

Geosci. Model Dev. Discuss., referee comment RC2
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Comment on gmd-2022-62

Anonymous Referee #2

Referee comment on "Simulations of aerosol pH in China using WRF-Chem (v4.0): sensitivities of aerosol pH and its temporal variations during haze episodes" by Xueyin Ruan et al., Geosci. Model Dev. Discuss., <https://doi.org/10.5194/gmd-2022-62-RC2>, 2022

Summary

This paper discusses aerosol pH in China, examining the sensitivity of aerosol pH to non-volatile cations, ammonia (NH₃) emissions, chloride (Cl⁻) emissions, aerosol aqueous phase chemistry, and assumed properties of the aerosol. Quantifying aerosol pH from observations and diagnosing its value in chemical transport models are needed to better understand impacts of aerosol pH on biogeochemical nutrient cycles and generation of reactive oxygen species that can cause aerosol toxicity and adverse health effects. Thus, the paper is an appropriate topic for GMD to publish.

This is a very good paper and should make a substantial impact on understanding processes affecting aerosol pH. The paper is fairly well written, although several spots need to be clarified. My suggestions of needed clarifications are given below.

Major Comments

- The authors conclude that non-volatile cations (NVC), ammonia (NH₃) emissions, and chloride (Cl⁻) emissions influence the aerosol pH over different areas of China. However, there is no presentation of the spatial distribution of NVCs, NH₃ emissions, or Cl⁻ emissions. It would be useful to see the overlap regions of NVCs and NH₃ emissions as well as the main locations for Cl⁻ emissions and SO₂ emissions. Please add these maps.
- Section 4 tends to repeat what was said in Section 3. Please review Section 4. I suggest writing it in a manner where the reader is reminded of the Section 3 result but spends more text focused on new information and discussion.
- Do the authors think the aerosol pH results would differ much with finer horizontal

resolution? I could imagine that the grid size of emissions and mesoscale flow patterns influences the range of aerosol pH. One of my comments below brings up this question again in terms of thinking of the average aerosol pH versus the range of aerosol pH during haze events and whether that range would change if the grid spacing were smaller.

Specific Comments

- I highly recommend using present tense instead of past tense.
- Line 15, in abstract: Why is it critical to estimate aerosol pH accurately in chemical transport models as well as policy development? Please add a phrase.
- Section 2.1.1. Does the WRF-Chem simulation include observational nudging so that the meteorology is represented well?
- Section 2.1.2. It would be good to add more information on how dust is treated in the model especially in relation to the ions associated with dust? Do iron, magnesium, and/or manganese affect the aerosol pH?
- Line 189. I am a little confused between dust and OIN in MOSAIC. I thought in WRF-Chem MOSAIC that dust is part of OIN (other inorganics). Therefore, it is not clear how the speciation profile is implemented when calcium, magnesium, sodium, and potassium are changed. It would also be good to know the speciation profile for the default simulation – please add a sentence in the second paragraph of Section 2.3. Please add a map to show where NVCs are high in concentration over China.
- Lines 192-198, please add maps of NH₃ and Cl⁻ emissions. It would be informative to explain the emissions sources of ammonia and chloride. How much did Cl⁻ emissions increase?
- Section 2.4, It is my understanding to calculate aerosol pH with ISORROPIA constrained by observations that gas-phase NH₃ and HNO₃ must be known. Could the authors please describe the measurements of NH₃ and HNO₃, or what values are used for these semi-volatile gases?
- Lines 243 and throughout the manuscript. It seems that the number of significant digits is too high for reporting aerosol pH, especially considering the standard deviations that are 20-50% of the actual value. Thus, for Line 243, I suggest reporting 4.2 +/- 2.2 and 5.7 +/- 1.4 for aerosol pH over the Gobi and Taklimakan Deserts, respectively. No need to use “~”.
- Lines 265-268, please explain why the doubling of NH₃ emissions caused large or small changes in aerosol pH for different regions of China. This explanation would be aided by the maps of NVCs and NH₃ emissions.
- Line 273, please include a figure showing that Cl⁻ concentration is underestimated compared to observations.
- Lines 273-275, deserves more description or explanation since the authors are advocating for future research on chloride emissions.
- Line 289. Is the analysis over Beijing averaged over several grid points or is it for a single location?
- Section 3.2, For the diurnal variation analysis, how did temperature and relative humidity vary? Is there a correlation between these state variables and aerosol pH? I would imagine that lower T, higher RH, which occur in the early morning, would have more aerosol water, diluting the hydrogen ion concentration.

- Line 315, Since there were not NH₃ observations made, what is the uncertainty in aerosol pH from ISORROPIA when using the empirical equation? This could be quantified by running ISORROPIA with +/-10% changes in NH₃ concentration.
- Lines 323-333. This paragraph reports results from Figure 4 but it does not provide any insight. Instead of giving details, I suggest discussing the meaning (or the point) of the results. For example, comparing CTL1 simulation to the default simulation could be written as, "When NVCs are increased, the aerosol pH increases by 0.9 on average with the largest increase occurring during clean periods because In contrast, when NH₃ emissions are doubled, the aerosol pH increase was smaller (0.4 pH units) compared to CTL1 simulation because With higher NH₃ emissions, the pH increased more in the more polluted regions because" . Please give explanations for each of the sensitivity cases.
- Lines 337-340. Why is aerosol pH sensitive to sulfate production in NCP? Why is the phase state assumption important to TD and GD regions? What are the "influencing factors" to the evolution of aerosol pH in a haze development cycle?
- Line 345, please explain more how NVCs (or aerosol composition in general) affect aerosol water amount?
- Sections 4.1.1 and 4.1.2 would both benefit from showing maps of the NVCs and NH₃ emissions. It would be interesting to see the juxtaposition of these cations.
- Line 388, I like Figure 5. Panel a) clearly shows non-linearity within each region. However, is Figure 5b truly non-linear? Eyeballing each region seems to show a linear response but with different slopes between regions. Perhaps a fitting line(s) could be added to the figure.
- Lines 405-411, I suggest moving Figures S4 and S5 to the main text since they are discussed at length and provide important support to the conclusion that models need to represent both stable and metastable aerosols.
- Sections 4.1.3 and 4.1.4, It seems that producing Figure 5 plots for aerosol phase state and for sulfate production would be interesting. Could panels be added to Figure 5 for these additional simulations?
- Line 443, could the authors explain the interfacial chemistry a little bit more? What is it?
- Lines 460-465, I think it is important to emphasize that aerosol pH during heavy pollution events remains < 5.0 noting that there is never a time when S(IV) + NO₂ formation of S(VI) contributes significantly. Please add! Of course, this is for Beijing region and at dx=36km, which may average out some extreme situations where pH could go higher. When examining individual grid point temporal variations, are there times when pH > 5.0? What might happen if dx=12km (i.e. what might be the impact of the grid spacing on the results here)?
- Lines 470-480 or so. The discussion of Figure S8 is very useful. I suggest moving the figure into the main manuscript.
- Lines 489-495, it may be beneficial to add a schematic describing what is said in the text here.
- Line 499, why does the acid effect prevail over the dilution effect?
- Section 4.3 provides useful information, but Pye et al. (2020) already presented these results. This section could be omitted or moved to the supplement.
- Section 5. The Conclusions fall short in bringing the results to the greater context (or implications elsewhere). For example, instead of repeating "A priori assumption that aerosols are stable or metastable...", it could say that across China both stable and metastable state of aerosols exist, thus both states should be represented in regional and global models.
- Section 5. The Conclusions did not say anything about the S(IV) + NO₂ contribution to S(VI) yet this is part of the Abstract.
- Section 5. The Conclusions should also have more text about future needs. Why do we need more high-resolution observations? What is meant by "high resolution"? Do we need higher temporal resolution, or higher spatial resolution, or both? Would it be useful to have measurements throughout the boundary layer? What is the influence of

boundary layer mixing on what is being measured? It seems that there is still a lot to be learned about winter-time haze and aerosol pH, and the authors have an opportunity to give their expert opinions on what should be prioritized.

Technical Comments

- Line 16, change "reported" to "report"
- Line 18, add comma to read as "state assumption, and heterogeneous production"
- Line 47, remove "for nowadays"
- Lines 99-106, Lines 110-119, use present tense
- Line 110, cite Grell et al., 2005 and Fast et al., 2006 when introducing WRF-Chem model
- Section 2.3, please use present tense
- Line 187, just cite Fig. S3. No need to specify each of the panels.
- Line 206, remove "The last" and change "production as which" to "production for which"
- Line 268, cite Figure S2.
- In the paper, Figure S3 is cited before Figure S2. Please review the text and order of figures.
- Line 278, "In particular, PM_{2.5} pH decreased by 1.9 for TD and 1.1 for GD, reducing aerosol pH values to 4.8 and 4.0, respectively, whereas the metastable state assumption had little impact"
- Line 293, use present tense ("were" to "are")
- Line 303, remove "On the other hand". I'm not sure what is being contrasted.
- Line 315, remove "so"
- Line 315, This sentence about NH₃ observations should be in section 2.4. Please add the empirical equation to the supplemental text (or in the main text).
- Section 3.2, Figure 4b is not discussed.
- Lines 337, reword the sentence removing "In addition". Maybe "For NCP where severe and frequent haze events occur, PM_{2.5} pH is very sensitive to the magnitude"
- Lines 347-354 are stated in the Results section and do not need to be repeated here.
- Line 362, change "minimum" to "minimal"
- Line 364, change "may" to "can". We know aerosol thermodynamics makes this sentence true. Same thing with Line 366 ("may" to "can"). You could also support these statements with supplement information using ISORROPIA calculations.
- Line 376, no need for both "In addition" and "also" in the same sentence. This occurs many times in the paper. Please proofread and try avoid using "in addition" and "also".
- Line 378, change "But" to "However,"
- Line 416, change to "all size bins"
- Line 421, change "might be" to "is" as you just spent two paragraphs showing the consequence of this assumption.
- Line 431, could you be more explicit about "differ by regions"? Where would the sulfate production be buffered?
- Line 438, the authors may want to note that H₂O₂ oxidation may be small because of low OH during the time of year investigated for the study.
- Line 450, please state why CTL3meta was chosen for further analysis instead of any of the other simulations.
- Line 460, change to "under heavy pollution events was 3.6 +/- 0.5".

- Line 485, delete "also"
- Line 486, change to "high on more polluted"
- Line 512, change to "both models using the same"
- Table 1, add vertical domain and grid (i.e., number of vertical levels, how many levels in the boundary layer). Also add information about observational nudging of the meteorology.
- Figure 1a. The six sub-regions are hard to read. Try using gray for the geography and a darker color for the acronyms.
- Figure 2, change CLT to CTL (check all figures for this misspelling)
- Figure 3 panels are in a different order than Figure 2
- Figure 4b, could WRF RH line be black (to be consistent with observations) and maybe dashed.
- Figure 7, are these results for all the simulated days or for just the polluted days?
- Table S2, change to "ranges and mean" because of the order of the columns.
- Table S3, where are the "decreasing regions"? Be more descriptive. Also add the time period averaged over for these results.
- Figure S3a. Should the observations be plotted as markers for when the measurements are taken (like in S3b)? A line for the observations could be misleading.
- Figure S3. The last two sentences are not clear. Why are they included in the figure caption?
- Figure S4. Is it surface relative humidity or RH at 2m?