Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-950-RC1, 2017

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modeling reactive ammonia uptake by secondary organic aerosol in CMAQ: application to continental US" *by* Shupeng Zhu et al.

Anonymous Referee #2

Received and published: 8 November 2017

General Comments

This work describes the effects of including NH3 uptake onto secondary organic aerosol (SOA) in the CMAQ model. A range of NH3 uptake coefficients are used, taken from a recent lab study. The authors find that the addition of this reaction significantly lowers gas phase NH3 concentrations, especially when higher uptake coefficients (10ˆ-3) are used. Lower NH3 concentrations then cause less ammonium nitrate to be formed, and higher HNO3 gas phase concentrations. During the winter, this effect is dominant, and PM2.5 and PM10 levels decline. During the summer, lower NH3 concentrations increase the aerosol acidity significantly (pH drops by ∼2),

which then triggers SOA production by acid-catalyzed pathways, especially by IEPOX species. This work will be of interest not only to modelers but also to those who study the chemistry of either inorganic or organic aerosol species in the lab and in the field.

The primary limitation of the study is that once NH3 is taken up by SOA in the model, it disappears. As described in the introduction, NH3 can be taken up into SOA by either neutralizing organic acids (producing ammonium salts) or by reacting with aldehyde species to produce NOC (nitrogen-containing organic carbon species, such as imines and imidazoles), most of which are still quite basic and could react with inorganic acids. The relative importance of these two competing reactions is not known, but this study neglects both options. The result is the counterintuitive conclusion that including NH3 uptake to aerosol particles in the model reduces both NH3 (gas) and NH4+ (aerosol) concentrations, while also increasing HNO3 (gas) and decreasing NO3- (aerosol) concentrations. To a great extent, NH3 uptake to SOA must either produce NH4+ in the aerosol particle (by neutralizing an organic acid) or produce basic NOC species that can still neutralize HNO3. NH3 uptake that generates neither of these products, as assumed in this manuscript, does not appear to be a viable option. While the state of knowledge of this chemistry is not quantitative enough to nail this down, and the authors allude to this in the last paragraph in the paper, these issues should be discussed more vigorously in the manuscript.

Specific Comments

It would be helpful to mention whether aerosol in the model are externally or internally mixed.

p. 11 line 8: This sentence implies that both California's central valley and the South Coast Air Basin have high NH3 emissions from intensive agriculture. Is this really true in the latter case?

p. 11 line 9: Where do organic acids fit in the order of NH3 neutralization with H2SO4 and HNO3? If NH3 uptake to SOA results in neutralization of organic acids, does this

affect any of the manuscript's conclusions about HNO3 (g) concentrations increasing and nitrate concentrations decreasing in response to NH3 uptake?

p. 12 line 4: The prediction of almost no nitrate in summer aerosol over the southeast U.S., due to sulfuric acid neutralizing all of the available NH3, should be testable against regional PM observations. Is the prediction consistent with this dataset?

p. 12 line 9: This sentence is an example of the strange reasoning caused by the lack of a product formed by NH3 uptake in the model. "The reduction in NH3 due to the SOA uptake, directly impacts the available NH3 that could be condensed into the particle phase, and reduces the NH4+ concentration considerably."

Technical Corrections

p. 3 line 31: the phrase in parentheses does not make sense.

p. 9 line 10: the sentence with the phrase "east remote source and go under. . ." does not make sense. In the following sentence, when the authors write "the introduction of NH3 does not have much impact on this spot" do they mean "the addition of NH3 uptake to the model does not have much impact at this location"?

p. 11 line 10: the meaning of "association form of NH4+" is unclear.

p. 13 line 21: "wide" should be "widespread"

p. 16 line 14: The growth of AISO3 with respect to the uptake coefficient is linear, not exponential, since the uptake coefficients were varied exponentially.

p. 20 line 16: the meaning of the parenthetical phrase "based high NOx assumption" is unclear.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-950, 2017.