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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding nitrate formation in a world with less sulfate" *by* Petros Vasilakos et al.

Anonymous Referee #1

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This paper adds to an ongoing discussion of the importance of aerosol acidity on gas-particle partitioning, and how errors in modeled aerosol pH adversely affect model predictions. The subject is certainly of interest to readers of ACP.

However, the authors' arguments are not always stated clearly, particularly in the introduction. There are so many citations to prior literature throughout the paper that it is often unclear as to which aspects are new in the present manuscript. In some cases, studies are cited in support of a point that was not the conclusion (or even the subject) of the paper. The authors need to do a better job placing this work in the context of prior literature. In particular, one of the principal conclusions echoes the title of another paper currently under review for ACP by the same research group: Guo et al. (2017), The underappreciated role of non-volatile cations on aerosol ammonium-sulfate molar

ratios.

Specific Comments by line number

8 Suggest deleting "exacerbated by reductions in SO2 emissions." These reductions do not exacerbate the bias. The bias in pH leads to a bias in predicted response to SO2 emissions reductions.

10-11 This is the first of many sentences in this paper that overuse semicolons. More importantly, the authors do not have available direct observations of PM2.5 pH for either 2001 or 2011 and should not imply they do. Instead I recommend something like "modeled PM2.5 pH using 2001 emissions compare favorably with pH inferred from observed species concentrations. Using 2011 emissions, however, leads to simulated pH increases of one unit, which is inconsistent with observations from that year."

12-13 Instead of saying NVC are responsible for the (nonexistent) trend, clarify that overestimated NVC lead to this erroneous predicted increase in pH.

13-15 This sentence is unclear. Please rephrase or delete.

20-26 Consider breaking this sentence up. Also, it should not be necessary to cite two papers twice in the same sentence.

30 It is inappropriate to cite West et al. (1999) in support of an observed negative trend over 2001-2011 and beyond.

32 "ammonia ... is either constant or increasing." It is now mid-2018. Does this statement still hold, as implied by the use of present tense? Then please provide a more recent reference. Alternatively, if the authors intend to limit their statement to the 2001-2011 period, then use an appropriate tense to convey that meaning.

35 "will become increasingly neutralized." I believe one of the points the authors are making is that the conceptual model of "neutral" aerosol is inapt. If so, I suggest deleting this unhelpful phrase, so that the sentence reads "have created the expectation that

ammonium sulfate will be replaced, at least in part, by ammonium nitrate." Alternatively, please explain further what "neutralization" means in this context.

38-48 I realize that the authors are criticizing the adequacy of the conceptual model regarding molar ratios, but even so the arguments should be stated clearly. If, in this conceptual model, the molar ratio of ammonium to sulfate is what is salient, then how are NVCs at all relevant? In stating that modeling studies have corroborated this (mistaken) view, have these studies misapplied thermodynamic models? Or were those incorrect conclusions (that ammonium sulfate would be replaced by ammonium nitrate) based on the incomplete conceptual model rather than the full thermodymamic model? ISORROPIA itself uses the critical molar ratio in its calculations. Can the authors elaborate on when or to what extent this is appropriate?

112-120 The stated aim of this study is to address the underlying reasons for the nitrate subsitution paradox. However, it seems that the resolution to this paradox has already been published in several papers by this research group, as summarized in lines 65-82, with further discussion in the subsequent paragraphs. Please clarify how this study represents an advance over that previous work. "The role of internally-mixed nonvolatile cations in PM2.5 as a source of the pH bias is then assessed." Again, to what extent is this new, and distinct from the Guo et al. (2017) manuscript under review?

135 Please provide a reference for the Air Pollutant Emissions Trends Data. If these are constant scaling factors, consider providing them in a table in the article Supplement.

138 Please clarify whether this is the same version of ISORROPIA as used in the release version of CMAQ v5.0.2.

143-148 Were these offline calculations computed separately for each of the three modes in CMAQ, or were the calculations done once by summing just the i and j modes? Given that CMAQ itself uses ISORROPIA, and HPLUS is one of the variables output by CMAQ, why was it necessary to run ISORROPIA again offline for each

grid cell and hour of each year? In presenting seasonal and annual average pH and nitrate partitioning ratios, are these calculated from hourly values?

160-171 The first sentence of this paragraph states that CMAQ captures the observed decreasing trends in SO4, NO3, and NH4. However, a few lines later the text states that ammonium levels "remain rather constant", and later in the same paragraph "aerosol nitrate concentrations remain relatively constant ... with small increases over the Eastern US." It is unnecessarily difficult to understand exactly what message the authors wish to convey.

161 Here and throughout the Results and Discussion section there are many references cited, but it is often not clear why they are being cited. In some instances, the authors mean that their current results are in agreement with results reported previously. However, the distinction between "Results" (of the current manuscript) and "Discussion" (including comparison with prior literature) should be stated explicitly. In this particular example, "CMAQ captures the observed downwards trends (six references cited) over the CONUS during the course of the decade," are those references supporting the assertion that inorganic species have been declining? Or that CMAQ generally represents species concentrations? This is especially confusing given the comment above, that ammonium and nitrate are largely unchanged between 2001 and 2011 in the current manuscript.

176 The methods section states that ISORROPIA is called offline using hourly CMAQ outputs, but the caption to Figure 1 indicates the calculation is performed using annual averaged CMAQ concentration fields (and presumably also annual average temperature and relative humidity). Given the strongly nonlinear dependence of aerosol partitioning on T and RH, I am skeptical of the value of a calculation based on annual average inputs to ISORROPIA.

183-187 "This trend suggests that pH will keep increasing... [four more references]." This discussion of the implications is repetitive and out of place here, especially since

the authors later argue that the modeled increase is in disagreement with WINTER observations and is erroneous, at least partially due to overestimated NVCs.

201-202 What is the meaning of citing Guo et al. (2015) and Xu et al. (2015) here? Those papers do not document the SEARCH data. Is the analysis performed here repeating work done in those papers?

205 The caption to Figure 2 states "Blue and red lines are the CMAQ predicted pH for 2001 and 2011 respectively," but the methods section states that ISORROPIA was called offline using CMAQ inputs, and the y-axis label indicates ISORROPIA. Which is it? Also, the caption appears to have been truncated.

207 Why is Guo et al. (2015) being cited here, along with Figure 2? Are the same data presented in Guo et al. (2015)? Or is the current result consistent with that previous study?

215 "due to the increased relative effect of NVCs (Weber et al. 2016)". Is the conclusion that NVCs are relatively more important made by Weber et al. (2016)? Again, please clarify what findings are new in the present manuscript.

215-217 Comparing Figure S5 to Figure 2, it is not at all obvious that the CMAQ values in S5 "better track" the observations by time of day than those in Figure 2. If this is an important point, it should be straightforward to substantiate it, such as via temporal correlations.

219 Of course the increase in pH is not proportional to the reduction in sulfate, since pH is logarithmic. The fact that aerosol responds non-linearly through volatilization of ammonia was stated previously.

224-225 It is strange to relate the pattern of the bias (difference between CMAQ predictions and SOAS measurements) to the pattern of the NVC concentrations. Moreover, I do not see the pattern referred to: the green line is between the red and blue lines up to about 8 in Fig. 2g, after which the model is negatively biased.

242-244 Foroutan et al. (2017) do not discuss pH at all.

293-294 If psi depends on the effective Henry's law constant for HNO3, which depends on H+, then psi is not a constant.

565 Figure 3 caption: are the Weber et al. (2016) mesasurements from the Centerville site? Do the CMAQ lines correspond to averages over the Eastern US domain or results at a single grid cell?

Technical Corrections by line number

22, 186 Surratt is misspelled.

90-93 Again, there is no need to cite the same three papers twice in the same sentence.

97 "find only minimal differences between predicted pH" is awkward. Perhaps "differences in predicted pH" or "differences in pH predictions."

130-131 "to eliminate potential biases of temperature and relative humidity on pH predictions." It would be clearer to state "to eliminate the effect of differences due to temperature and relative humidity on pH predictions."

149-153 This is a run-on sentence.

200 Clarify that these urban sites are in Atlanta, Georgia and the rural sites are also in Georgia.

202 sites is misspelled.

285 "out" should be "our"

287-289 The authors should be consistent as to whether this is "sulfate substitution" or "nitrate substitution."

303 Should this also be "nitrate substitution" rather than "nitrate partitioning"?

581 Caption is missing the word "change". The caption says "winter" and "summer"

but the figure titles say "January" and "July."

424-431 The same paper is listed twice, with differing author lists.

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