation during the winter in Delhi”**

### Overall comment:

This manuscript analyzes ground based CIMS field measurements in Delhi during the winter. In combination with a 0D box model, the authors assess how high NO surface concentrations at night impact the radical budget in Delhi. Insights also come from an interesting comparison of their measurements in Delhi to their measurements in Beijing, a city with lower nighttime NO surface concentrations.

The paper presents interesting conclusions about the unique chemical environment in Delhi and discusses implications for how the current chemistry should inform further emissions reductions. Overall, the content of the paper will be of interest to the atmospheric chemistry community, and I recommend publication after addressing the concerns listed below.

### General remarks:

There is a lack of clarity throughout the manuscript distinguishing the effects of boundary layer dynamics and the effects of chemistry on observed concentrations. For example, the high NO surface concentrations observed at night are largely attributed to high nocturnal NO emissions but without any quantitative justification for this attribution. Though large NO emissions at night can be a big contributor to high nighttime NO concentrations at the surface, the height of the nocturnal surface layer also exerts control on nighttime NO concentrations. This is important to address, especially when assessing the differences between Delhi and Beijing and when assessing the impacts of possible emissions controls. One could imagine a scenario in which the nocturnal boundary layer dynamics are dramatically different between the two cities, meaning that the differences in chemistry observed would be driven largely by dynamics rather than by emissions. This is an important aspect to address, at the very least through a simple comparison of NO emissions inventories between the two cities and perhaps also with an assessment of what meteorological/dynamical conditions are coincident with particularly high- and low-NO surface concentrations at night.

As the authors hint at several times, nighttime NO<sub>3</sub> chemistry is generally understood to be most important in the nocturnal residual layer, decoupled from the fresh NO emissions at the surface. The products of the chemistry in the residual layer can then impact concentrations at the surface when sunlight-driven convection begins in the morning. However, the 0D box model used in this work does not account for any residual layer chemistry. The authors attest that residual layer chemistry is likely important, concluding that differences between their model and their measurements are likely driven by mixing from the residual layer. Given the importance of the residual layer for nighttime NO<sub>3</sub> chemistry, it seems remiss to not include some sort of accounting of residual layer chemistry in the box model, especially since the box model is then used to assess overall oxidant budgets. Something as simple as a 1D 2-box model (one box for the surface layer, one box for the residual layer, with mixing between boxes) could address this. I also recommend including some discussion of the overall structure of the nocturnal boundary layer (including distinguishing the surface vs residual layer) in the introduction when introducing nocturnal chemistry.

Specific comments:

Line 48: is the 10% by mass?

Line 160: R6 and R7 are only defined in the supplement, so the reference here is confusing.

Line 162: “outlined in more detail below” should be changed to “outlined in more detail in the supplement”

Line 163: should reference Eq 1

Lines 160-165: How are you parameterizing the ClNO<sub>2</sub> yield? I could only find details about N<sub>2</sub>O<sub>5</sub> uptake, but not on the yield of ClNO<sub>2</sub> from N<sub>2</sub>O<sub>5</sub> hydrolysis.

Lines 176-177: Can you give some sort of justification for whether these select VOCs are representative of total VOC reactivity?

Lines 211-212: Boundary layer dynamics can also play a role in the high NO concentrations, in addition to the emissions and low O<sub>3</sub> concentrations mentioned here!

Line 215: Here the high OA concentrations at night are attributed to dynamics. The effect of dynamics can affect NO and O<sub>3</sub> concentrations as well!

Lines 231-232: Are NO emissions in Delhi dramatically different between day and night? Or are the NO concentration differences observed between day and night primarily a result of dynamics?

Lines 232-235: This sentence is really important in acknowledging the effects of both dynamics and emissions on observed concentrations. I recommend making sure this idea permeates throughout the manuscript.

Line 237: Is the “little daytime NO” a result of differences in emissions or differences in dynamics?

Line 235-238: Consider adding a plot in the supplement of the relative importance of different NO<sub>3</sub> loss pathways over the diel cycle.

Figure 2: I think there is a typo in the legend to the right of the top panel (“daynight” should be “nighttime”).

Lines 248-259: This acknowledgment of the importance of residual layer chemistry is really important—I think it should be included somehow in your box model, perhaps through the use of a 1D 2-box model.

Line 253: Can you include a little more description of how you quantify “atmospheric mixing,” including what time intervals it is calculated over?

Line 257: Can you use these estimates to figure out something about the mixing timescales and residual layer concentrations of  $\text{N}_2\text{O}_5$ ,  $\text{ClNO}_2$ , etc.?

Lines 267-272: I think it's important to note that CHON compounds can also be derived from  $\text{RO}_2 + \text{NO}$  reactions during OH-initiated oxidation.

Line 288: Can you provide some quantitative justification (i.e., data) for saying that the aerosol oxidation state in Delhi is "very low"?

Line 293: Can you be more quantitative here (rather than just "unusually low")?

Line 300: Can you include a few other important details about the Beijing measurement site (was it also ground-based, was it also at a background urban site)?

Line 303: I think a comparison of NO emissions inventories between Delhi and Beijing is an important part of this comparison to help distinguish whether observed differences are due more to dynamics versus due more to emissions.

Line 305: Replace "where" with "when."

Line 309: Because  $\text{N}_2\text{O}_5$  is also thermally stabilized, a comparison of temperatures between Delhi and Beijing is another important factor to consider here.

Line 325-326: I suggest adding the following italicized phrase for clarity: "*At a given pCl concentration, larger nighttime concentrations of  $\text{N}_2\text{O}_5$  result...*"

Figure 6: Why are constraints on  $\text{O}_3$  and initial  $\text{ClNO}_2$  different between scenario 1 and scenarios 2 and 3?

Line 387: Are these large concentrations of NO a result of emissions or dynamics? This has important implications for the conclusions you later draw about emissions reductions, etc.