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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Assessing the ammonium nitrate formation regime in the Paris megacity and its representation in the CHIMERE model" *by* H. Petetin et al.

Anonymous Referee #2

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This study investigates the sources of NH3 and HNO3 and their contribution to aerosol nitrate formation in the Paris megacity, through analysis of observational data and model predictions from the CHIMERE model. Through comparison of model predictions with observations of inorganic gas and aerosol species the authors also examine the suitability of the CHIMERE model in predicting ammonium nitrate levels in the city. The results are potentially useful to the broader community. However, in my assessment the manuscript would benefit from some additional work: (1) there are aspects of the study (model and observational analysis) design that need further elaboration so that the results presented can be viewed in the right context; and (2) the manuscript

would benefit from a tighter editorial review by the authors to help remove awkward sentences and phrasing in many parts of the discussion. These are further elaborated below:

1) The authors use the terminology "urban background" throughout the manuscript. It is suggested that the observational information (Section 2) analyzed is representative of this urban background. Yet the data is from locations within the city center or urban core ("heart of Paris") – how is this site then representative of the urban background? The use of the terminology is somewhat nebulous – the authors should clearly state what they imply by urban background and how a location in the center of the city is representative of this.

2) Section 2 describes the measurement data analyzed in this study. If I understand this discussion correctly, the locations where the aerosol composition, the gas-phase concentrations, and the meteorological data are collected are not exactly co-located – in fact it appears that they are separated by a few kilometers. Information on the characteristics of these locations should be included. It is not apparent what the local influences are at these locations, how similar or different these influences may be and how they impact the variability in the data collected at these locations. The authors assume that the atmosphere across these locations is relatively homogeneous so that gas-phase measurements at one location can be combined with aerosol composition measurements at another location for prevalent meteorological conditions from a third location to examine gas-particle partitioning of airborne nitrogen compounds – how does one ascertain if this assumption holds? What is the spatial representativeness of each of these locations? Could one site be influenced by local conditions (emission sources, urban morphology) more than the other? It may be reasonable to combine these data from different locations, but this needs to be more clearly justified.

3) The description of the measurement locations and its spatial and temporal representativeness is also important for better understanding the discrepancies between the measurements and model predictions. For instance in section 2 it is mentioned

that six sampling sites were implemented – were model predictions also compared at these locations? Were the error/bias characteristics similar to the city center site? Based on measurements alone at a city center site it is not readily apparent how one could apportion the role of local versus "imported" pollution to the city. In principle, a model such as CHIMERE could help with such interpretations, but the bias characteristics of the model for reduced and oxidized nitrogen are so large that such inferences are not apparent. This aspect of the discussion needs to be explained more clearly. If the variability in the measurements is indeed influenced by local sources (e.g., Figure 7 shows strong correlation between peak NH3 and BC, suggestive of influence of local emissions at least on several days), how does one discern this from the import?

4) The sensitivity analysis presented in section 4.4.3 is interesting and can potentially be insightful. However, in its current form the discussion is a bit confusing - it was difficult for me to understand how the sensitivities were estimated for the model and the observations. I would think that the ISORROPIA estimated change in NO3 (ΔNO3) to a perturbation in a parameter (Δx) would be the same irrespective of the model or measurements. Instead the differences in ratio x/ NO3 between the model and the measurements drive the differences in Sx. The differences in x as discussed in the manuscript however could arise from several factors other than the representation of the thermodynamic partitioning and influence the resultant inferred NO3 response. How does one infer if the lack of responsiveness in the model is due to uncertainties in the process representation (e.g. gas-particle partitioning) or input data (e.g., emission inventory) or other reasons?

5) At several places in the manuscript the authors discuss the NH3 rich conditions in Paris, in spite of NOx emissions, and attribute this to low HNO3. Again, this characteristic could simply be due to the location of the monitoring site. One would expect relatively lower amounts of NOx oxidation products (like HNO3) in urban cores and the reverse downwind. Thus a better description of the site characteristics is needed to put the results in context.

6) Pg 23734, line 10: the sentence is awkward – increasing ammonium nitrate should result in increasing PM, not the reverse as implied – the sentence should be reworded.

7) Pg 23744, line 10: it would be useful to state emissions of which species were impacted the most when anthropogenic emissions were shut-off. For instance it is not clear what the magnitude of NH3 emissions were in the base case, how these may have got perturbed in the sensitivity, and what their impact was?

8) Pg 23746, line 15-20: defining the S ratio based on molar concentration will be more meaningful for inferring rate of conversion of S(IV) to S(VI).

9) Fig 3 and associated discussion: It would be useful to also show total S for the two simulations. The results conveyed in Figure 3 are not adequately discussed.

10) Pg 23746, line 13: "enrichment in NH3 of air masses" should perhaps read "enrichment of NH3 in air masses".

11) What do "daily concentrations" in the left panel of Figure 2 represent – daily averages?

12) Pg 23748: it is suggested here that NH3 in Paris is associated with transport events and not to a specific source region – what does this mean? Is there not a dominant flow pattern associated with the anti-cyclonic regime? If so, is there a predominant source upwind of Paris along this flow? Is the suggestion that there are no local sources of NH3 in Paris (though Figure 7 does not necessarily suggest that)? How are the model sensitivity results used here? This discussion on this page needs to be clarified.

13) Pg 23749, line 14: should dry deposition not remove NH3 in the stable layer where emissions are also injected? Or are the authors suggesting that there are no nocturnal NH3 emissions?

14) Pg 23748, line 22: the increasing background line in Figure 7 is not apparent.

15) Pg 23749, line 15: "out" should be "our"

16) Pg 23750, line 25: While the model sensitivity runs do indeed indicate that most of the NH3 originates from outside, there is also a systematic low bias. How does one then rule out missing local emissions? Is the lack of diurnal variation in both the base and the noIDF runs and their dissimilarity with the observed diurnal variation indicative of a possible local source?

17) Pg 23753, line 10-20: there appears to be a sizeable impact of dry deposition even during the day and not just at night as suggested. Also, it would be useful to get a sense of magnitude of the modeled NH3 deposition velocities.

18) Pg 23754, line 20-25: what is the connection between black carbon episodes and HNO3 peaks? Please clarify.

19) Pg 23755, line 1: “are sufficient the 4 and 5 June” is awkward.

20) Pg 23755, line 5-10: this sentence is too long and awkwardly worded.

21) Pg 23756, line 1-5: Given that HNO3 is efficiently removed from the atmosphere via dry deposition, can import of HNO3 be a dominant source for the Paris metro area?

22) Pg 23757, line 1-5: Is N2O5 hydrolysis as a source of HNO3 represented in CHIMERE?

23) Pg 23757, line 10: it is suggested that dry deposition rate of HNO3 may be too low in CHIMERE. What are typical deposition velocities for HNO3 in CHIMERE? How do they compare with those reported in literature?

24) Pg 23757, line 15-20: what is a quadratic error?

25) Pg 23758, line 5-10: “poor contribution” should perhaps be “low contribution”

26) Pg 23759, line 10: “uncertainties on daytime” should perhaps be “uncertainties in daytime”.

27) Pg 23760, line 1-5: Uncertainties in predicted OH are speculated to contribute to

errors in modeled HNO3. If the OH concentrations are significantly off, it should also be reflected in other secondary species – did the authors see similar discrepancies in other secondary species. Biases in dry deposition of HNO3 could likely drive the model biases and it seems some more quantitative analysis of the modeled dry deposition rates vs chemical production rates will be useful.

28) Pg 23760, line 20-25: why would flat terrain result in more dispersive conditions?

29) Pg 23762, line 5-10: Given that the model has a high HNO3 bias and a low NH3 bias may be the reason it produces reasonable aerosol NO3 – is that plausible?

30) Pg 23767, line 5-10: How do the wind regimes dictate local HNO3 formation? This needs to be more clearly explained.

31) Pg 23767, line 10-15: the conclusions should state more specifically what new light this study has shed on debate on contributions of agricultural emissions.

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