

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2022-237

Anonymous Referee #1

Referee comment on "Chloride (HCl/Cl^-) dominates inorganic aerosol formation from ammonia in the Indo-Gangetic Plain during winter: modeling and comparison with observations" by Pooja V. Pawar et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-237-RC1>, 2022

This manuscript expands on the analysis of previously published work by using WRF-Chem to attempt to model the observations described in Acharja et al 2020 and Acharja et al 2021. The authors need to clarify that the same dataset was the topic of the previous papers that thoroughly describes the aerosol trends and chemistry. These papers are cited in a few places but adding a sentence that explicitly makes the connection needs to be included. To keep the differentiation between the current and previous papers, and to make the modelling results more impactful, the analysis needs to be more clearly framed using the model to understand the mismatch in the model and the observations of NH_3/NH_4 partitioning even though NH_x was well reproduced. The main result highlighted in the title of the manuscript is important but the modeling is not needed to determine that NH_4Cl is an important form of particulate ammonium. The manuscript would greatly benefit from a more focused and streamlined discussion.

The discussion of the data used could use some clarification. While there is in-depth discussion of how PM_{10} and $\text{PM}_{2.5}$ were separated there is no discussion of how the gases were separated and measured. This detail is important to add even if it appears in the other paper referenced describing the methods. Were both PM_{10} and $\text{PM}_{2.5}$ used in the modeling? Which size cut are you using for the comparison of the model and measurement?

On Line 123 you state that the $\text{PM}_{2.5}$ impactor was cleaned regularly – what about the PM_{10} impactor?

The discussion of detection limits (Line 132). For the ozone data, you state that data below the LOD were rejected – did you just omit them and treat as NA or replace with zero or fill with the DL? Were any of the MARGA data below the LOD, how did you treat

those data?

How was the MARGA calibrated? Were blanks taken? I didn't see this information in the other papers referenced from your group. The internal calibration standard just accounts for dilution not verification of the concentrations measured. Did you do comparisons with other sampling techniques to help validate the MARGA data?

In the WRF-Chem description section the description of the various methods/algorithms is hard to follow. I believe you are using MOSAIC with MTEM-MESA-ASTEM as described in Zaveri et al 2008. The authors need to revise the wording in Line 157 and Line 161 – ASTEM was new in 2008 and is not now (unless something else has been added). Instead of describing and naming the various components (MTEM, MESA, ASTEM) since they are in the cited paper, I suggest focusing on what MOSAIC does and doesn't do well. This information is sort of in there but gets lost. Adding more recent papers that use the same WRF-Chem setup would improve the section.

Since the focus of this manuscript are the modeling results and discrepancies between the observations and model I suggest a reorganization of the Results and Discussion section. The section should start with 3.2.1 and 3.2.2. Some description of the temporal trends can be discussed which then nicely flows to potential processes that are missing - like dew and fog (section 3.1.1) or potential issues with the current model setup (partitioning/sources/Cl chemistry, etc).

Line 216-230: The discussion of fog/dew should be shortened since you don't fully investigate this process and one of the other papers from this study looked at the role of fog. This discussion seems like a distraction from the main points of the paper – no need to describe the figures in the supplement just say you looked at this and details can be found there. I think these are more helpful to your main points as they processes that aren't included in the model. The discussion of dew as a potential nighttime source should include Wentworth et al 2016. Wentworth, G.R., Murphy, J.G., Benedict, K.B., Bangs, E.J., Jr, J.L.C., 2016. The role of dew as a night-time reservoir and morning source for atmospheric ammonia. *Atmospheric Chemistry and Physics* 16, 7435–7449. <https://doi.org/10.5194/acp-16-7435-2016>

Section 3.1.2 focuses more on understanding what the data is telling us about sources in the area, rather than how the emissions inventory might be right/wrong. Can you frame the discussion in this section differently to highlight the connection to the modeling results and getting the right NH₃/NH₄ partitioning?

Line 335: The pH dependent reaction of SO₂ oxidation by O₃ is an aqueous phase reaction. There is evidence of a heterogenous oxidation reactions on sea salt (<https://agupubs.onlinelibrary.wiley.com/doi/pdf/10.1029/2006JD008207>) but that is not what the authors are referring to from Seinfeld and Pandis. Please clarify the statement that begins on Line 335 and consider removing the rest of this paragraph and the following paragraph. It is sufficient to say that gas phase oxidation is much slower than aqueous phase oxidation and due to nearby sources much of the sulfur is present as SO₂.

Line 342: What is limiting SO₂ production to sulfate? Is it just the proximity of the source to the measurement site? This statement is confusing.

Line 388-9: The statement about HCl enhancing Cl concentrations is confusing. Perhaps restate to says HCl is available for conversion to Cl.

Section 3.4 – This discussion would be clarified with a table defining the modeling scenarios and what the change in total HCl emissions look like: No HCl (0 tons/yr), Base Case (3x Sharma; X tons/yr), 3xBase (Y tons/yr) or something similar. These names are more intuitive than Sensitivity experiment # and make the discussion easier to follow. You could easily do this as part of table 2 or 3.

Table 3: how do you end up with different amounts of NH_x across the different sensitivity experiments? Is this a function of the change in lifetime of NH₃ and NH₄? Experiment 3 with the highest HCl emissions doesn't have the lowest total NH_x so that doesn't entirely make sense to me. Line 486 – total ammonia = NH_x? The sentence this is apart of doesn't clearly explain why total ammonia would increase. Can you elaborate for the reader?

Line 417: How confident are you in the emission inventories of SO₂? Is it just a chemistry issue or are there issues with the conversion of SO₂ to SO₄? And as you mention at the end of the paragraph aqueous processing is important. This seems like it might be the more likely culprit than adding these gas phase mechanisms. Have you done sensitivity studies to see how much more SO₄ you can get from these different oxidation pathways? Do any of the observation days have similar cloud/fog as the model? Do they agree better?

Line 421: define TMI

Line 529: NH₃ is a trace gas – why separate it out?

Line 567: If NH_x generally agrees then why does the emission inventory for NH₃ need to be adjusted? Is there a reason a sensitivity test with NH₃ wasn't performed to reduce emissions? For instance, your best HCl emissions (test 3) with lower NH₃?

Figure 4: This might be more effective as a ratio plot – model/obs where 1 indicates agreement. Then you could put all 3 line together.

Figure 6: This timeline suggests there are periods when Cl and NO₃ are low. Does the model do better predicting NH₃ and NH₄ during these times? This would support your push for better HCl chemistry. The Pink and Red are too close in shade and color to clearly read the plot.

Figure 7: This figure seems unnecessary.

Figure 8: Group by component (put HNO₃ and NO₃ next to each other). I also suggest leaving a space in the HCl and Cl⁻ plots for the no HCl case to make it more obvious that there wasn't any Cl.