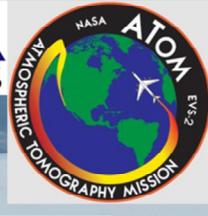


Global Survey of Aerosol Acidity from Polluted to Remote Locations: Measurements and Comparisons with Global Models

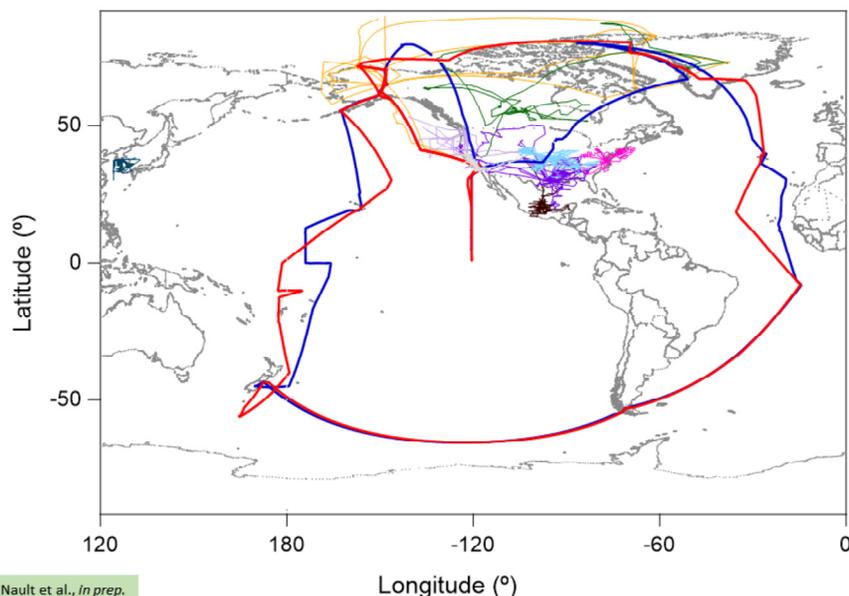
B.A. Nault, P. Campuzano-Jost, D.A. Day, W.W. Hu, B.B. Palm, J.C. Schroder, R. Bahreini, H. Bian, M. Chin, S. L. Clegg, P. Colarco, J. Crouse, J. Dibb, M.J. Kim, J. Kodros, F. D. Lopez-Hilfiker, E.A. Marais, A. Middlebrook, J. A. Neuman, J. B. Nowak, J. Pierce, E. Scheuer, J. A. Thornton, P.O. Wennberg, and J.L. Jimenez

Dr. Benjamin A. Nault
University of Colorado Boulder
EGU General Assembly 2020
Friday, 08th May 2020



Summary

Campaigns used to investigate submicron ammonium balance and pH



- MILAGRO (Mexico, 2006)
- INTEX-B (NW US, 2006)
- ARCTAS-A (NA Arctic, 2008)
- ARCTAS-B (NA Boreal, 2008)
- CalNex (California, 2010)
- DC3 (US, 2012)
- SEAC⁴RS (US, 2013)
- WINTER (US, 2015)
- KORUS-AQ (South Korea, 2016)
- ATom-1 (around the world, 2016)
- ATom-2 (around the world, 2017)

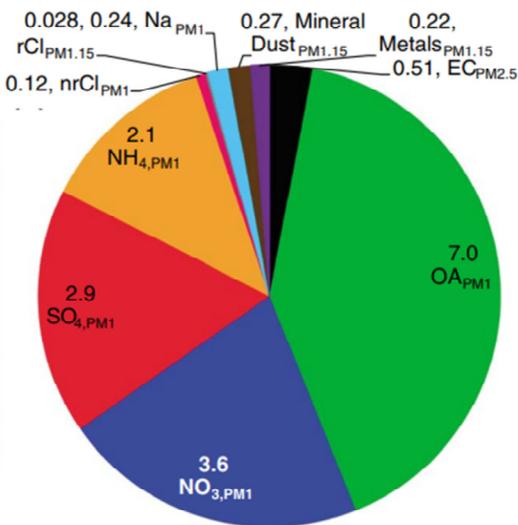
Nault et al., *in prep.*

3

11 different aircraft campaigns have been used to investigate how the aerosol composition and aerosol pH changes from polluted to remote locations. These campaigns stretch a range of locations, from urban areas (MILAGRO—Mexico City, CalNex—Los Angeles, WINTER—New York and northeastern US, and KORUS-AQ—Seoul) to remote continental regions (ARCTAS-A, ARCTAS-B, INTEX-B, DC3, and SEAC⁴RS), to remote oceanic regions (ATom-1 and ATom-2). The advantages of these missions is that they have both aerosol chemical composition (Aerodyne AMS) and gas-phase measurements of HNO₃ for all and NH₃ for CalNex, and measurements ranging from near surface (100 – 300 m) to near the tropopause (10 – 12 km).

Full Presentation

General composition of particulate matter (PM)



- Organic aerosol or organic matter (OM) composes largest fraction of PM (Jimenez et al., *Science*, 2009)
- Focused on urban OA production & sources (**Nault et al., ACP, 2018**) and global OA production, source, & health impacts (**Nault et al., in review**)
- Inorganics included many compounds, but in submicron, dominate by **sulfate (SO₄)**, **nitrate (NO₃)**, and **ammonium (NH₄)**

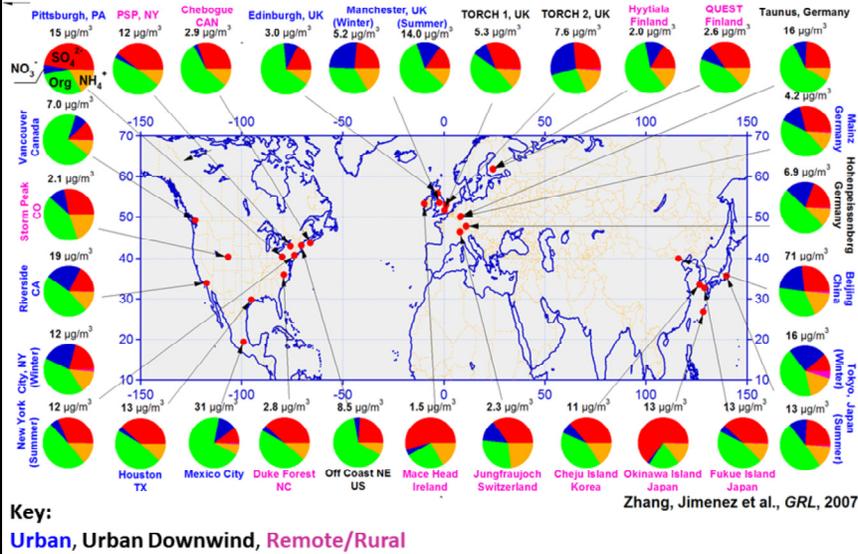
Hayes et al., *J. Geophys. Res. Atmos.*, 2013

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Aerosol controls many processes, including radiative balance, cloud formation and lifetime, fertilization, health affects, visibility, and boundary layer dynamics. To understand how these processes are impacted by aerosol, both the composition and concentration, and what emissions and chemistry impacts the composition and concentration, need to be known.

Recent work has shown the importance of the inorganic fraction of the aerosol as well as our lack of understanding in what controls the concentration we observe in the inorganic fraction.

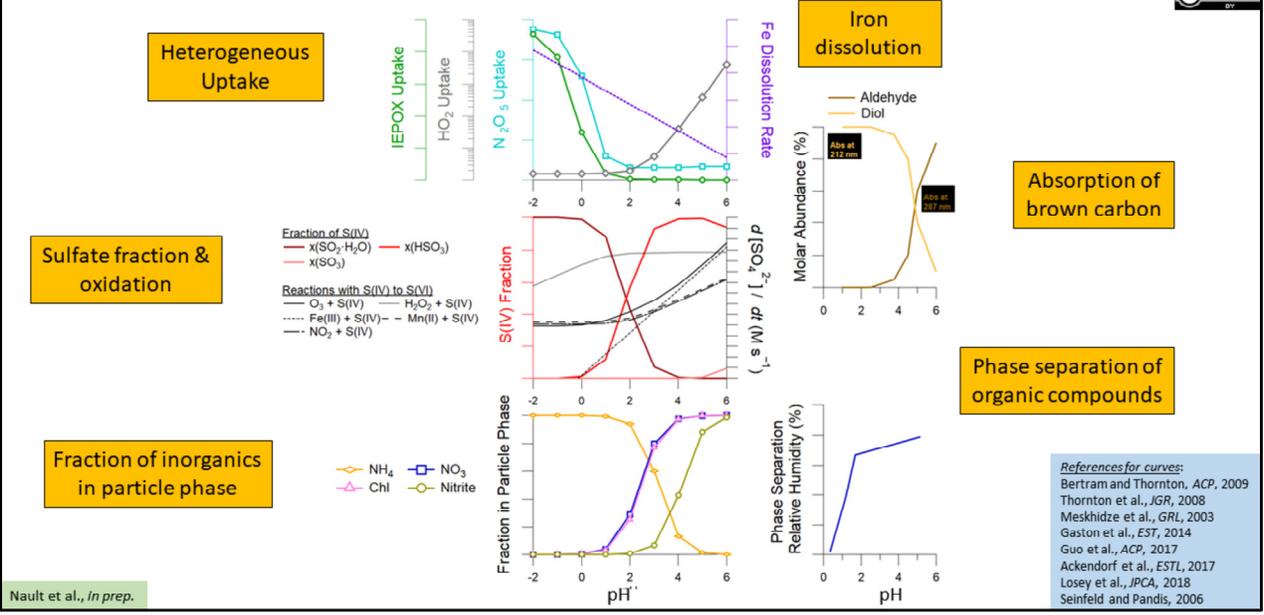
Inorganic aerosol composes an important fraction of aerosol; however, lacking knowledge in remote areas and impact in atmosphere



- Missing observations for remote ocean
- Missing observations for different altitudes
- Missing observations for continental background

The inorganic fraction composes an important to dominating fraction of the submicron aerosol mass concentration around the world. However, there is a lack of observations throughout the remote ocean, throughout different levels of the troposphere, and the remote continental regions (Siberia, throughout Africa and South America, etc.) as observational constraints to compare against chemical transport models to investigate what aspects are uncertain when it comes to what controls the inorganic fraction.

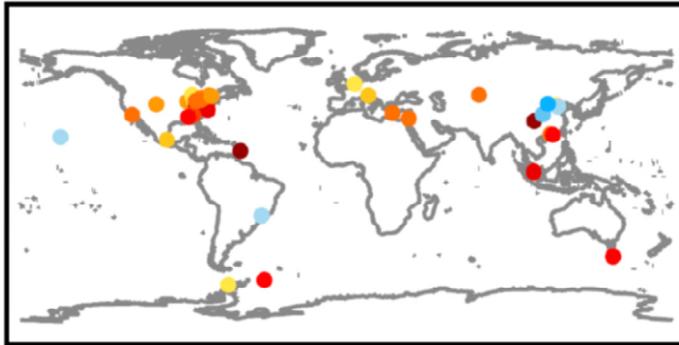
Importance of inorganic aerosol to the atmosphere and earth system—Chemistry



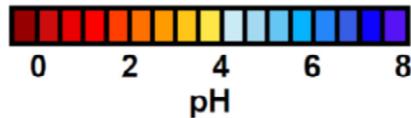
One important property the inorganic aerosol controls is aerosol pH.

Aerosol pH impacts many chemical and physical processes, as highlighted above from a literature review and compilation. This includes organic uptake, such as IEPOX, inorganic uptake, iron dissolution, oxidation of S(IV) to S(VI), inorganic partitioning, whether organic aerosol will absorb UV light or not, and phase separation.

Missing measurement constraints on aerosol pH and ammonium balance in more remote regions of the atmosphere



- From an aerosol pH review (Pye et al., *ACP*, 2020)
- Measurements mostly ground base, on land, and near pollution



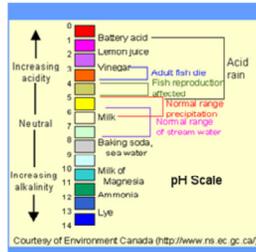
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However, similar to the aerosol composition, there is a lack of observations pertaining to aerosol pH around the world. Part of this is the analytical challenge in measuring aerosol pH. The other part is that the best way to estimate aerosol pH is w/ thermodynamic models, but to estimate reliable aerosol pH, both aerosol composition/mass concentration as well as the volatile gases (e.g., HNO_3 and/or NH_3) need to be measured, limiting where aerosol pH can be estimated.

Questions being investigated across multiple campaigns:

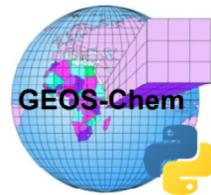


1) How does inorganic aerosol composition change from polluted to remote locations? Is there a trend?



2) How does aerosol pH change from polluted to remote locations?

3) How well do chemical transport model capture the observations? How does that impact our understanding of inorganic aerosol?

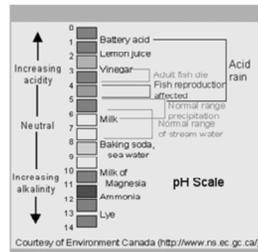


In this study, three I've looked at three questions.

Questions being investigated across multiple campaigns:



1) How does inorganic aerosol composition change from polluted to remote locations? Is there a trend?



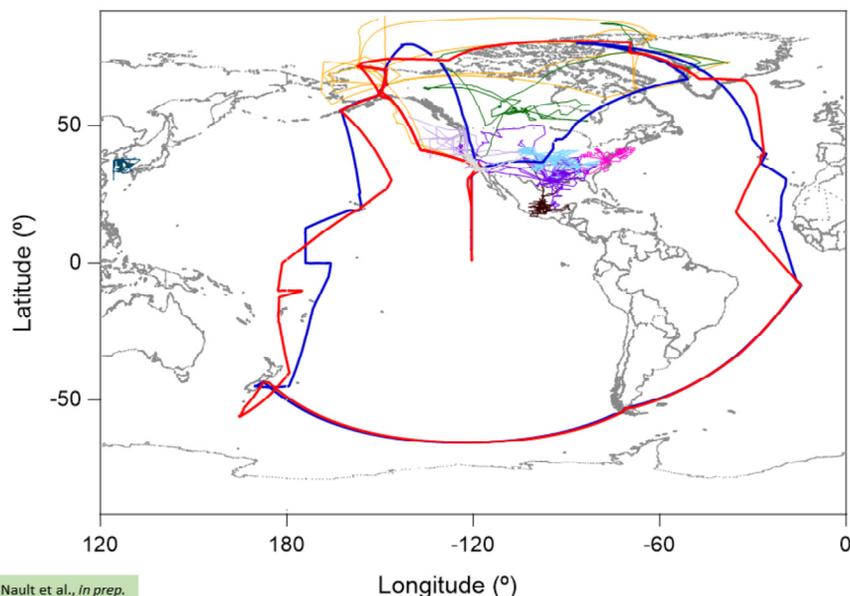
2) How does aerosol pH change from polluted to remote locations?

3) How well do chemical transport model capture the observations? How does that impact our understanding of inorganic aerosol?



First, we'll focus on the composition.

Campaigns used to investigate submicron ammonium balance and pH



- MILAGRO (Mexico, 2006)
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- KORUS-AQ (South Korea, 2016)
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- ATom-2 (around the world, 2017)

Nault et al., *in prep.*

12

11 different aircraft campaigns have been used to investigate how the aerosol composition and aerosol pH changes from polluted to remote locations. These campaigns stretch a range of locations, from urban areas (MILAGRO—Mexico City, CalNex—Los Angeles, WINTER—New York and northeastern US, and KORUS-AQ—Seoul) to remote continental regions (ARCTAS-A, ARCTAS-B, INTEX-B, DC3, and SEAC⁴RS), to remote oceanic regions (ATom-1 and ATom-2). The advantages of these missions is that they have both aerosol chemical composition (Aerodyne AMS) and gas-phase measurements of HNO₃ for all and NH₃ for CalNex, and measurements ranging from near surface (100 – 300 m) to near the tropopause (10 – 12 km).

Ammonium balance 101



$$\text{Ammonium balance (AB)} = \text{NH}_4^+ / (2 \times \text{SO}_4^{2-} + \text{NO}_3^-) \text{ (in moles)}$$



AB = 0

AB ≈ 0.5

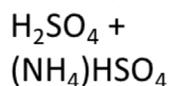
AB = 1

Chemical Formulas

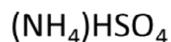
Assumed:



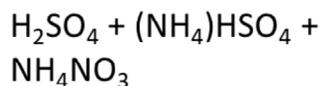
Actually:



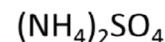
Assumed:



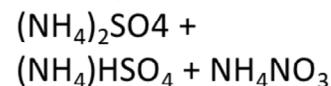
Actually:



Assumed:



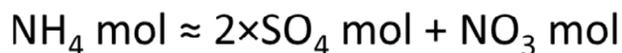
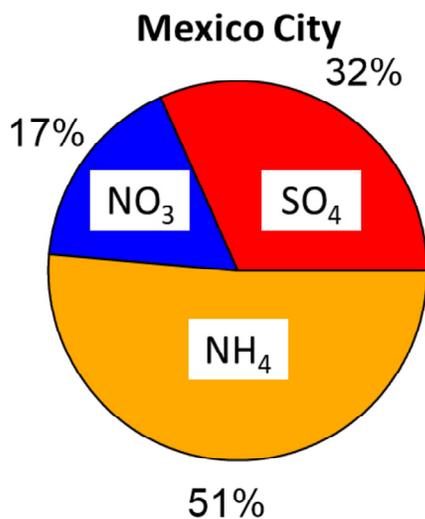
Actually:



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Briefly, ammonium balance is introduced, as this is the first metric that is discussed for the measurements. Ammonium balance is defined as the charge balance, in molar units, of the main cation ammonium to the main anions sulfate and nitrate. An ammonium balance of 1 is defined as ammonium's charge completely balanced by nitrate and sulfate; however, due to thermodynamics and the difficulty of measuring hydronium ions, the actual chemical composition will be different than pure ammonium sulfate and ammonium nitrate (assumed vs actual). A thermodynamic model provides valuable insight into what the actual chemical formula of the aerosol is compared to what is assumed by ammonium balance.

Comparison of inorganic aerosol composition and NH_4 balance



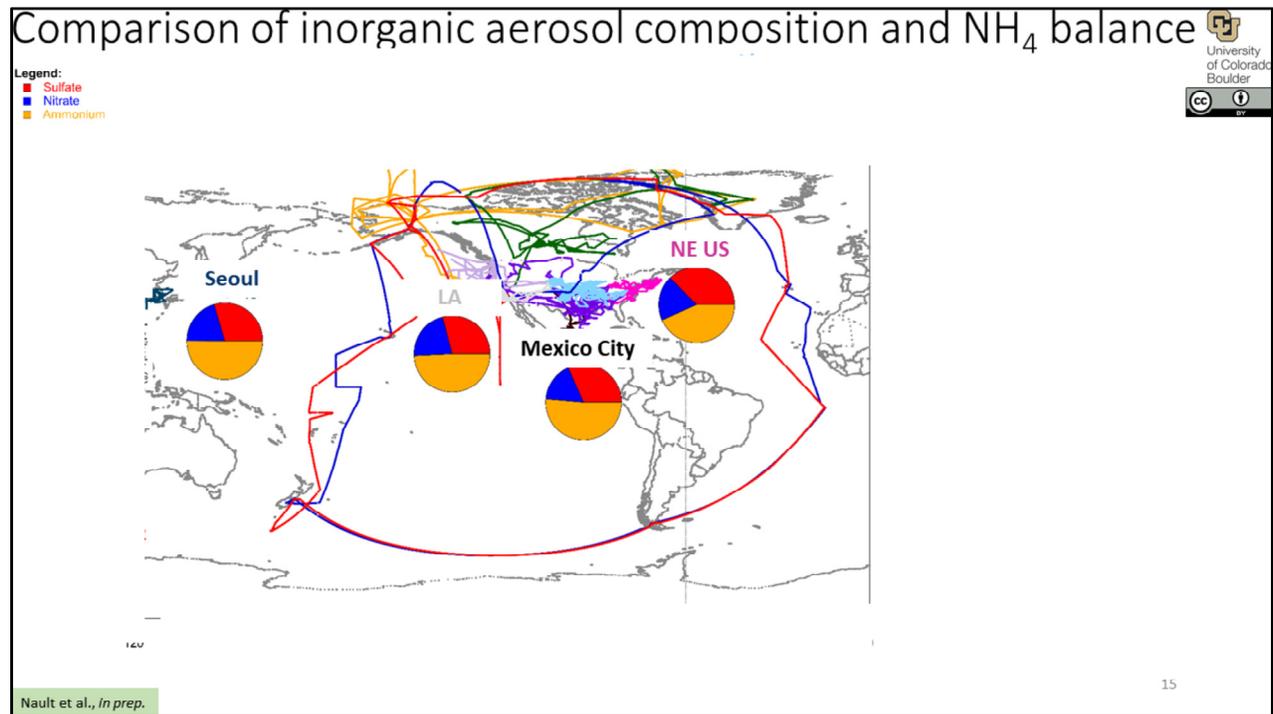
Mixture of $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)\text{HSO}_4$, & NH_4NO_3

Need thermodynamic model to know actual chemical composition

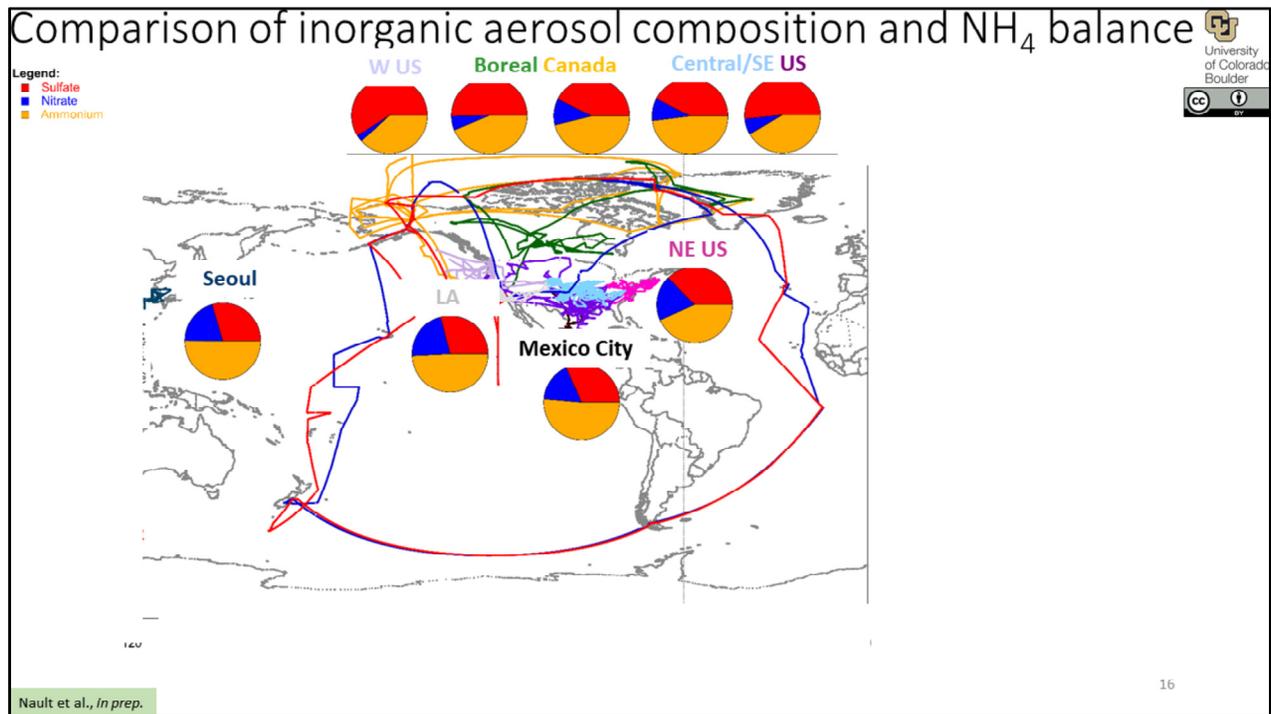
Nault et al., *in prep.*

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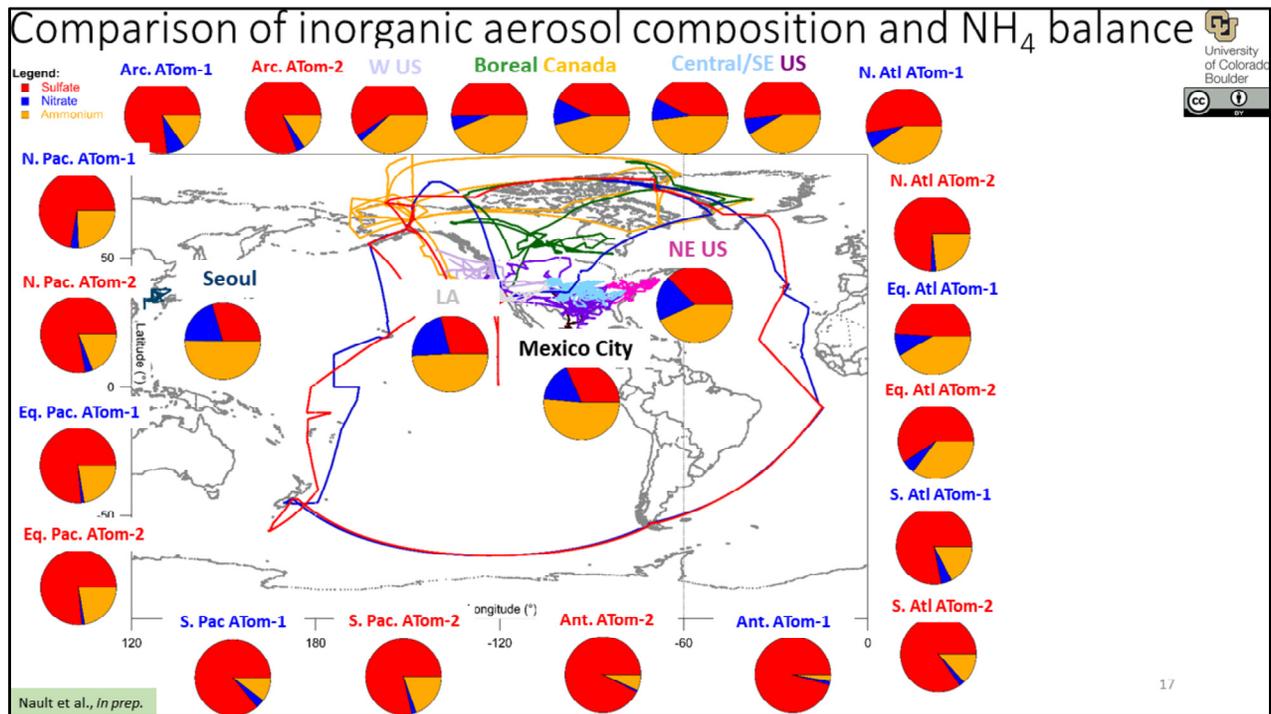
In the next slide, pie charts to compare the various campaigns will be shown. However, unlike the typical pie chart that is in mass concentration, these pie charts are representing the charge balance of the inorganic aerosol. E.g., this example from Mexico City, the ammonium charge is completely balanced by nitrate and sulfate, as ammonium = nitrate + 2×sulfate. However, keep in mind, that the actual composition will be different due to thermodynamics.



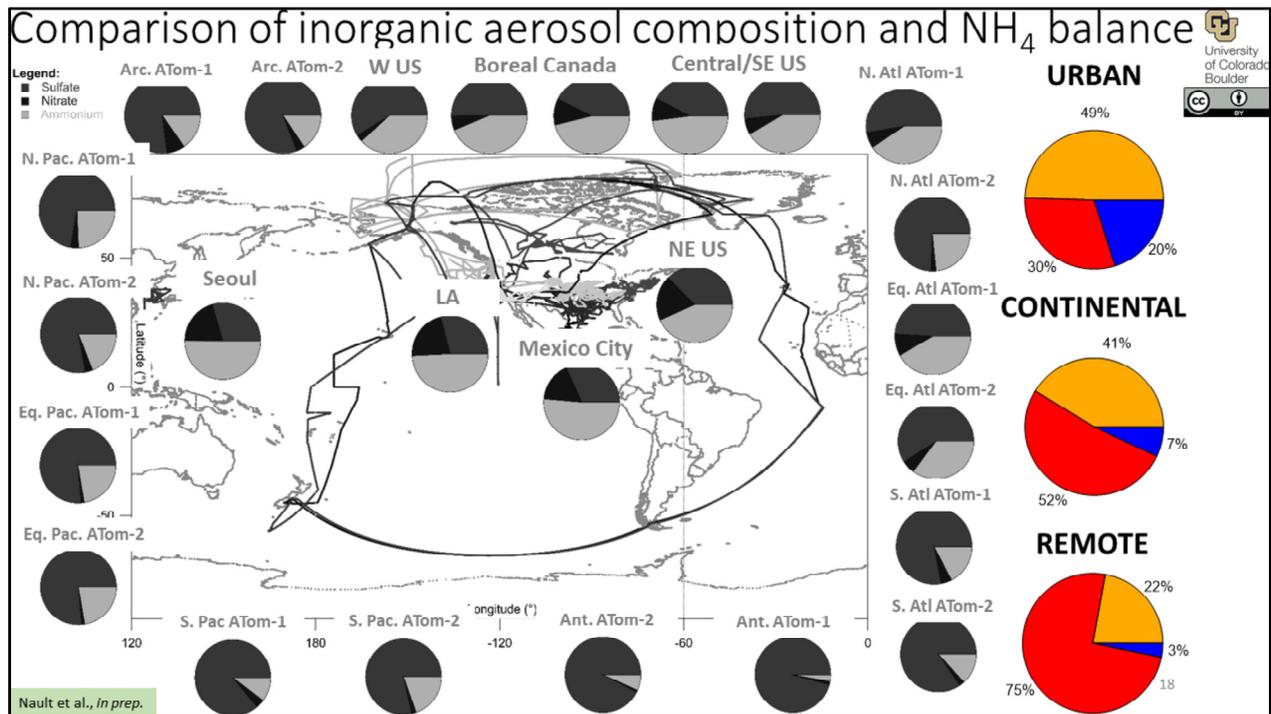
First, I'll show the urban regions. For all the urban regions, the ammonium charge is balanced by nitrate and sulfate.



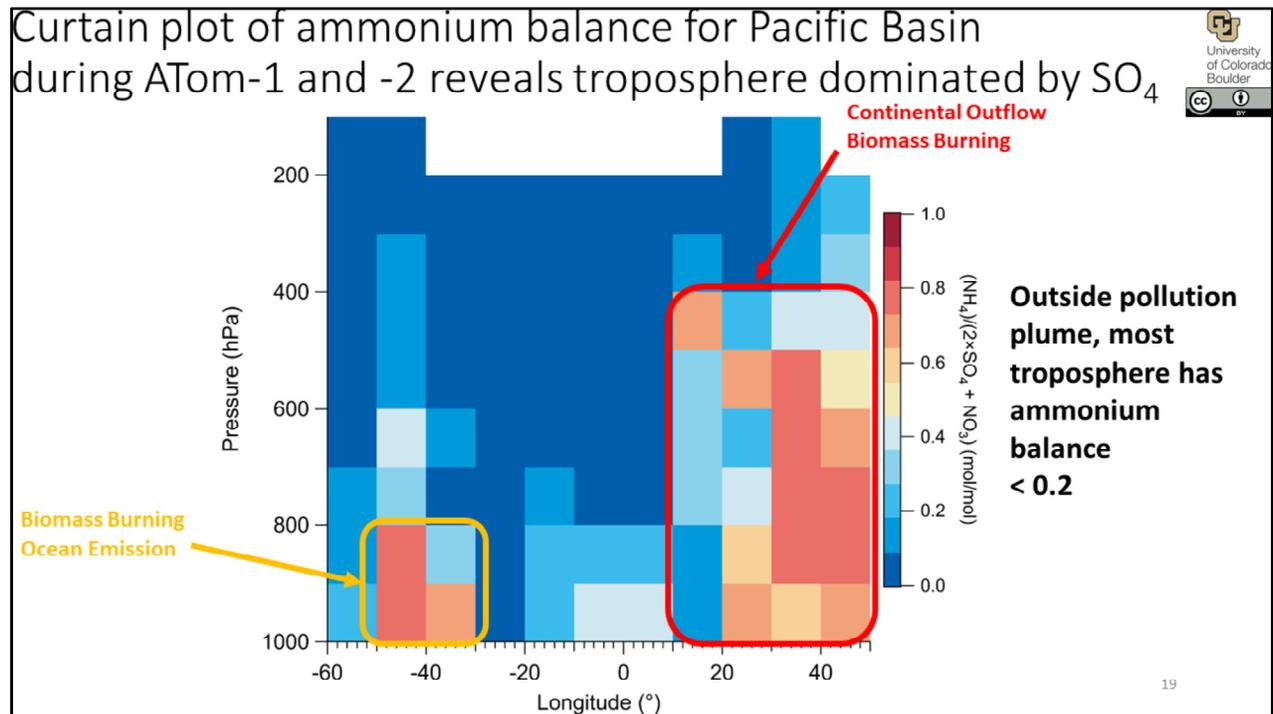
Moving to continental background observations, the nitrate charge balance decreases. This is due to moving away from NO_x emission sources, moving the equilibrium as ammonium nitrate is volatile. Also, the ammonium starts decreasing as the air masses move from ammonia emission sources (urban areas, agriculture, etc.).



Going to the remote ocean regions, outside of pollution transport regions (e.g., northern Atlantic) or areas impacted by biomass burning (e.g., equatorial Atlantic), sulfate dominates the charge to the point that there is almost no ammonium (Antarctica). This suggests that hydrogen is becoming important in maintaining a charge balance.

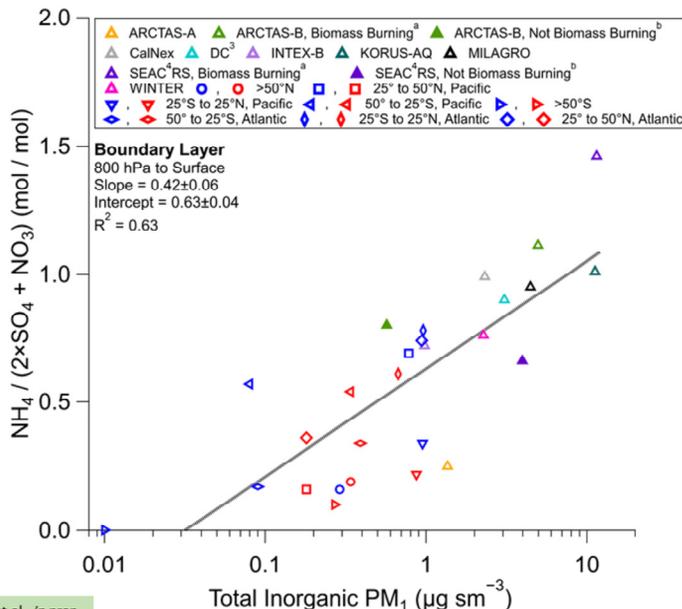


As that is a lot of pies, here is a summary, where each region has been averaged into the three pie charts. Urban areas have near complete charge balance; whereas, the continental regions show the charge balance goes away as sulfate starts dominate the charge, and ammonium nitrate evaporates. Finally, remote oceanic regions show that sulfate dominates the charge with minimal nitrate and low ammonium, indicating that hydrogen is becoming important in maintaining a charge balance.



Instead of campaign or ocean basin average, we can also see how ammonium balance changes with altitude (or pressure). Plotted here is the average ammonium balance from ATom-1 and ATom-2, for the Pacific Ocean observations, plotted versus pressure. Red = ammonium balance = 1 (ammonium charge balancing anion charge) and blue = ammonium balance = 0 (hydrogen charge balancing anion charge). For pollution and biomass burning plumes, ammonium balance is high. Outside these plumes, the ammonium balance is very low.

Ammonium balance decreases with PM_{10}

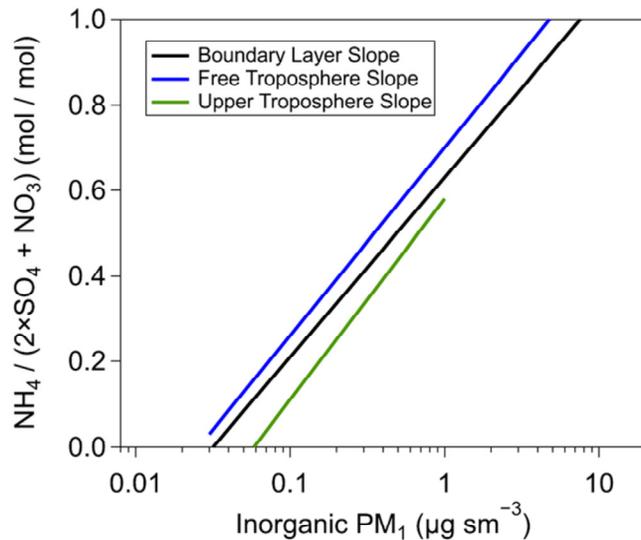


- Strong correlation of ammonium balance w/ inorganic PM_{10}
- Suggests that away from major point sources (urban areas, forest fires, agriculture), minimal NH_x emissions while SO_4 is still being produced

Now, we look to see if there is a trend, and specifically, look to see if there is a trend in chemical coordinates. Chemical coordinates provide a way to minimize the influence of transport and meteorology on the observations and to focus on emissions and chemistry that impacts the observations (e.g., Woody et al., ACP, 2016).

For observations collected in the boundary layer (observations between surface and 800 hPa), there is a strong correlation for ammonium balance (y-axis) versus total inorganic mass concentration (x-axis) for all campaigns. The x-axis is a metric of pollution/emissions, has higher values are from urban regions and biomass burning and lower values are for remote regions such as Antarctica. Since ammonium balance decreases as the aerosol is removed from continental pollution, this suggests that total ammonia ($NH_x = NH_3 + NH_4$) emissions decrease while continuous sulfuric acid production occurs. The sulfuric acid production comes from the slow oxidation of natural and anthropogenic SO_2 and the oxidation of oceanic emissions, such as dimethyl sulfide.

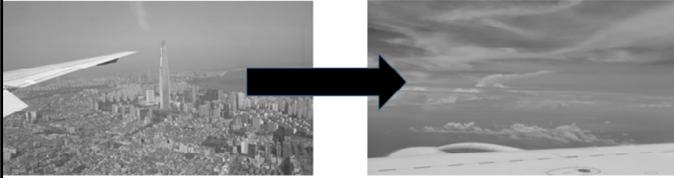
Ammonium balance decreases with PM_{10} at the same rate for all levels in troposphere



- Suggests similar chemistry/emissions controlling ammonium balance throughout troposphere
- High ammonium balances above boundary layer controlled by forest fires & thunderstorms
- Away from land sources, little NH_3 emissions with continued production H_2SO_4

Comparing the slopes from boundary layer (surface to 800 hPa), free troposphere (800 to 400 hPa), and upper troposphere (400 to 250 hPa), I find statistically similar slopes for all three regions of the atmosphere. This suggests that the emissions and chemistry controlling ammonium balance is similar for all three regions. Also, the higher ammonium balance and inorganic mass concentrations observed in free and upper troposphere is due to injection from biomass burning and/or deep convection.

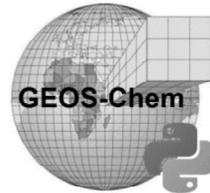
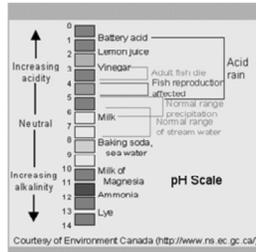
Questions being investigated across multiple campaigns:



1) How does inorganic aerosol composition change from polluted to remote locations? Is there a trend?

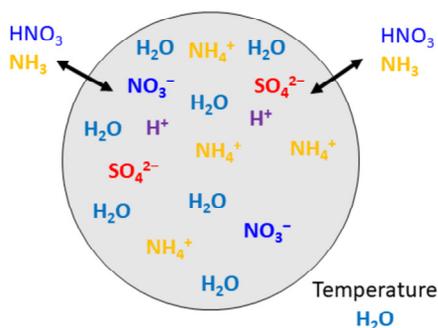
2) How does aerosol pH change from polluted to remote locations?

3) How well do chemical transport model capture the observations? How does that impact our understanding of inorganic aerosol?



Next, I'll look at how aerosol pH changes w/ the observations.

E-AIM thermodynamic model to predict aerosol pH



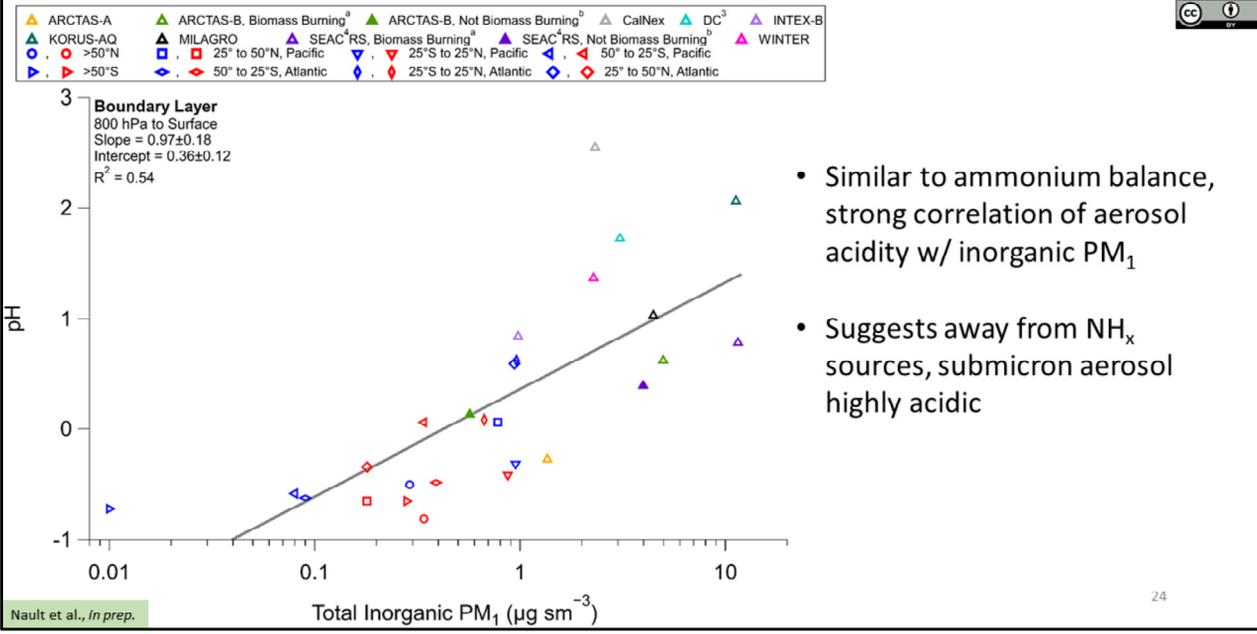
- Input = Temperature, relative humidity, aerosol composition, gas-phase species
- Calculates equilibrium between gas & aqueous and aqueous & solid phases
- Activity of water & ions calculated w/ Debye Hückel eq to account for high ionic strength/interactions
- $\text{pH} \approx -\log_{10}(\gamma_{\text{H}^+} H_{\text{aq}}^+)$

Clegg & Brimblecombe, *J. Chem. Eng. Data*, 1995
Clegg et al., *JPC*, 1992
Clegg et al., *ACP*, 2007
Friese & Ebel, *JPCA*, 2010

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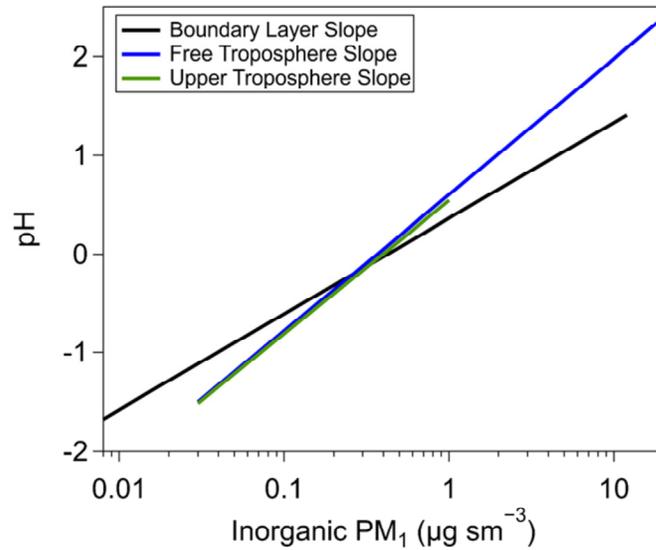
Briefly, as I mentioned earlier, best method to estimate aerosol pH is via a thermodynamic model due to the analytical challenges of measure aerosol pH. For this study, I used the E-AIM model, which has been compared against ISORROPIA and shown similar values. For this study, the inputs include aerosol composition/mass concentration (sulfate, nitrate, and ammonium), gas-phase mixing ratio (HNO₃ for all missions and NH₃ for CalNex), temperature, and relative humidity. E-AIM is used to estimate aerosol liquid water and hydronium ion mass concentration to calculate aerosol pH. The output of the model is compared w/ observations to determine level of accuracy for the model.

Aerosol acidity decreases with PM₁



Similar to ammonium balance, to determine if there is a trend for aerosol pH, I plot pH (y-axis) vs inorganic aerosol mass concentration (x-axis) for the boundary layer (surface to 800 hPa) for all campaigns. There is a strong correlation for aerosol pH vs aerosol mass concentration, again, showing that as you move from polluted regions (high mass concentration, urban and biomass burning) to low mass concentration (remote regions, such as Antarctica), ammonium cation decreases and hydronium increases, making aerosol more acidic. This further supports that total NH_x (NH₃ + NH₄) emissions decrease as you move from continental regions.

pH decreases with PM_{10}
at the same rate for all levels in troposphere



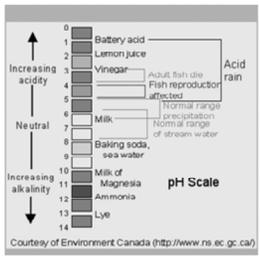
Nault et al., *in prep.*

Again, similar to ammonium balance vs inorganic mass concentration, aerosol pH vs inorganic aerosol mass concentration for three tropospheric levels show statistically similar slopes, suggesting similar emission and chemistry is controlling the decrease in pH with decreasing inorganic aerosol mass concentration.

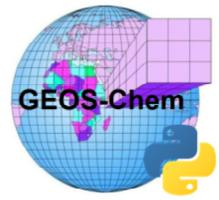
Questions being investigated across multiple campaigns:



1) How does inorganic aerosol composition change from polluted to remote locations? Is there a trend?



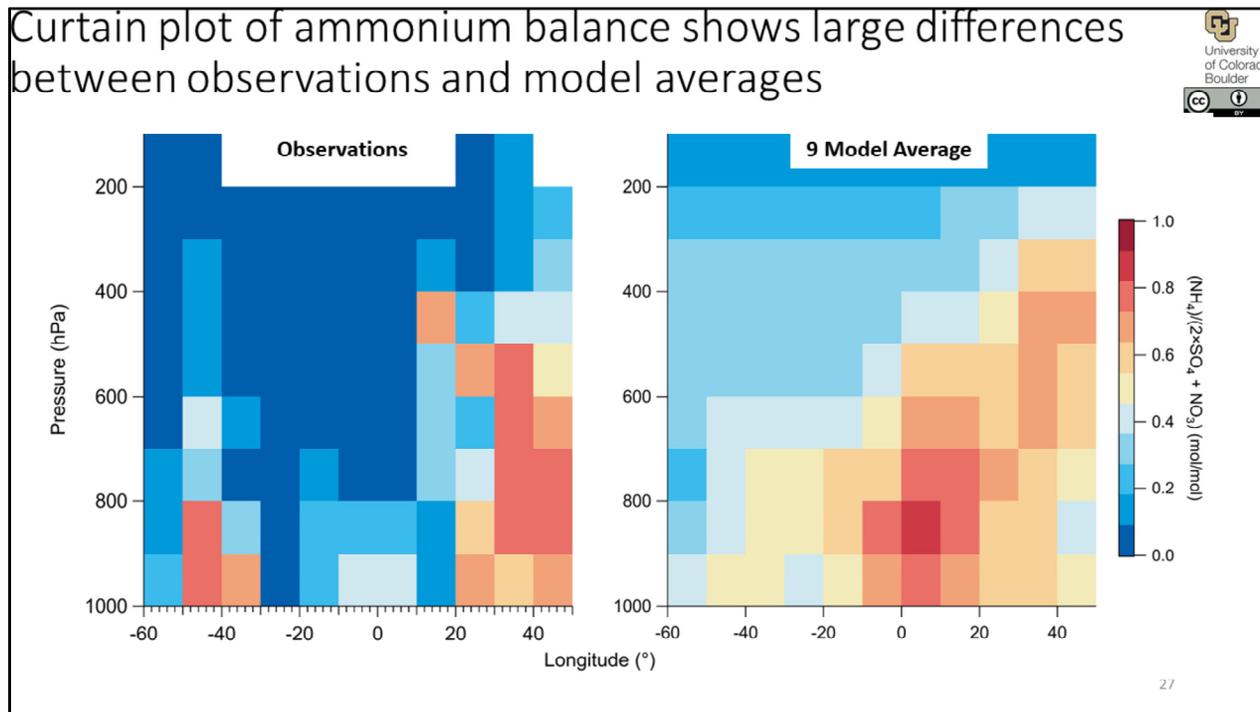
2) How does aerosol pH change from polluted to remote locations?



3) How well do chemical transport model capture the observations? How does that impact our understanding of inorganic aerosol?

Finally, I'll compare the results from the observations with numerous different chemical transport models.

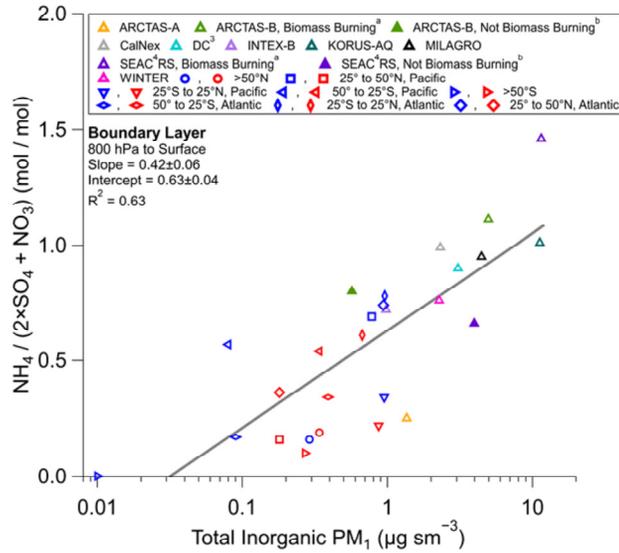
Curtain plot of ammonium balance shows large differences between observations and model averages



I've looked 9 different chemical transport models. First, we can see how the model average compares for ammonium balance over the Pacific Ocean. Again, the observations are the average ammonium balance observed during ATom-1 and ATom-2 over the Pacific Ocean for the different pressure levels.

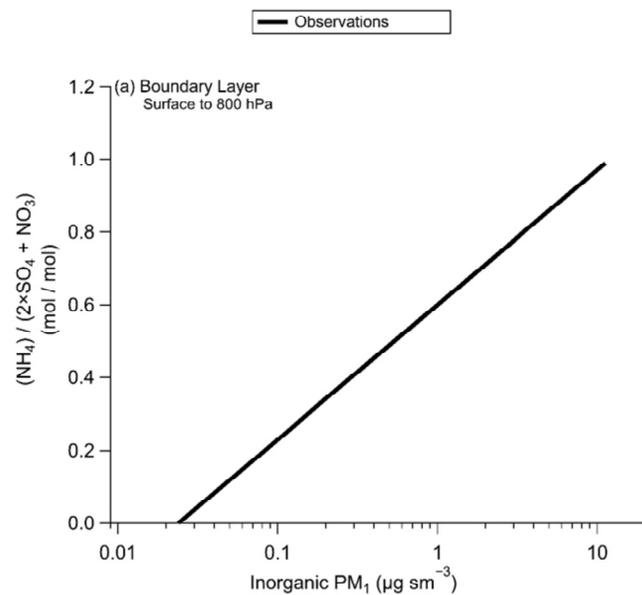
The 9 model average is on right for the similar location the DC-8 sampled over the Pacific. The 9 model average shows a similar pollution outflow region in the northern Pacific, with higher ammonium balance. But unlike the observations, the 9 model average generally shows moderate to high ammonium balance and does not show ammonium balance less than 0.2 throughout the Pacific troposphere.

Use chemical coordinates to investigate biases



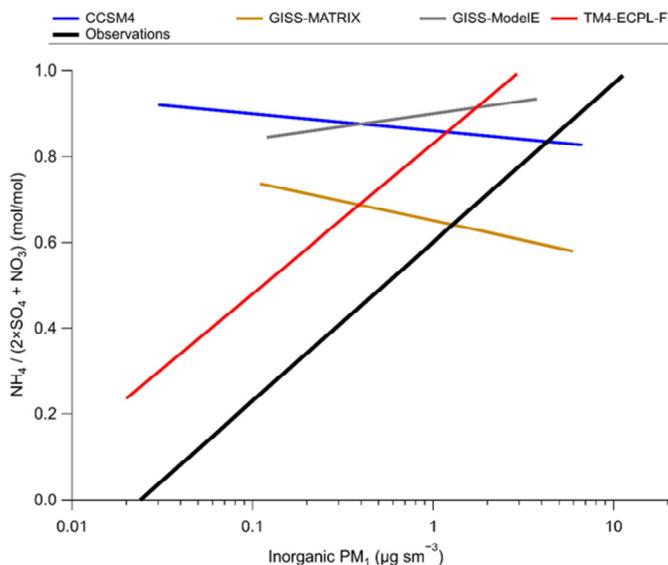
To further investigate the differences between the observations and model, I'll use the chemical coordinates I introduced earlier. Again, this is to minimize the impact of transport and meteorology and to really investigate if the differences are due to chemistry and/or emissions.

Use chemical coordinates to investigate biases



To do that, I'll take the slope for ammonium balance versus inorganic mass concentration for the boundary layer.

Similar to prior studies, the models show a range of skill for ammonium balance trends



- Older chemical transport models show very large disagreement compared to observations

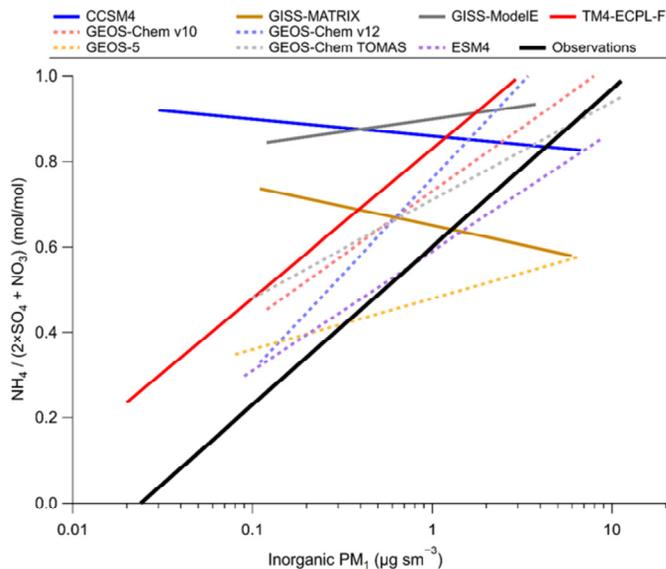
Nault et al., *in prep.*

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And compare the slope from the observation with the slopes from different chemical transport models. This minimizes seeing if point to point the models are getting the same values as the observations, but instead, are the models getting the same trend as observations.

Taking older models used during AEROCOM II, the trends from the models are different than observations. These models either show no change for ammonium balance versus inorganic mass concentration, or the opposite change (ammonium balance decreasing with increasing inorganic mass concentration).

Similar to prior studies, the models show a range of skill for ammonium balance trends—Boundary Layer



- Older chemical transport models show very large disagreement compared to observations
- Newer models generally better capture trend
- Still large offset for models vs observations

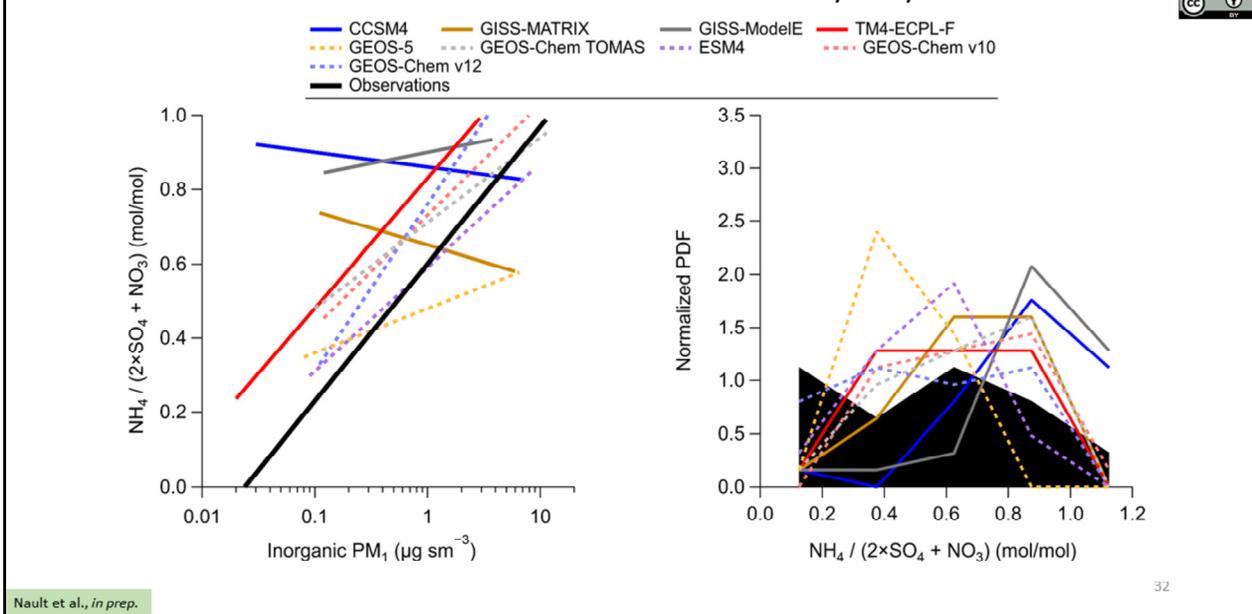
Nault et al., *in prep.*

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Comparison of the slope with newer chemical transport models improves in that they mostly show a decreasing trend for ammonium balance versus inorganic mass concentration.

However, there is still a large offset compared to observations. Thus, though the trends are similar to observations, the models appear to be estimating higher ammonium balances than observations indicate.

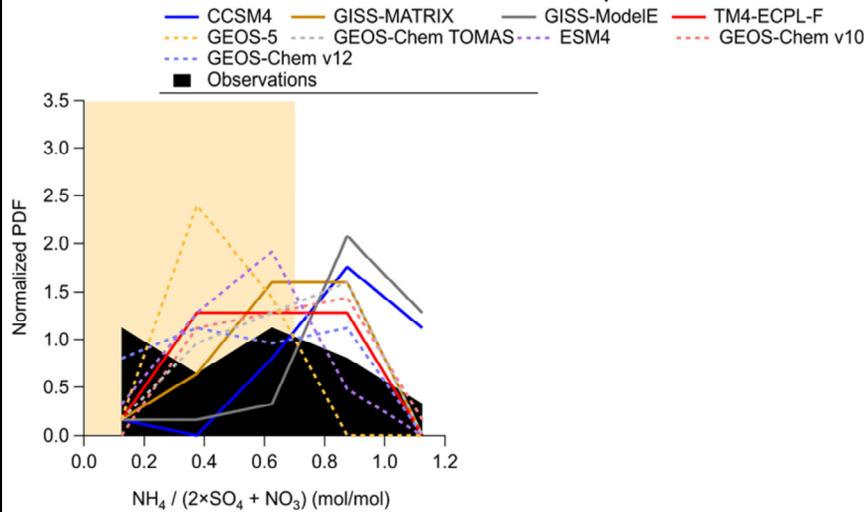
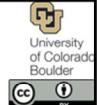
Similar to prior studies, the models show a range of skill for ammonium balance distribution—Boundary Layer



The difference in ammonium balances (the offset) can be further explored with a normalized probability distribution function (PDF). The PDF of ammonium balance for boundary layer. Note, since the ammonium balance values are less than 1, the PDF values are greater than 1 so that the sum = 1.

Observations (black) show a spread of ammonium balance from ~ 0 to ~ 1 . However, the models do not show this spread, and generally show more occurrences of ammonium balances > 0.5 (instead of equal occurrence of ammonium balances from 0 to 1).

Using thermodynamic model, ammonium balance < 0.7 are liquid in Boundary Layer



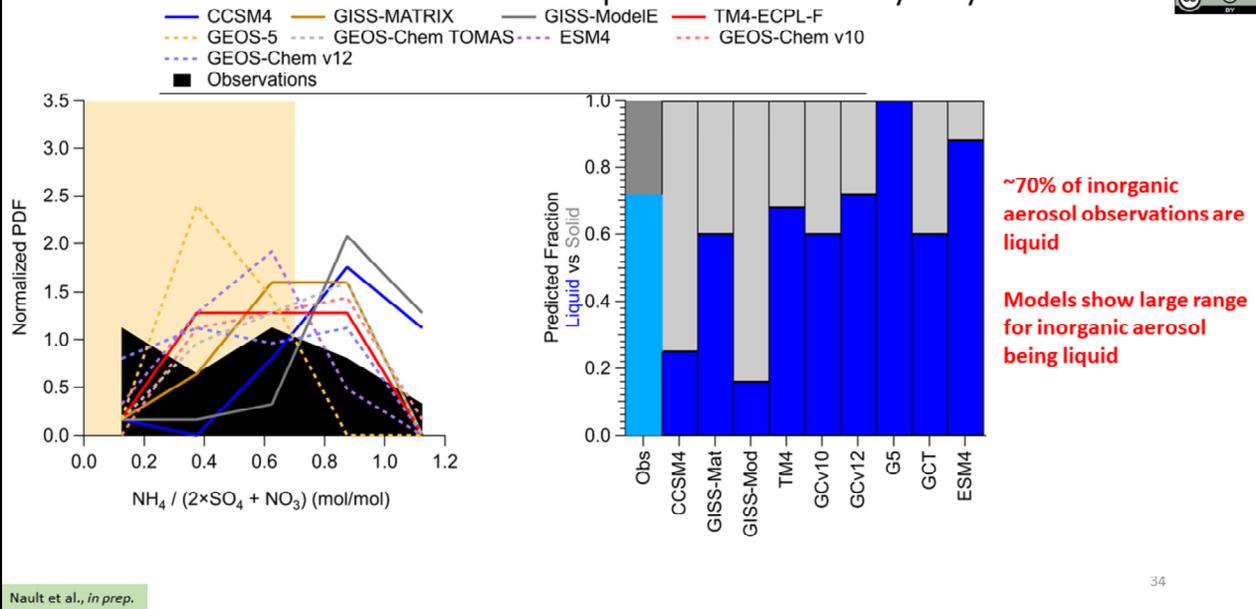
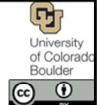
Nault et al., *in prep.*

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This difference in ammonium balance is important due to deliquescence/efflorescence of inorganic aerosol. Ammonium sulfate salts have different values (ammonium sulfate > ammonium bisulfate > sulfuric acid), meaning that the models with higher ammonium balances will have different estimations for amount of aerosol liquid water than observations.

I used the E-AIM thermodynamic model to estimate at what ammonium balance would be liquid (yellow background) vs solid (white background) for the average temperature and relative humidity of the boundary layer.

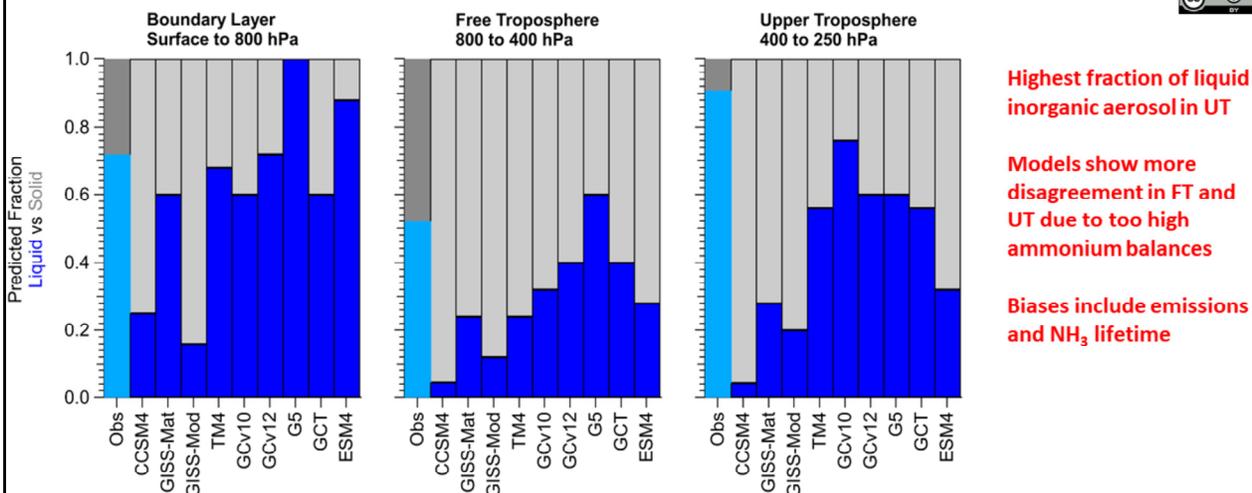
Using thermodynamic model, ammonium balance < 0.7 are liquid in Boundary Layer



I then transposed that estimate of solid vs liquid into the bar graph on right, where I represent the predicted fraction of inorganic aerosol that is liquid (blue shade) vs solid (grey shade), where observations are the different shades to better contrast.

The predictions from observation show that ~70% of the inorganic aerosol is liquid. The older models generally under-predict this fraction while the new models generally better predict the fraction, in the boundary layer.

High bias leads to models predicting more solid sulfate aerosol



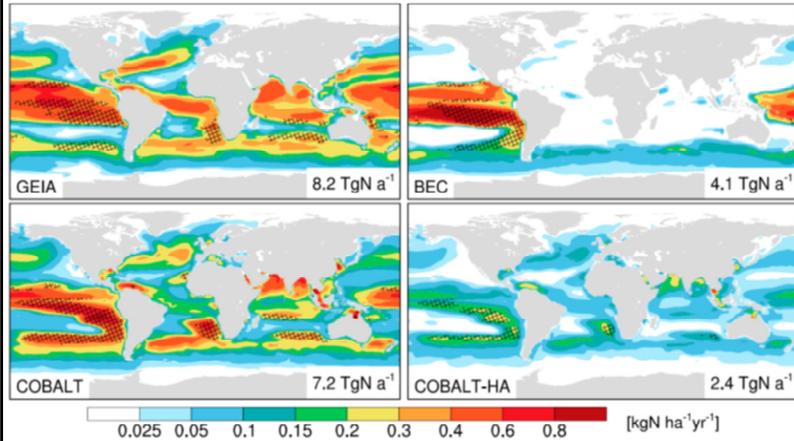
Highest fraction of liquid inorganic aerosol in UT

Models show more disagreement in FT and UT due to too high ammonium balances

Biases include emissions and NH₃ lifetime

However, outside the boundary layer, where relative humidity decreases, the difference in ammonium balance for the amount of inorganic aerosol that is liquid vs solid become more apparent, especially in the upper troposphere. Since the observations predict very low ammonium balances in the upper troposphere, this leads to very high amount of water in the inorganic aerosol as sulfuric acid typically retains water for tropospheric conditions. There are two important things that come from this analysis. First, these differences in liquid vs solid aerosol between observations and model would impact the models predictions of radiative balance and liquid phase chemistry (and aerosol pH). Second, these differences suggest that the models either overestimating NH₃ emissions or lifetime.

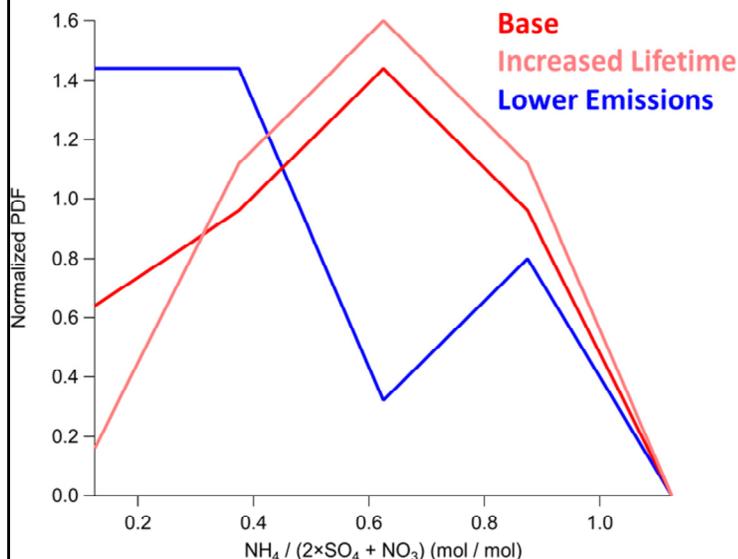
Large discrepancy in oceanic NH_x emissions from different emission inventories



- GEIA is 3.5× higher than updated estimates from Paulot et al.
- GEIA similar or lower than older estimates (up to factor 3 lower)

A paper in 2015 showed that many emission inventories greatly over-predict the NH_x emission from oceanic regions due to the general lack of data in this region.

Uncertainty in NH_x emissions and lifetime impacts our understanding of the aerosol radiative effect—Boundary Layer



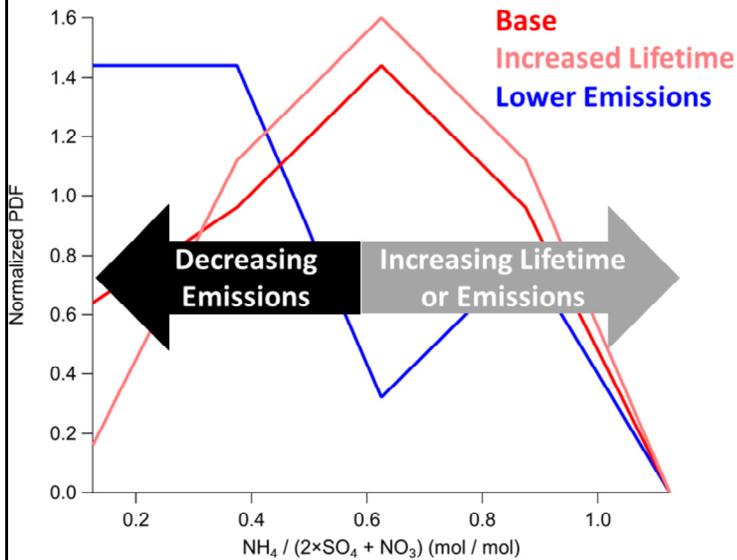
- All sensitivity analysis conducted with GEOS-Chem v12
- Base = Ocean Emissions
- Increased lifetime = reduced wet deposition
- Lower emissions = ocean emissions from Paulot et al. 2015

Nault et al., *in prep.*

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Thus, I ran a sensitivity analysis with GEOS-Chem to see how changes in NH_3 lifetime and changes in NH_3 emissions will impact ammonium balance. The base case (red) from GEOS-Chem is compared with increasing the NH_3 lifetime (light red) or lowering the NH_3 emissions, specifically oceanic NH_x oceanic emissions (blue). Increasing the NH_3 lifetime slightly shifts the PDF to the right (higher ammonium balance) whereas lowering the oceanic emissions strongly shifts the PDF to the left to be more similar to the observations.

Uncertainty in NH_x emissions and lifetime impacts our understanding of the aerosol radiative effect—Boundary Layer



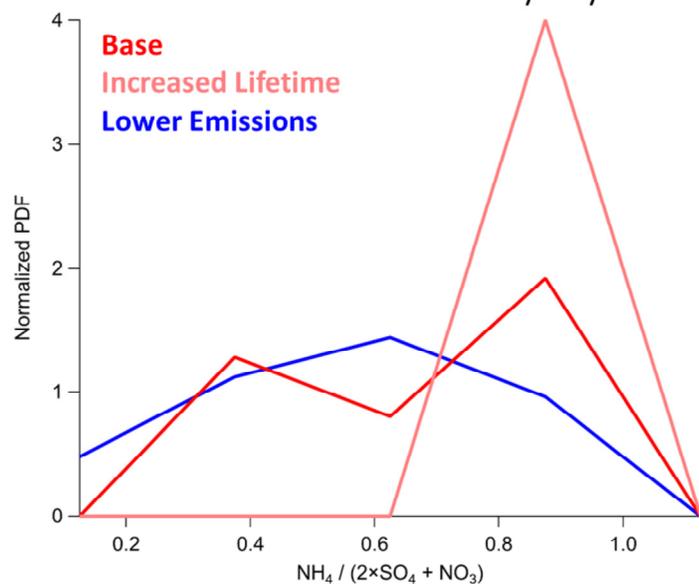
- All sensitivity analysis conducted with GEOS-Chem v12
- Base = Ocean Emissions
- Increased lifetime = reduced wet deposition
- Lower emissions = ocean emissions from Paulot et al. 2015

Nault et al., *in prep.*

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This highlights the shifts.

However, ammonium balance only sensitive to lifetime outside boundary layer



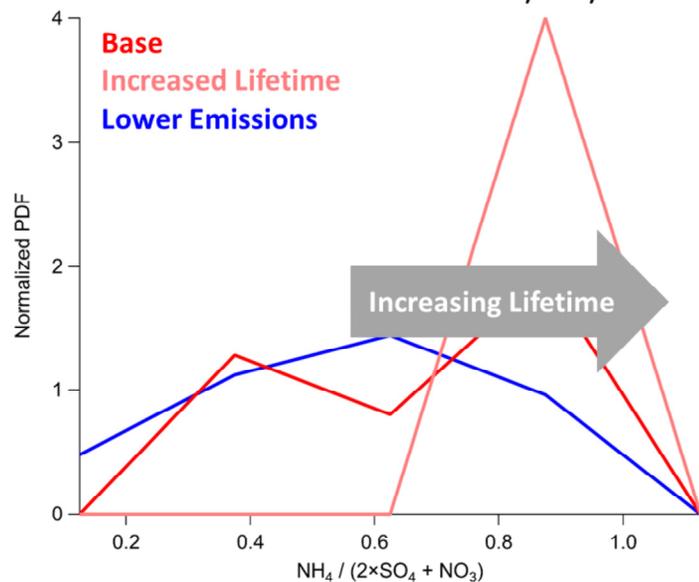
- All sensitivity analysis conducted with GEOS-Chem v12
- Base = Ocean Emissions
- Increased lifetime = reduced wet deposition
- Lower emissions = ocean emissions from Paulot et al. 2015

Nault et al., *in prep.*

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A similar analysis of this sensitivity is done for the upper troposphere. Increased NH_3 lifetime shifts the PDR all the way to high ammonium balances, similar to boundary layer. However, unlike boundary layer, decreasing NH_3 emissions has no impact on the upper tropospheric ammonium balance. Thus, something else is leading to the higher ammonium balances predicted in the model for the upper troposphere (to be determined).

However, ammonium balance only sensitive to lifetime outside boundary layer



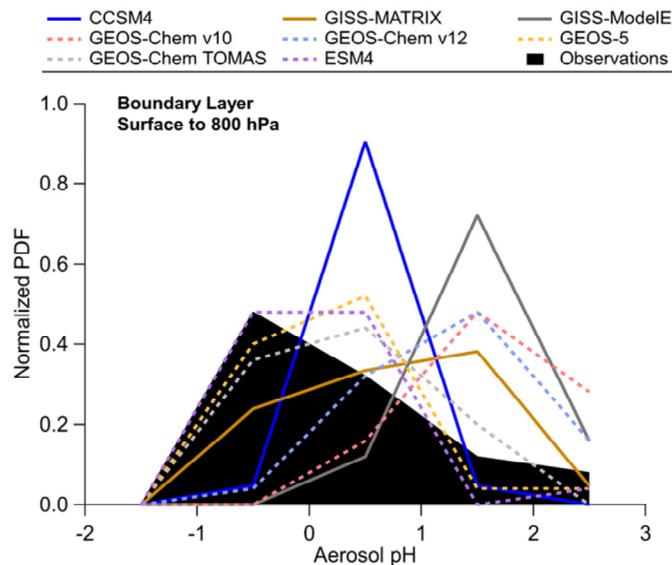
- All sensitivity analysis conducted with GEOS-Chem v12
- Base = Ocean Emissions
- Increased lifetime = reduced wet deposition
- Lower emissions = ocean emissions from Paulot et al. 2015

Nault et al., *in prep.*

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This highlights the results from the sensitivity.

Similar to ammonium balance,
the models show a range of distributions for aerosol acidity

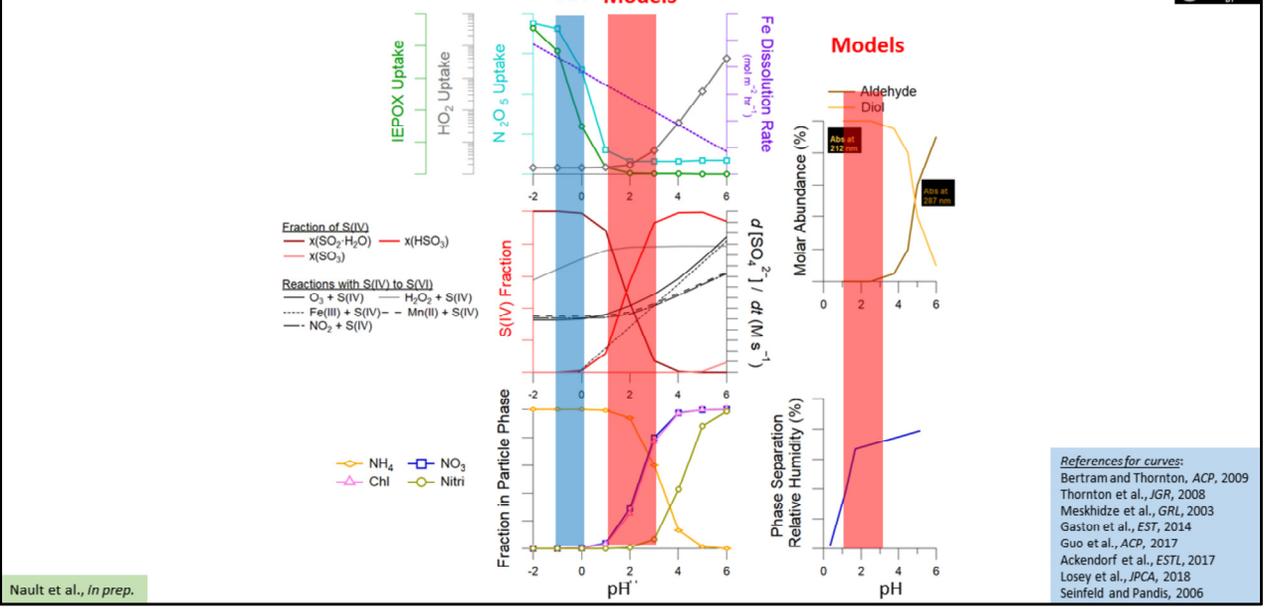


Nault et al., *in prep.*

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Finally, briefly, is the comparison of the predict aerosol pH from the chemical transport models compared to observations for the Boundary Layer. The models show better distribution, more similar to observations, than the ammonium balance. However, there are still high instances of aerosol pH greater than what the observations indicate.

Imply different chemistry for boundary layer compared to observations



The higher aerosol pH from the chemical transport would lead to different aerosol chemistry, if the models included all the processes highlighted here. This indicates the importance of not only evaluating the models chemical composition vs observations, but also their chemical properties such as aerosol pH.

