Modeling of Reactive Ammonia Uptake by Secondary Organic Aerosol in CMAQ: Application to Continental US

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Background

- Ammonium salts such as ammonium nitrate and ammonium sulfate make up an important fraction of the total $PM_{2.5}$ mass, and ammonia (NH_3) emissions are expect to increase in future due to warming climate and growing agricultural activities.
- Interactions between gas-phase ammonia and secondary organic aerosol (SOA) are poorly understand and are not taken into account in current air quality models.
- Liu et al. (2015) reported for the first time chemical uptake coefficients for ammonia onto SOA:
  - On the order of $\sim 10^{-3}$-10^{-2} initially, decreasing significantly to $< 10^{-5}$ after 6h of reaction.

Methodology

- The Community Multiscale Air Quality (CMAQ) model was modified to taken into account for the reactive uptake of ammonia by SOA based on the uptake coefficient (γ) reported by Liu et al. (2015).
- Air pollutant emissions are obtained from the National Emissions Inventor (2014) compiled by the US Environmental Protection Agency (EPA) for the CB06 mechanism.
- Simulations are conducted for two different periods: the winter period from Jan.1 to Feb. 28, and the summer period Jul.1 to Aug. 31. Four scenarios are considered for each period: (a) base case, (b) $\gamma = 10^{-3}$, (c) $\gamma = 10^{-4}$, and (d) $\gamma = 10^{-5}$.

Species	Period	Observation Mean *	Simulation Mean *	Correlations %	Network	Number of Sites
O_3	Winter	27	34	51	AQS	664
O_3	Summer	41	51	57	AQS	1262
NH_3	Winter	0.8	0.4	26	AMoN	19
NH_3	Summer	1.4	2.2	20	AMoN	46
$PM_{2.5}$	Winter	12.3	13.0	31	AQS	166
$PM_{2.5}$	Summer	12.6	21.9	18	AQS	176
PM_{10}	Winter	19.7	16.0	14	AQS	229
PM_{10}	Summer	26.6	28.6	8	AQS	225
NH_4^+	Winter	1.3	1.2	46	CSN	187
NH_4^+	Summer	0.8	1.0	32	CSN	187
NO_3^-	Winter	2.4	3.1	40	CSN	187
NO_3^-	Summer	0.5	0.9	18	CSN	187
SO_4^{2-}	Winter	1.9	1.5	54	CSN	193
SO_4^{2-}	Summer	2.9	3.2	33	CSN	193

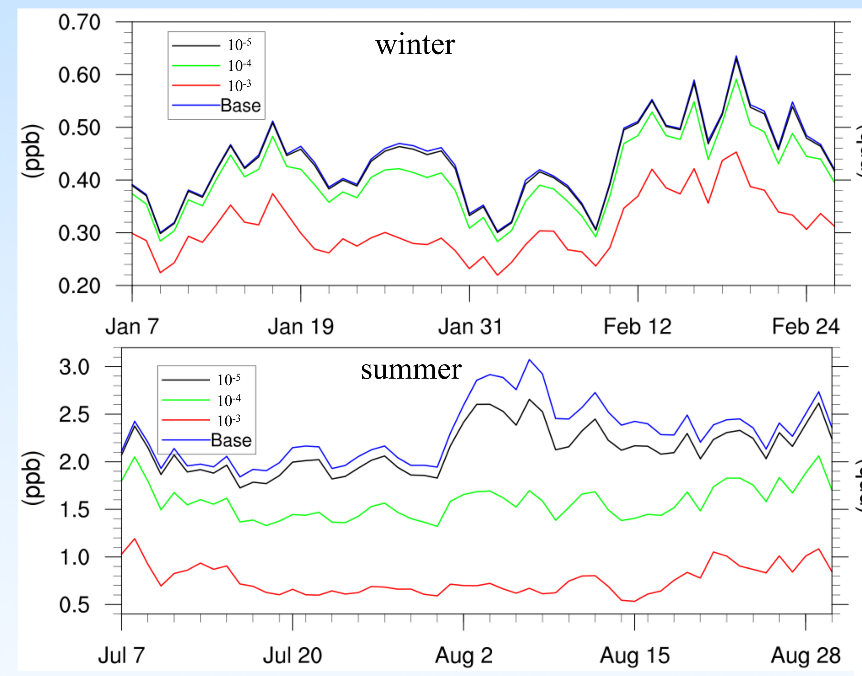
* Note: O_3 is given in (ppb). All others are given in (μg/m^3).

Model Validation

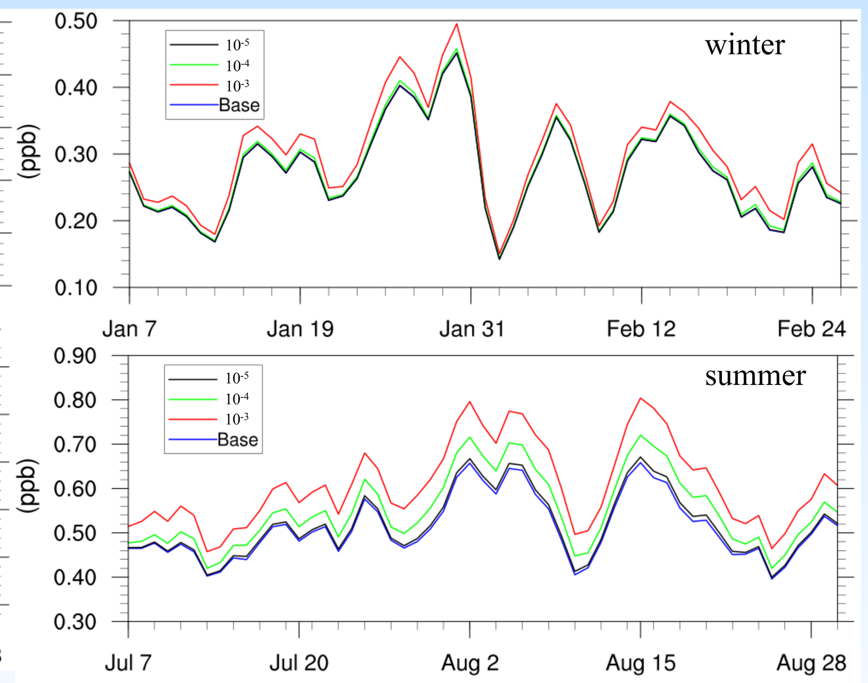
- The simulation results are compared with different observation networks:
  - $PM_{2.5}$, PM_{10} and O_3 with hourly EPA's Air Quality System (AQS).
  - NH_3 with bi-weekly data from Ammonia Monitoring Network (AMoN) network.
  - NH_4^+, NO_3^- and SO_4^{2-} with daily measurement from EPA's Chemical Speciation Network (CSN)

Comparison between each uptake scenario

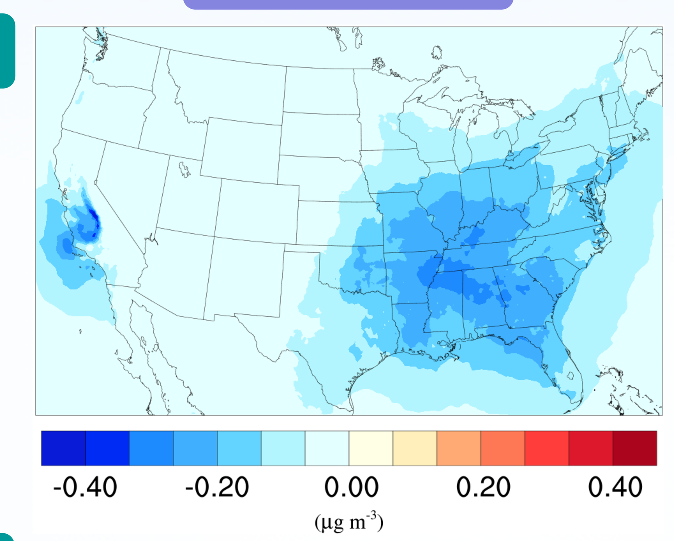
Impact on NH_3

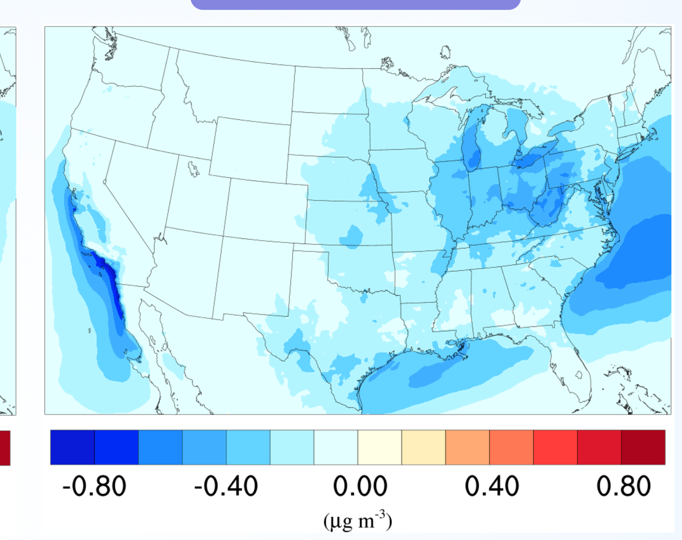


Impact on HNO_3

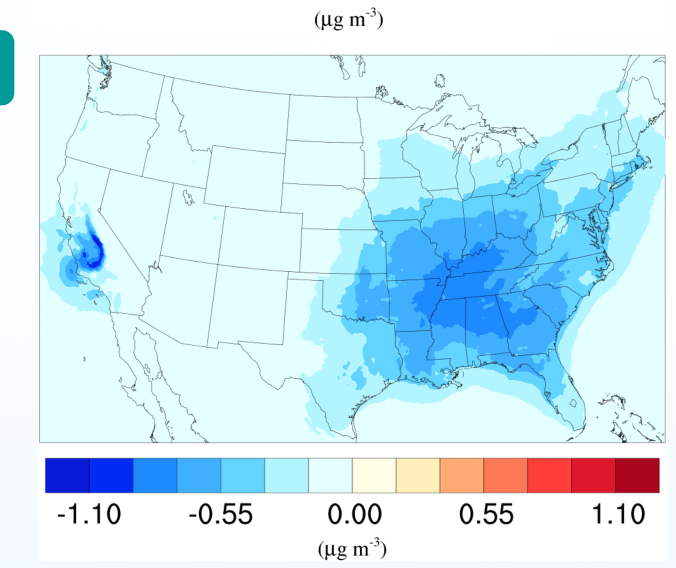


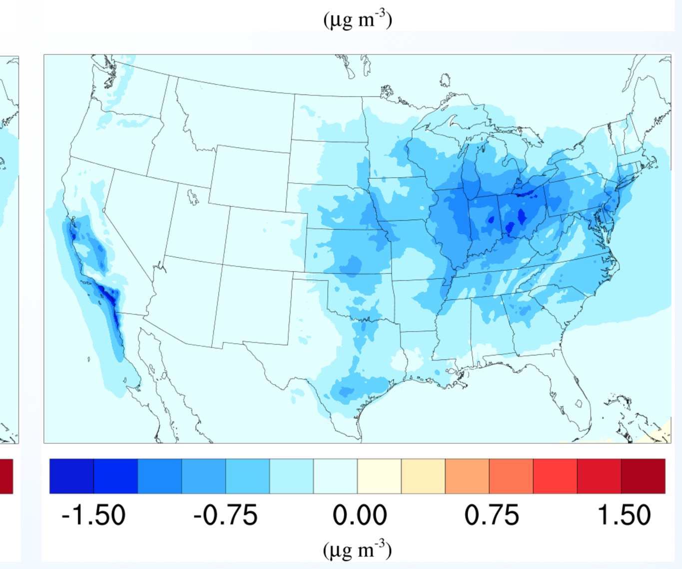
Impact on NH_4^+ — Diff 1e-3 vs base (Winter, Summer)





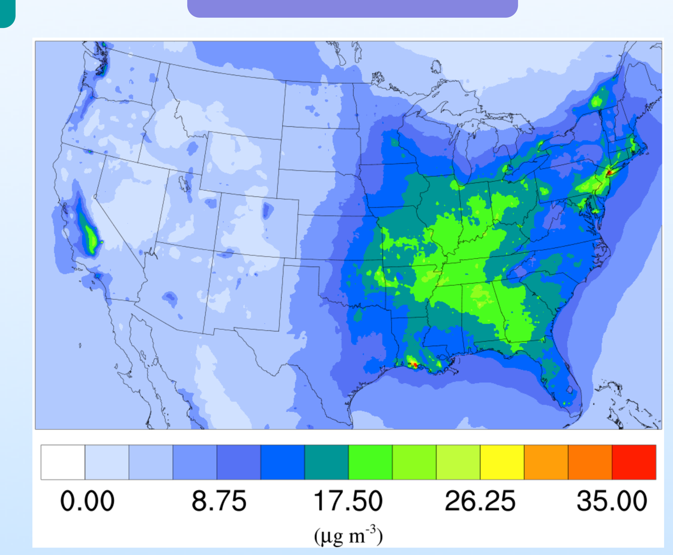
Impact on NO_3 — Diff 1e-3 vs base

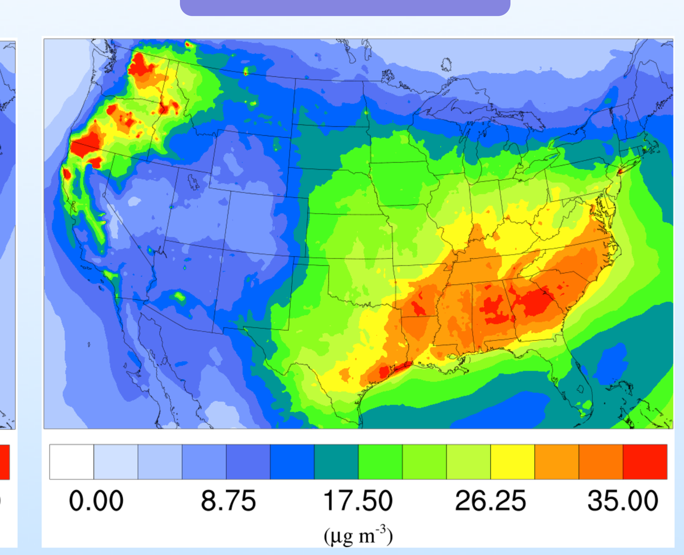




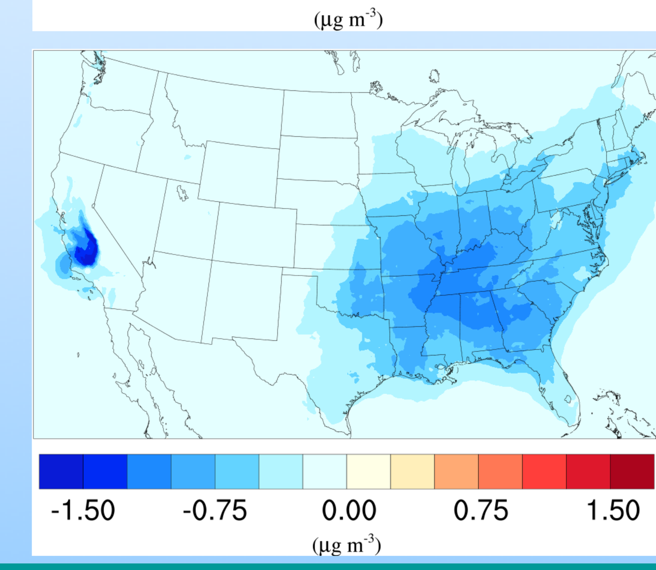
Impact on $PM_{2.5}$ (Winter, Summer)

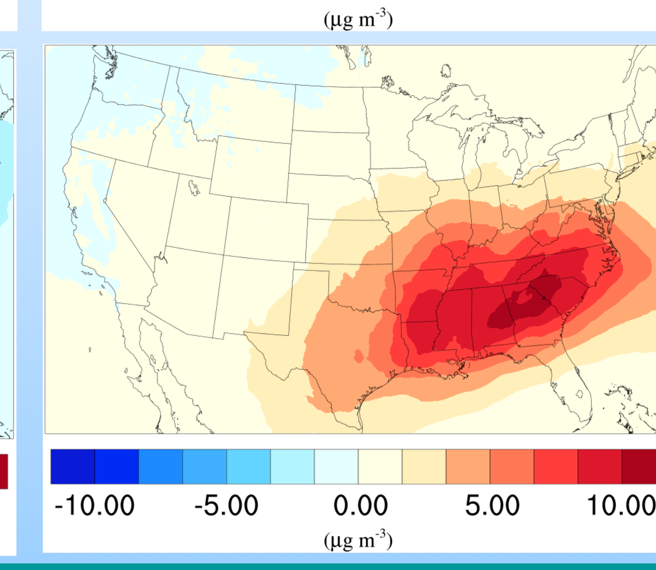
Base Avg.





Diff 1e-3 vs base

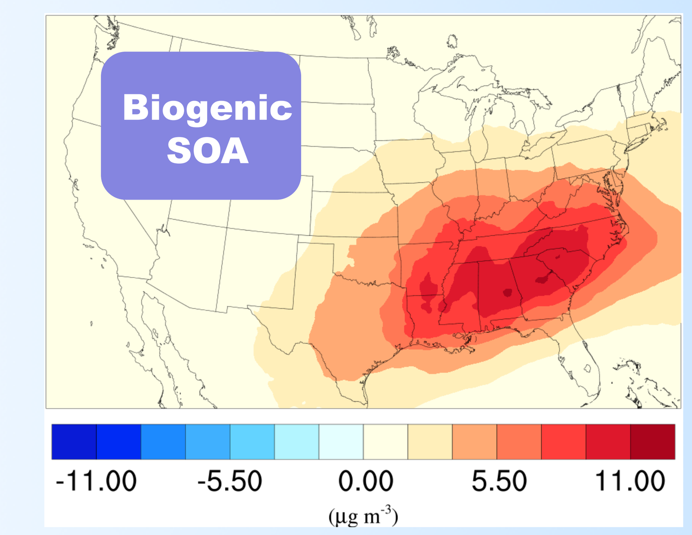


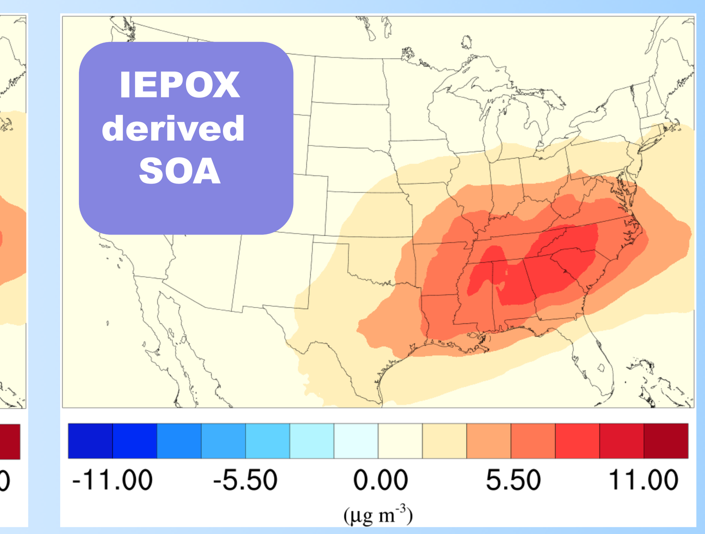


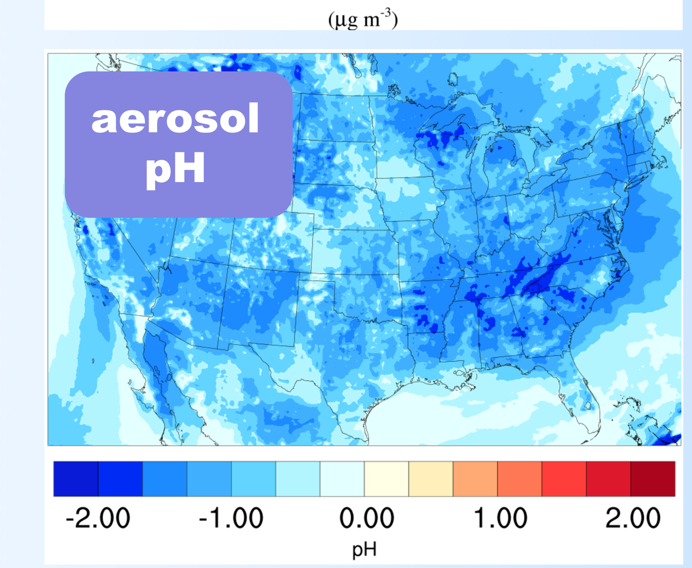
Air Quality Impacts

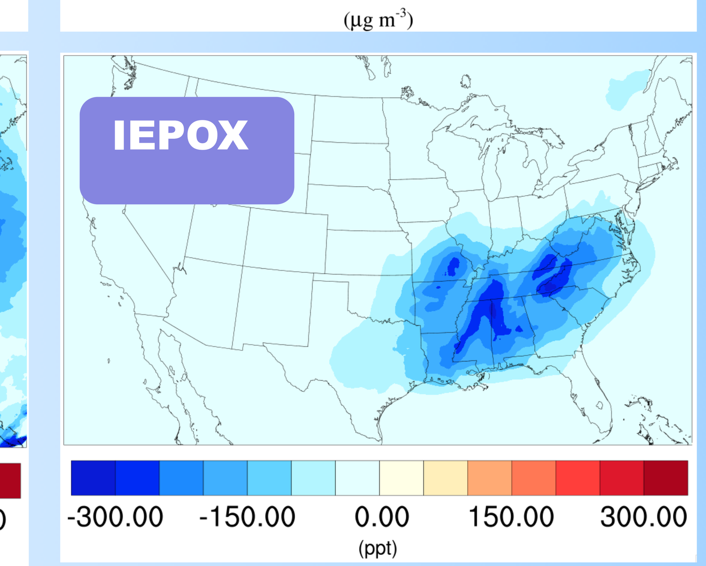
- Change in domain wide mass concentration between $\gamma = 10^{-3}$ case and the base case: summer (sum.), winter (win.)
- NH_3: -31.3% (win.), -67.0% (sum.); HNO_3: +8.5% (win.), +19.6% (sum.)
- NH_4^+: -13.2% (win.), -28.2% (sum.); NO_3^-: -10.6% (win.), -24.3% (sum.)
- $PM_{2.5}$: -3.4% (win.), +12.4 (sum.);
- The increase in $PM_{2.5}$ is caused by the increase of Biogenic SOA (+49% in summer $\gamma = 10^{-3}$ case). ~80% of such increase is caused by isoprene epoxydiol (IEPOX) derived SOA through the acid-catalyzed ring-opening reactions (Pye et al. 2013). This is due to the increase of aerosol aqueous phase acidity caused by the reduction in NH_4^+ after adding the NH3 uptake mechanism.

Diff 10^{-3} vs base (Summer)









Conclusions and Future works

- The reactive uptake of NH_3 by SOA could have significant impact on the concentration of both gas phase (NH_3, HNO_3) and particle phase (NH_4^+, NO_3^-, biogenic SOA) pollutants.
- More significant impact in the summer period than the winter period. There is an overall increase of total $PM_{2.5}$ in the summer while a overall decrease in the winter.
- Future laboratory studies should be conducted to identify the nature of the chemical interaction between NH3 and SOA species to help model explicitly the uptake process and provide more accurate model representation.

References

Liu, Y., Liggio, J., Staebler, R., and Li, S.-M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmospheric Chemistry and Physics, 15, 13 569–13 584, 2015.

Pye, H. O. T., and Coauthors, 2013: Epoxide pathways improve model predictions of isoprene markers and reveal key role of acidity in aerosol formation. *Environ. Sci. Technol.*, **47**, 11056–11064.