

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2022-237-RC2>, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2022-237

Anonymous Referee #2

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-RC2>, 2022

General Comments

The Authors present an observational dataset of water-soluble gas-particle inorganic atmospheric species to study the impacts of HCl on aerosol compositional changes in the IGP. They find that regionally high NH_3 allows local sources of atmospheric HCl to substantially partition to the condensed phase through correlational analyses and implementation of HCl emissions estimates into an atmospheric chemical model that includes an equilibrium thermodynamic model. Overall, the results are an interesting case study that builds on prior observations of the unusual and substantial presence of NH_4Cl in $\text{PM}_{2.5}$ in India. Generally, the components of this work are suitable and of interest to the readership of ACP. However, in its current state there are several substantial inaccuracies that need to be addressed in the interpretation of the model data and potential drivers for mismatches between models and observations. There is substantial excess material in the manuscript that does not directly drive the main thesis of the work around HCl/Cl⁻ importance to aerosol loadings and composition that would greatly improve this work if removed. In many cases, these additional considerations are highly speculative without the necessary supporting observations. There are many technical corrections needed to improve clarity, particularly with respect to thermodynamic partitioning of the $\text{NH}_4\text{-NO}_3\text{-SO}_4$ system, but these are rather minor. Pending these major revisions, the manuscript should be suitable for publication in ACP.

Major Revisions

- Throughout the manuscript, the authors lean on the concept that ammonium salts are formed in aerosols from their gas phase precursors. While this is possible, most

aerosols have sufficient liquid water that a solid salt is not the product, but rather that dynamic exchange between the gas and condensed phase sustains or alters the condensed phase composition. The writing of salt formation and neutralization reactions throughout the manuscript conflict with the use of an equilibrium thermodynamic model and some effort should be made throughout to accurately relate the relevant processes. There are many instances where this needs to be considered and they are presented in the detailed comments below, which may not comprehensively identify all occurrences. The Authors are encouraged to revise the manuscript thoroughly to address this.

- Given the focus of this manuscript is on an evaluation of the MARGA analyte dataset, enough information needs to be presented on its operation, calibration, and quality control to demonstrate that high quality data was obtained. Specific QA/QC for these datasets and for instrument operation are required. Details of the MARGA from other field campaigns do not lend credibility to the QA/QC obtained here. Every move and new setup of an instrument requires a revisit and verification of functionality. Lay out your figures of merit (accuracy, precision, etc) required to operate the instrument and how these are obtained. Were background corrections done? How? And so on... See more detailed comments for this section below.
- Sections 3.3 and 3.5 have numerous issues and require major revision for accuracy. See detailed comments below.
- The manuscript is long for the investigation being performed. There is substantial redundancy between some sections and in some other cases, an entire paragraph can be distilled into a single sentence. Identifying further opportunities to improve the concision of the manuscript will also improve its clarity, and raise its impact. A few places where this would be very helpful are identified, but since the role of the Reviewer is not editorial in nature, a recommendation to review the manuscript for other opportunities to reduce manuscript length is presented as a major revision. One major distraction throughout the manuscript is the speculative referencing to HONO chemistry and its role in NH₄⁺ aerosol chemistry. This should be removed entirely from the manuscript, as there is not sufficient supporting data to enable a proper set of chemical inferences on the controls and relationships between HONO and aerosol composition presented. A couple brief comments on the linkages might be important, if there is prior data for this specific region that suggests this is the case from a detailed analysis. Otherwise, keep the manuscript focused on the influence of HCl/Cl⁻.

Detailed Comments and Technical Corrections

Page 1, Lines 34-36: This summary of the model performance is unclear and confusing. Please revise this and other aspects of the abstract after addressing all comments.

Page 2, Line 51: This sentence could use some clarification. Is the intention here to identify NH₃ as a PM_{2.5} precursor gas? Instead of writing 'ammonium' three times, perhaps you can state that it is the typical counter ion for the three anions stated?

Page 2, Line 70: Remove 'etc' and use 'for example' earlier in this sentence.

Page 3, Line 111: Is this length of 1 cm correct? Seems too short to get air to an instrument to condense the aerosol inside a building. Please revise for clarity. Also, this instrument is only sampling particles? Or both gases and particles? If you have two size cuts, are these being modulated or do you have two separate channels for analysis? The sampling rate suggests that the observation intervals are 1 hr? Please clarify. This section could use a bit more organization. It is hard to tell if the measurements are close to real time or collected and analysed later?

Page 4, Line 119: 'analyzed in the analyzer box using the ion chromatography (IC)' – Confusing and unclear. Please revise with technical description on how sample analysis was performed by IC. This is too superficially presented.

Page 4, Line 122: 'absorbing solution' – What is this? For the gas collection? It's not described at all. What was used? At least some basic description is needed here.

Page 4, Line 125: While this statement to see earlier work is fine, a clear metric of what qualified as viable data by the ion-balance method and what does not still needs to be presented here.

Page 4, Line 128-131: NO_x analyzers are standard instruments. Suggest giving the manufacturer and models of the instruments instead of these descriptions, along with time resolution and performance metrics relevant to the campaign instead of their principle of operation.

Page 4, Line 133: 'lowest'? There is only one detection limit for a given instrument or method. Suggest removing this to improve clarity.

Page 4, Lines 138-139: This statement can likely be removed so long as it follows the criteria and rationale presented above. If it does, it is redundant with that material and makes it confusing why this is worth noting here? Or are these below the threshold criteria, but there is a clear local plume passing by the station? Please clarify why this is important to mention if the data do not meet the thresholding criteria.

Pages 4-5, Lines 153-166: Way too much detail on the composite modules. None of these details is used to investigate the controls on the gas-particle partitioning system. Suggest removing altogether to reduce manuscript length or moving it to a section of SI, if the Authors wish to retain it. Given the superficial inspection of the model results, the level of detail given seems like a restatement of material presented by the model developers elsewhere.

Page 5, Line 163: Sentence makes sense without 'however'. There is no contrast required here. This is simply a fact. Delete. Look for other sentences that start like this (e.g. thus, therefore, on the other hand, etc). These tend to confuse the point of sentences when used where they are not needed. If you can remove these from a sentence and not lose the purpose of your writing, the simplification should be preferred.

Page 5, Line 192: Based on other online IC measurements of atmospheric composition, this seems like too many significant digits? Please confirm by providing the figures of merit in the methods that show these values are consistent with instrument performance, or revise to provide appropriate values here.

Page 6, Lines 203-205: Can the NH₃ be coming from volatilization off of ground surfaces or from metabolism of microbes driving surface sources with a T-dependence? See more work from Murphy and Moravek on bidirectional exchange of NH₃ from surfaces as substantial sources of atmospheric NH₃.

Page 6, Line 207: There is more recent work explicitly investigating dew-NH₃ interactions since the report by Ellis et al by Wentworth and Murphy (and references therein).

Page 6, Line 225: 'indicating strong evidence' - Well no. This is evidence that fog water can act as a reservoir. What you can say is that fog water enhancing NH₃ pulses in the morning is consistent with what would also be expected from the evaporation of dew. If you didn't measure the dew water NH₄⁺ and the accumulation of dew water, then you don't have strong evidence. Also, why are these surface sources missed in the discussion of model-observation mismatches later on? It seems to have been forgotten? Or were the sections written by different contributors in the Author list?

Page 6, Line 229: Guttation presented out of context like this seems extremely speculative, given the composition of the NH₃-surface interaction literature. What about soil or stomatal interactions? The processes of guttation is not widespread amongst plant species and no literature is convincingly cited here to suggest this is necessary to point towards as a major consideration in this work. Suggest removing and perhaps visiting some more of the major contributors to NH₃ bidirectional exchange present in the literature to bolster likely processes governing the observed NH₃ and its diurnal patterns.

Page 7, Line 236: The arguments aren't very convincing about the morning pulse of NH₃. Is NH_x conserved and/or increasing in the morning when integrated throughout the boundary layer? If yes, then I would agree with the strength of these conclusions more. I suspect this isn't possible to speak directly on, so would caution the Authors to be a bit more careful in their writing here.

Page 7, Lines 247-249: This sentence is mixing a lot of things together. Why is it

important to mention the proximity to Delhi here? Revise for clarity.

Page 7, Lines 252-254: How is this relevant to dairies being a source of NH_3 ? Even the disposal in waste water is less likely to be a major source of NH_3 compared to lagoons or active application of manure to fields, followed by volatilization. Revise for accuracy and clarity.

Page 7, Lines 254-256: This argument needs to be revisited. The bivariate polar plot takes such mixing considerations into account. Revise and draw conclusions from these plots using them as they are intended to communicate information about sources.

In the final sentence, they are higher due to the lack of turbulent mixing, meaning that plumes from point sources are diluted to a lesser extent. Diffusion rates are a fundamental property of a gas molecule and these change with temperature or pressure, but not with wind speed.

Page 7, Lines 257-260: This belongs in a separate analysis. If you are driving phase partitioning of NH_4^+ from NH_3 , then it does not have sources in industry or power plants. Be careful with the phrasing!

Suggest discussion of NH_4^+ , Cl^- and NH_x to follow presentation and discussion of HCl results. OR, present the NH_4^+ and NH_x and then make a separate section about HCl/ Cl^- to communicate that this has explanatory power for interpreting the drivers of NH_4^+ formation.

Page 7, Lines 261-262: Thermodynamic partitioning of NH_3 to the condensed phase. While in PM as NH_4^+ it can be the free ion. It doesn't have to be a salt, although there does need to be a counter-ion to maintain charge balance. Revise.

Page 7, Lines 264-270: This needs work. Clarify that industrial sources seem probable, then speak directly on them as known HCl emitters. There is some inaccurate writing on the interactions of HCl and NH_3 as well. At high enough mixing ratios, these gases will homogeneously nucleate. In other cases, the excessive quantities of NH_3 may drive the partitioning of HCl to the condensed phase. Neither of these processes is technically a neutralization reaction and that word should be removed from this part of the discussion.

Page 7, Lines 270-273: I don't understand why these statements are being made? Are they potential HCl sources? Or is this general commentary on nearby industry? What do the authors mean by 'necessary' here?

Page 8, Line 286: 'Figure 3a shows that' is repetitive. Delete. Look for other instances of such repetitiveness to improve manuscript clarity and concision.

Page 8, Line 290: The writing here starts to use 'ammonia' instead of the chemical formula used up to this point. Is this writing from another Author that has not been revised for consistency? This seems to be the case, as evidenced by the use of 'vis-à-vis' which shows up in this same section (Page 9, Line 310). Please edit the manuscript for consistency in writing throughout.

Page 9, Line 317: 'in low NH₃ environments' can be removed

Page 9, Line 319: 'in the gas-to-particle partitioning process to produce ammonium salts...'
- I agree that the NH₃ and acids are transferred to the condensed phase, but a lot of recent work on particle acidity clearly demonstrates that aerosols rarely have even metastable salts present in them, so this is probably better presented as the neutralization reaction from above, in the presence of water, where a pair of non-volatile NH₄⁺ and acid anions are formed. What is depicted in these reactions is homogeneous nucleation of salts from the gas phase collision of NH₃ and the acids, which isn't the primary driver of aerosol mass composition and growth.

Page 9, Lines 327-328: This is not true according to thermodynamic equilibrium theory. All SO₂ in the condensed phase will be fully neutralized before any HNO₃ or HCl can partition. Please revise for accurate representation of the state of knowledge. All this observation communicates is that the concentrations of both gas phase precursors are substantially high enough to drive phase partitioning in this very local context. Also, the quantity of SO₂ is not a measure of H₂SO₄, so the comparison being made here is misleading and the logic of this argument needs revision.

Page 9, Lines 331-333: The presented data does not demonstrate anything about rate. Revise. All that can be said is that there is a lot of SO₂ that has not yet been converted to sulfate.

Page 9, Lines 335-341: I don't understand the logic of all this text? I'm not sure it is relevant given the limited nature of this dataset and drawing from studies in other locations? Suggest removing to reduce the length of this manuscript, since the focus is on HCl impacts on PM. These alternative mechanisms driving sulfate formation are quite speculative and not very well justified, so a major simplification should be made at the very least. It is also concerning that such speculation is allowed to occupy so much of the writing about sources of sulfate, but the contributions of the known chemistry are not visited except in passing. Suggest reversing these priorities. What can current chemistry explain? Then clearly state the link between these other studies that may make them relevant to filling in the remainder of the observations to motivate future campaigns.

Page 9, Line 344: 'also low daytime' – Should this be 'lower during the daytime'?

Page 9, Lines 345-346: Only in the local observations, it will be oxidized downwind.
Rephrase.

Page 10, Lines 352-353: This is only true if the accuracy of the measurements is very good. Please propagate the error of the measurements and put error bars on this trace. Typically, the resulting error from IC measurements applied to ANR results in a cumulative error near 50 %, given the challenges in quantifying NH_4^+ by IC.

Page 10, Line 353: 'utterly' - remove. The timeseries shows that this is not a universal truth. Figure 5 demonstrates that, on average, this was the case, so suggest redirecting this commentary towards that figure. The ANR actually demonstrates substantial variability, which appears to be muted here due to the very large number of datapoints put into the statistical evaluation. It would be worthwhile to comment on the range observed as well. There also seem to be synoptic scale events where all of the nitrate and chloride are evaporated from the condensed phase? Seems to be a missed opportunity in the case studies that followed to learn something insightful about drivers of their partitioning.

Page 10, Line 357: 'conversion rate' - This is not a rate. It is a ratio. This simply evaluates the equilibrium distribution of the NH_x pool between the two phases. The model assumes equilibrium, where the rate of formation is equal to the rate of loss in a dynamic system.

Page 10, Line 358: 'Previous studies have reported...' - Reported is not sufficient here. State exactly what the intention you have in using this ratio here is. You are evaluating the model against the observations, but it isn't clearly stated why the way you are doing it is the right way to go about things. What is the point of doing this for sulfate in the model, but chloride in the measurements? I cannot follow the logic.

Probably this whole sentence can be deleted and the references can be moved to the end of the prior sentence. Stating what previous studies have reported, when that is already a term in the prior sentence, doesn't really add value here, but it does add confusion when trying to follow this section.

Page 10, Line 367: Again. This is not a rate, which evaluates a change in concentration over time due to a given chemical process. Here you are observing the change in the particle fraction. That's it. I agree the HCl is promoting this increase in the particle fraction of NH_4^+ . Please clarify.

Page 10, Line 370: 'the reactions of ammonia with HCl' - Maybe, but I don't see any evaluation of the gas product (K_p) of NH_3 and HCl being performed here to suggest these are undergoing homogeneous condensation as NH_4Cl to the $\text{PM}_{2.5}$. Isn't it more likely that the HCl is partitioning into the aerosol, deprotonating in the aerosol water, followed by the ammonia partitioning and being protonated by the ionisation of the strong electrolyte HCl? This is the largely agreed upon process for aerosol growth and partitioning that has been communicated in the aerosol pH community over the past 10 years.

Page 10, Line 372-374: That is not what the anticorrelation between NH_4^+ and HONO means. It's could be generating nitrite in the aerosol due to the excess NH_3 available. The correlation here is also very poor, so this statement is highly speculative and should be removed, along with the references. A general comment on the inverse relationship, a clear statement of any speculation, then the need for further study is the most that seems appropriate here, given the limited nature of the dataset. The recommendation of the Reviewer is to remove all of this discussion as it is not relevant to the manuscript and there is not enough supporting measurements to really justify further comment.

Page 10, Line 381: The plots of NH_4 versus NH_4/NH_x in both the measurements and model does not make sense to present. This relationship has to be the case, since the terms are internally dependent, and the statements in the manuscript, plus entries in the table communicate everything shown in these figure panels anyways. This is an opportunity to streamline the manuscript. Suggest removing a) and C) from Figure 7 unless substantive discussion is added to explain the value that is not already clear from the existing statements.

Page 10, Line 385: It doesn't react. It's an aqueous solution that obtains charge neutralization through mole balance of NH_3 uptake before HNO_3 can partition. Revise all of this for equilibrium thermodynamic partitioning accuracy.

Page 11, Line 393: Section 3.4 is way too long and needs to be substantially condensed and simplified. Suggestions follow on some ways to do this, but likely that further gains can be made.

Page 11, Line 400: '7th to 16th' does not follow journal guidelines for presentation of dates.

Page 11, Lines 402-404: Why state the revised work twice? Instead, state who did the revision and why that is important to build upon in your work. Perhaps try to simplify the statements here and combine this sentence with the one that follows.

Page 11, Line 406: Is the base case 'experiment-2'? The organization of the model runs here is getting confusing and could use some work to improve clarity. Rename these or something.

Page 11, Lines 409-416: Example of simplification, where this can be a single sentence:

'Increasing the emissions of HCl in the model partition more NH₃ to the condensed phase, due to its high concentrations, reaching mass loadings of NH₄⁺ and Cl⁻ of 70 and 110 ug/m³, respectively'

Page 11, Lines 419-425: This is pure speculation. Remove. State instead that missing chemistry may underly the mismatch and move on. These findings from these studies may not be relevant to the Delhi observation site.

Page 12, Lines 426-432: Why all this speculation? The drivers of typical sulfate production are likely wrong in the model with so much pollution, meaning that OH or aqueous H₂O₂ is not being simulated correctly either. If the fundamentals can't be verified, there doesn't seem to be much justification for exploring or commenting on these other mechanisms. At a minimum, remove the comment about nucleation, as this is a very minor contributor to sulfate mass loading increases.

Page 12, Lines 435-436: Given the focus of this manuscript on HCl partitioning, suggest removing all discussion of HONO. No model can get this right in such polluted regimes and it is not diagnostic in an investigation of HCl partitioning unless you are drilling down into the thermodynamics.

Page 12, Lines 438-439: Not true. The effective aerosol pH will determine the gas fraction of HNO₃ observed. You also have not evaluated the total of the two species and compared them to the model, as you do for NH_x. It could mismatch simply because the HCl/Cl⁻ system is important and not included.

The following sentence on over-representation of NH₃ is more explanatory. More NO_x in the model should generate more HNO₃, so one would expect the total of HNO₃+nitrate in the model to exceed the observed sum.

Page 12, Lines 444-445: The extent of the partitioning and accumulation of NH₄NO₃ depends on T, aerosol water and pH, as well as other constituents. If the HCl/Cl⁻ system is a major contributor, its missing will lead to mismatches.

Page 12, Line 446: HONO rarely can partition to PM_{2.5} aerosol that is dominated by traditional inorganics (the pH is far too low). Remove from the manuscript.

Page 12, Lines 458-459: This is already stated in the methods. No need to repeat here.

Page 13, Line 466: Why not call these:

No HCl (experiment-1)

HCl base case (experiment-2)

3xHCl (experiment3)?

Would be much easier to follow.

And why wasn't a simulation with reduced NH₃ and 3xHCl in the model performed? The NH_x simulation in this run is substantially higher and the reason for that is not really clear? Shouldn't this be conserved across all three model runs?

Page 13, Lines 473-475: This should have been used diagnostically to conclude that there is something wrong with these simulations, or that the model includes some additional source of NH_x into the modeled system that may be important. The sum of NH₃+NH₄⁺ should be conserved across all three model runs if the emissions are the same in each run. Does this chemistry scheme include bidirectional exchange of NH₃ from surfaces? Such processes (e.g. dew and fog) are discussed earlier on. Some substantial work needs to be done to understand the driver of this issue, as it undermines the reliability of the comparisons being made, if the assumption is that NH_x should be conserved across all three sensitivity tests.

Page 13, Lines 482-487: Why use percentages here? The relative difference between the various cases isn't very useful as a metric. Why not use the absolute change in mixing ratio or mass concentration? On Line 483 should 'improves' be 'increases'? And for Lines 486-487: This doesn't make sense. See prior comments. This should be conserved, based on how these tests have been described. This is also 'total reduced nitrogen', not 'total ammonia' as ammonia is only NH₃.

Page 13, Line 488: Correlational analyses are weak tools for inferring chemical drivers. The model-measurement comparisons are much stronger in reaching robust conclusions. Suggest substantially reducing the content here that revisits the MARGA measurements and trends. This section is titled as though its purpose is to be comparing measurements to the model results? There are a lot of repetitive statements about the observations being

made here that were already presented in other sections that can be removed.

Page 13, Line 497: All the correlations are done under what conditions? Isolated from 19:00 to 9:00? For the Cl⁻ and NH₄⁺, is this correlation performed after accounting for the NH₄⁺ associated with sulfate and nitrate?

Page 13, Lines 500-501: This does not add value to the analysis. HONO is well known to form at night from hydrolysis of NO₂, but that isn't the focus of this work. Suggest removing this analysis from this section as well. There are not enough observational constraints on the HONO chemistry to justify all this speculation.

Page 14, Lines 509-510: Repeated information. Get rid of correlation coefficients. Focus on HCl/Cl⁻ system interactions with NH_x. Get rid of the rest.

Page 14, Lines 513-515: Remove.

Page 14, Line 517: Repeating chemical formulas. Delete.

Page 14, Line 520: Partitioning and chemical transformations are two different things. This needs to be described better throughout the manuscript.

Page 14, Lines 522-525: The case for why this is relevant to this study is not clear and seems irrelevant. It seems highly speculative, at best, based on the current framing of the discussion and operation of the model.

Page 14, Conclusions: Rewrite to reflect on revised contents of manuscript after major revisions.

Page 25, Figure 2 caption: Do not capitalize ammonium and chloride here.

Page 25, Figure 5 caption: Was SO₂ treated as a divalent molecule in this analysis? That does not seem appropriate. It is not H₂SO₄.

Page 25, Figure 7 caption: Panel b does not look like a linear fit? Regression equations and

values should be presented on the plots and the details of the regression (least square, linear, error-weighted, etc.) given in the caption here. This is insufficient in its current state.

Page 26, Table 1: Are correlations for HCl here actually meaningful? It's obvious that HCl is being partitioned into the aerosol, why look at the HCl using this approach? In a fresh plume that mixes at the observation site, I would expect a strong negative correlation between HCl and NH₄/NH_x. This campaign wide statistical analysis for looking at local point source chemistry is confusing and, while this may have been informative for the authors to go through all these comparisons, they are not really well justified. To the Reviewer, the thing to take away here is that the chloride is completely missing in the model, but explains a lot of the variability of NH₄/NH_x in the observations. Suggest revising this section of the analysis to simply focus on that point and remove some of this more distracting analyses.

I don't understand why the poor correlation observation between sulfate and NH₄/NH_x is not being commented on? Is it because sulfate is so small that the NH₄/NH_x ratio doesn't change appreciably when sulfate is neutralized?

Page 28, Figure 1: The symbol for Celsius appears to be lower case? The left panel y-axis should be 'Mass concentration'. Why are time stamps displayed with minutes and seconds? Makes the figure very busy and these meaningless quantities distracting. X-axis label should be 'Time of Day' instead of 'Time' in a diurnal plot.

Page 28, Figure 2: Panel letters need to be moved. Why not state the ratio actually being calculated for the gas-particle conversion ratios instead of these words? For the frequency % in panel a, can this information be moved to the figure caption?

Page 29, Figure 3: Same issue with time notation, axis labels, and temperature unit notation as Fig 1.

Page 29, Figure 4: Can the dates be presented in equal intervals and only the first dates for a given year listing that value? This information is not particularly important to the figure interpretation, so can be substantially simplified. The '-3' superscript also seems to be quite large?

Page 30, Figure 6: Same issue with dates on the x-axis here. Try to simplify.

Page 32, Figure 8: Label each plot with the species name instead of on the y-axis. Put one label for all the concentration plots on the left, after removing the HONO panel, then keep

the y-axis labels for T and RH (although these can likely also be removed since this data is shown convincingly in other figures). The HONO simulations returning what appears to be zero values, suggests further that this analysis does not belong in this work. Simplify and remove. In panel (j) shouldn't a green line at zero be plotted for Experiment-1 results to keep all the panels consistent?

Page 34, Figure 9: Remove HONO traces and axis.