Emissions and chemistry of submicron aerosols and precursor gases during wintertime over the NE US

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WINTER campaign overview

Main themes

Multiphase NOy chemistry

Daytime NOx oxidation: $NO_2 + OH \xrightarrow{M} HNO_3$

Nighttime NOx oxidation:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5$$

$$N_2O_5 + H_2O_{(l)} \longrightarrow HNO_3$$

$$N_2O_5 + Cl^-_{(aq)} \longrightarrow ClNO_2$$

WINTER campaign overview

Main themes

Secondary aerosol formation

Sulfate formation: $SO_2 + OH \longrightarrow H_2SO_4 \longrightarrow SO_4^{2-}$

$SO_2 + H_2O_{2(aq)} \,/\, O_{3(aq)} \longrightarrow SO_4^{2-}$

Ammonium nitrate: $NH_{3(g)} + HNO_{3(g)} \longleftrightarrow NH_4^+ + NO_3^-$

Organic aerosols: $VOC + Oxidants \longrightarrow SOA$

WINTER campaign overview

Main themes

Wintertime emissions

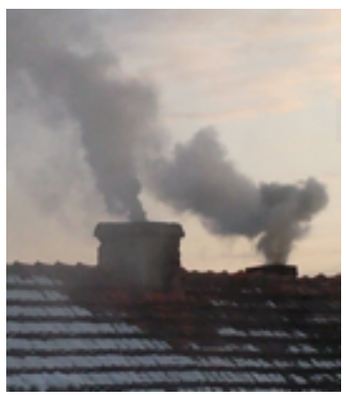
Power plants

SO_2, NOx

Vehicles

NOx,VOC

VOC,OA



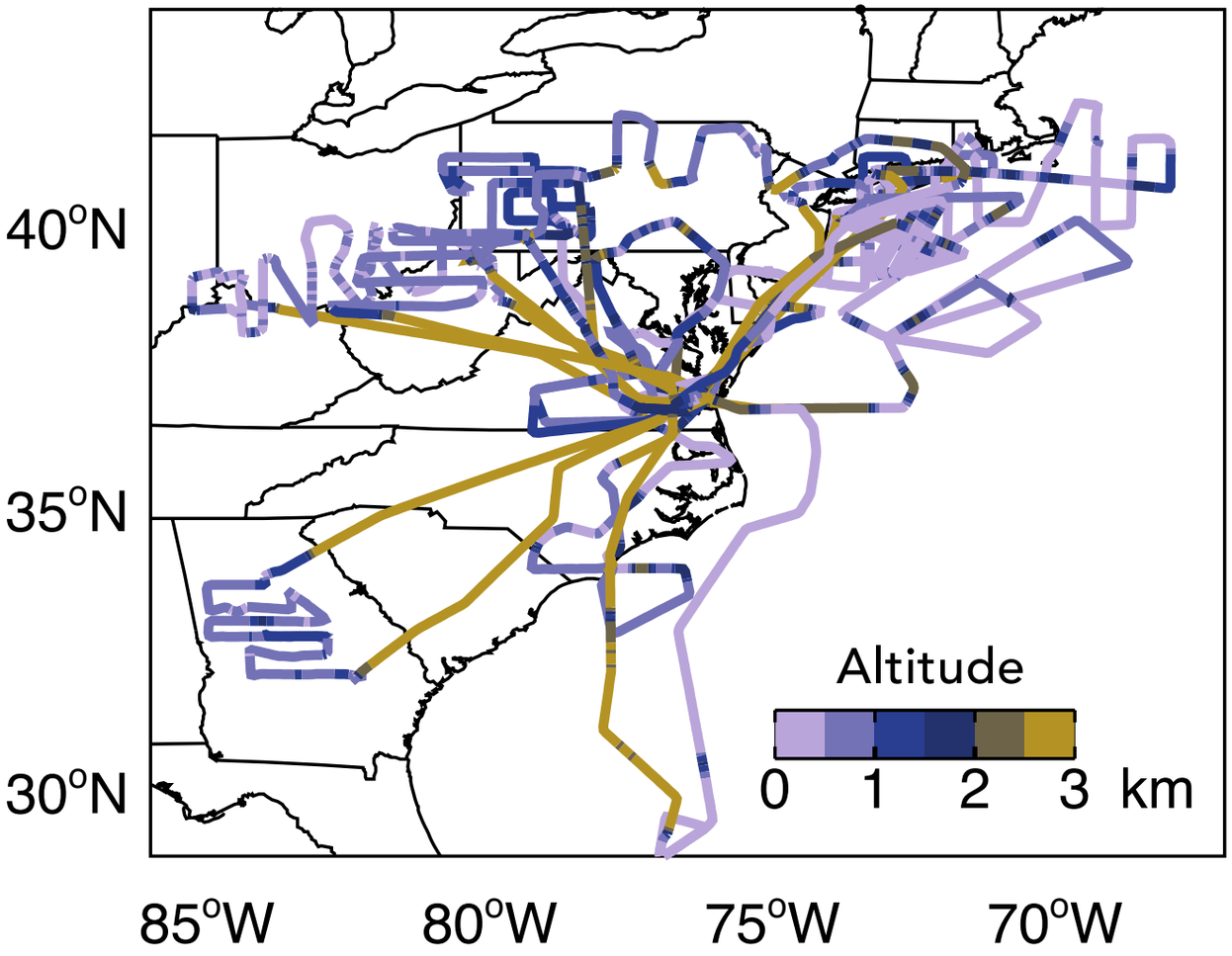
Home heating

Livestock

NH_3

WINTER field deployment

Feb. 1 – Mar. 15, 2015



- ✦13 research flights
- ✦71% of flight time < 1 km
- ✦50% of flight time at night

Measurements

Particles:

SO_4^{2-}, NO_3^-, NH_4^+,Organic aerosol,

Cl^-,Na^+,Ca^{2+},K^+,Mg^{2+}

(**AMS**, PILS, Filter-based)

Gases:

SO_2, NO, NO_2, NO_y,HNO_3,N_2O_5,

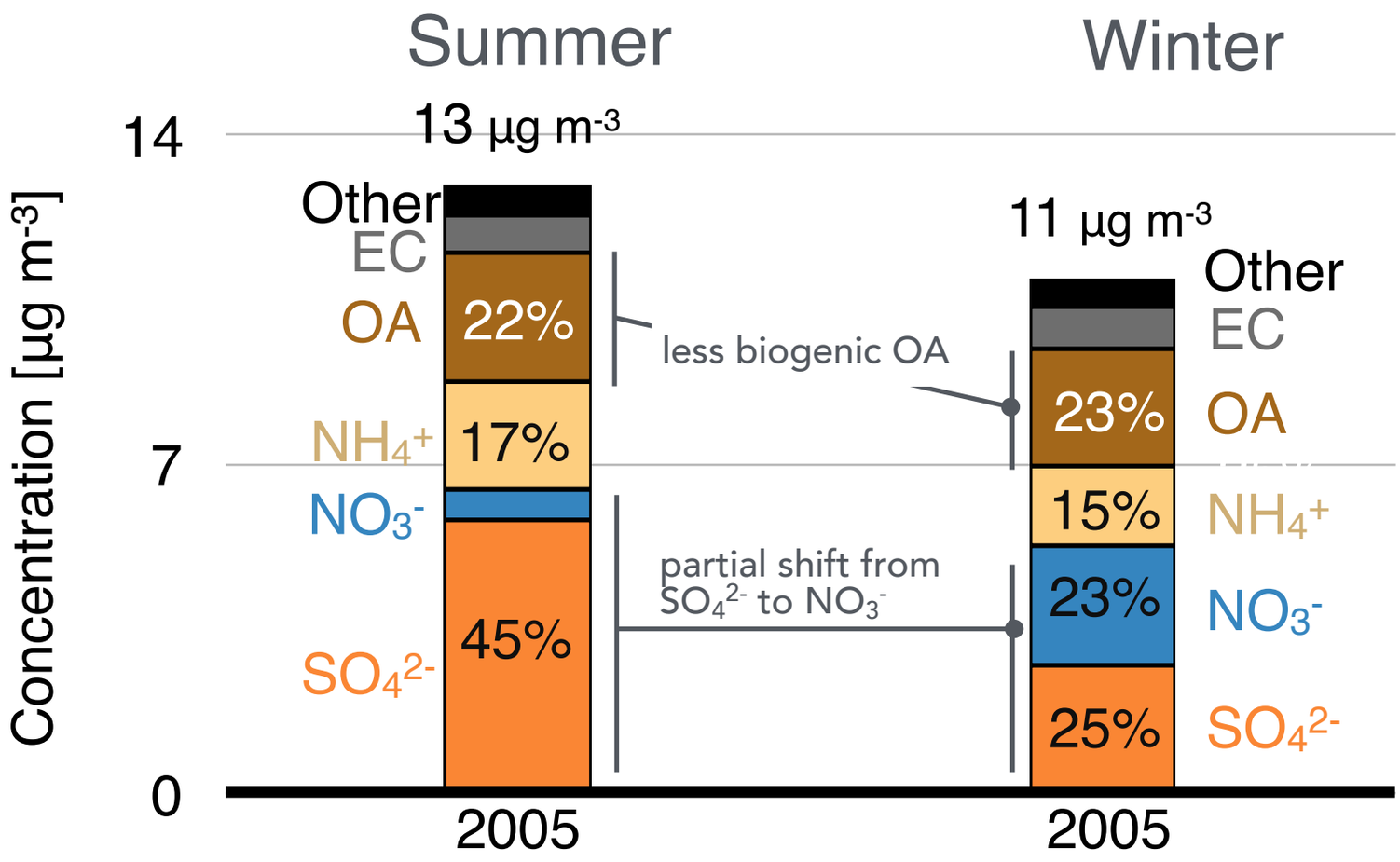
$ClNO_2$,HONO,ANs,PNs,O_3,CO,etc

Meteorological variables, aerosol size distribution, actinic flux

Modeling: GEOS-Chem

Summer vs. wintertime aerosols over eastern U.S.

Chemical Speciation Network surface observations [U.S. EPA]



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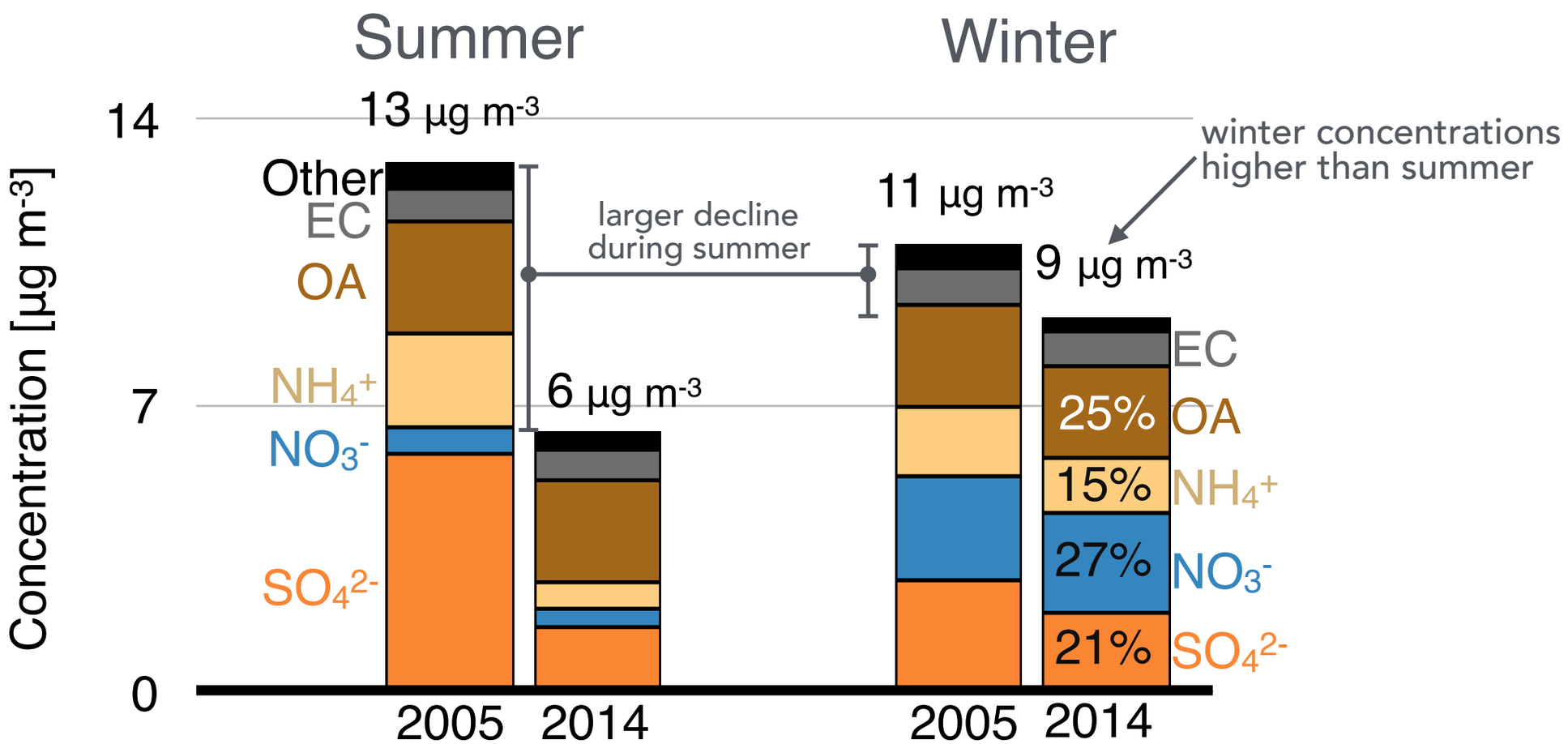
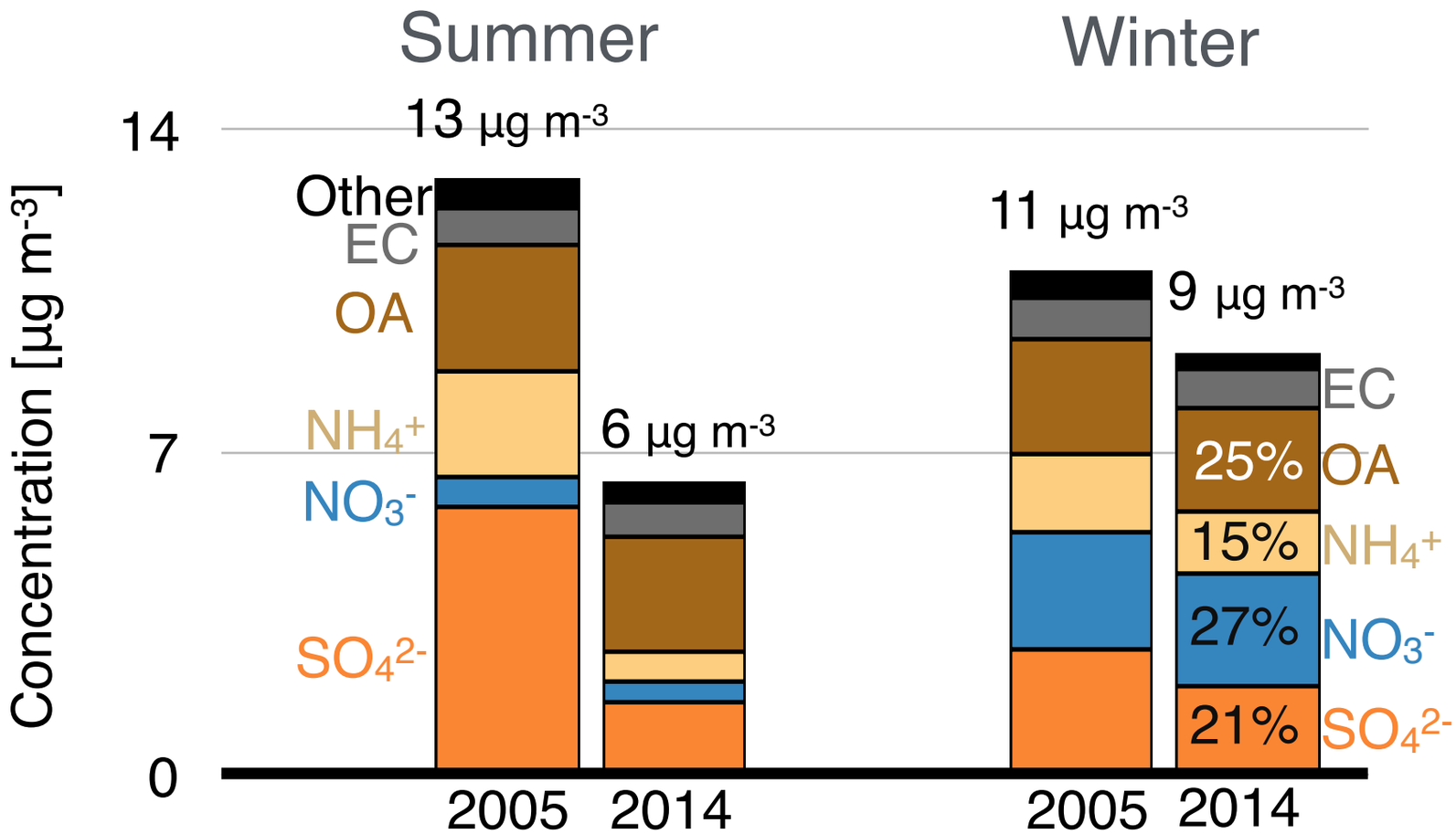
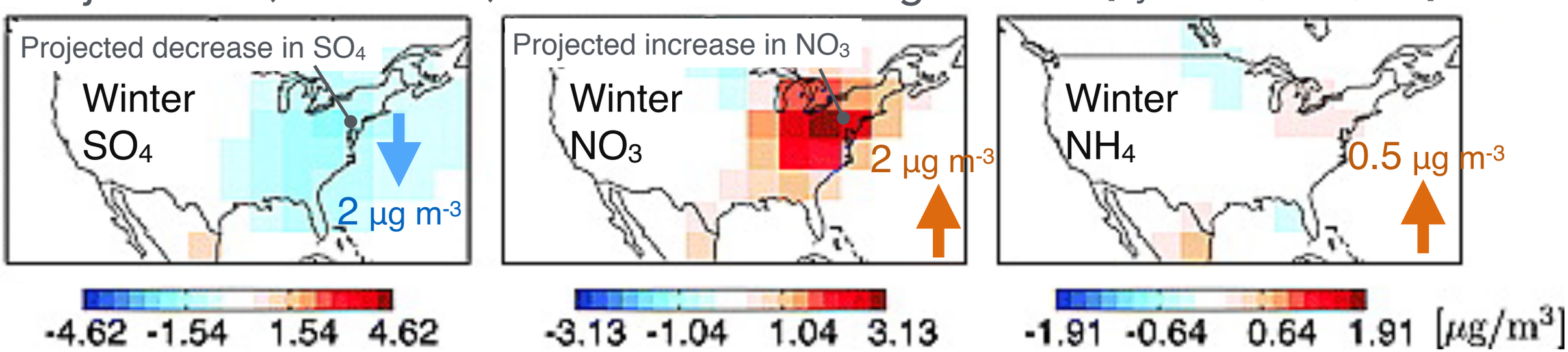


Wintertime aerosols over eastern U.S.

Chemical Speciation Network surface observations [U.S. EPA]



Projected Δ (2050-2000) from emission changes alone [Pye et al., 2009,JGR]



GEOS-Chem modeling for WINTER

System:

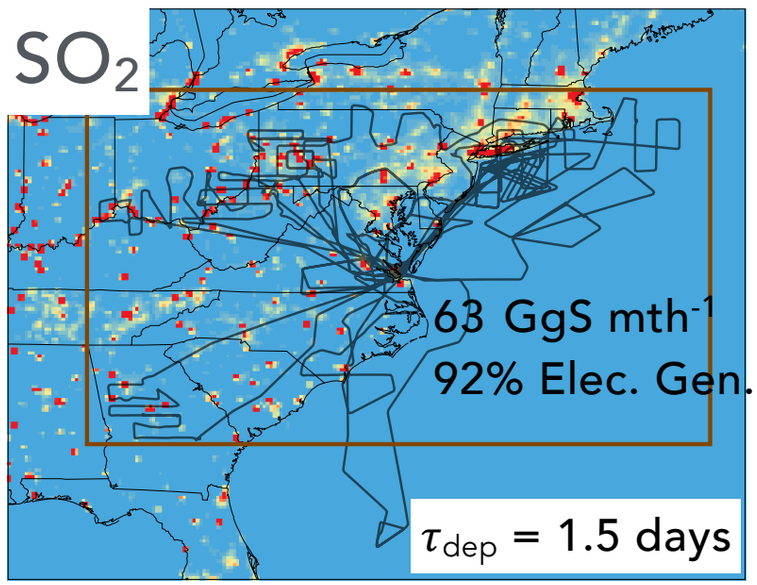
- v10-01, NASA GMAO GEOS-FP meteorological fields
- 0.5°×0.625° nested-grid model, 47 vertical layers
- NEI 2011 (v6.0) emissions scaled to 2015.
- Gas-phase, aqueous-phase, & heterogeneous chemistry.
- Gas-particle equilibrium using ISORROPIA for inorganics.

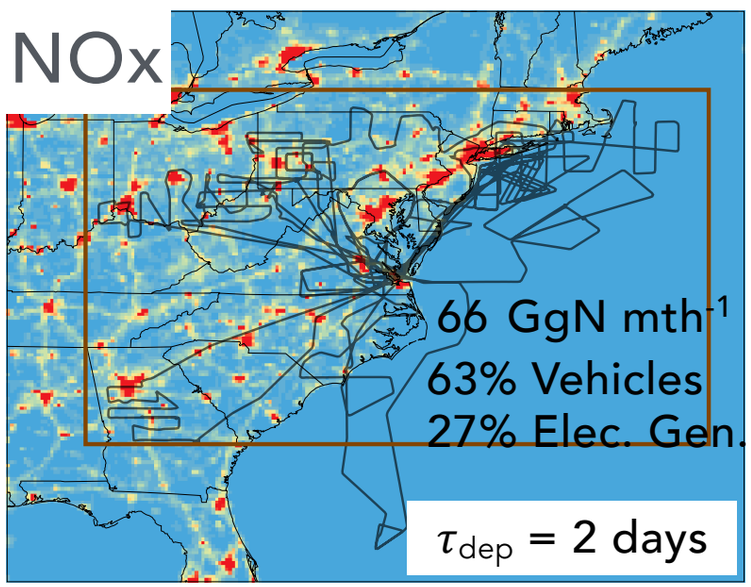
Modifications to GEOS-Chem:

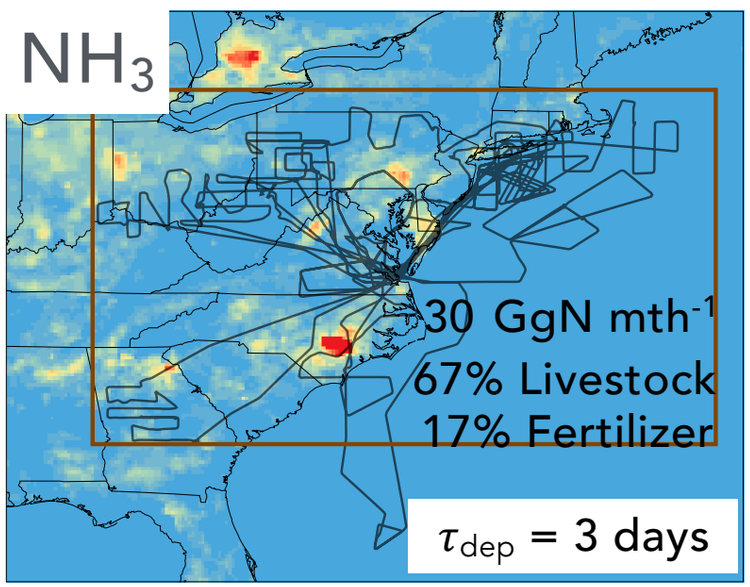
- Fe/Mn catalyzed SO_2 oxidation [Alexander et al. 2009, JGR]
- N_2O_5 heterogenous reaction [Bertram & Thornton, 2009, ACP]
- HNO_3 dry deposition [Wesely and Hicks, 2000, Atmos Env.]
- Simplified POA-SOA chemistry [Hodzic and Jimenez, 2011, GMD; Kim et al., 2015, ACP].

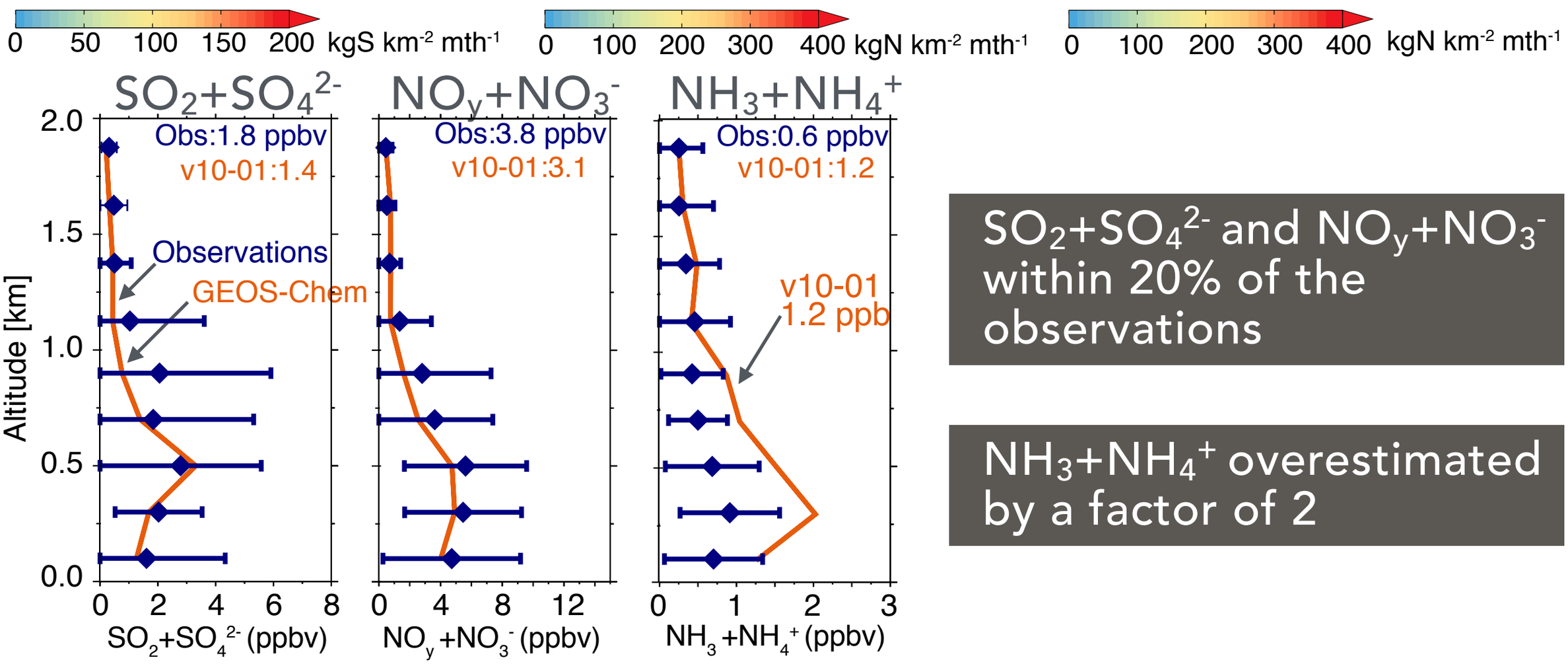
Emissions & lifetimes of SO_2, NO_y, NH_3

Emissions: NEI 2011 scaled to 2015









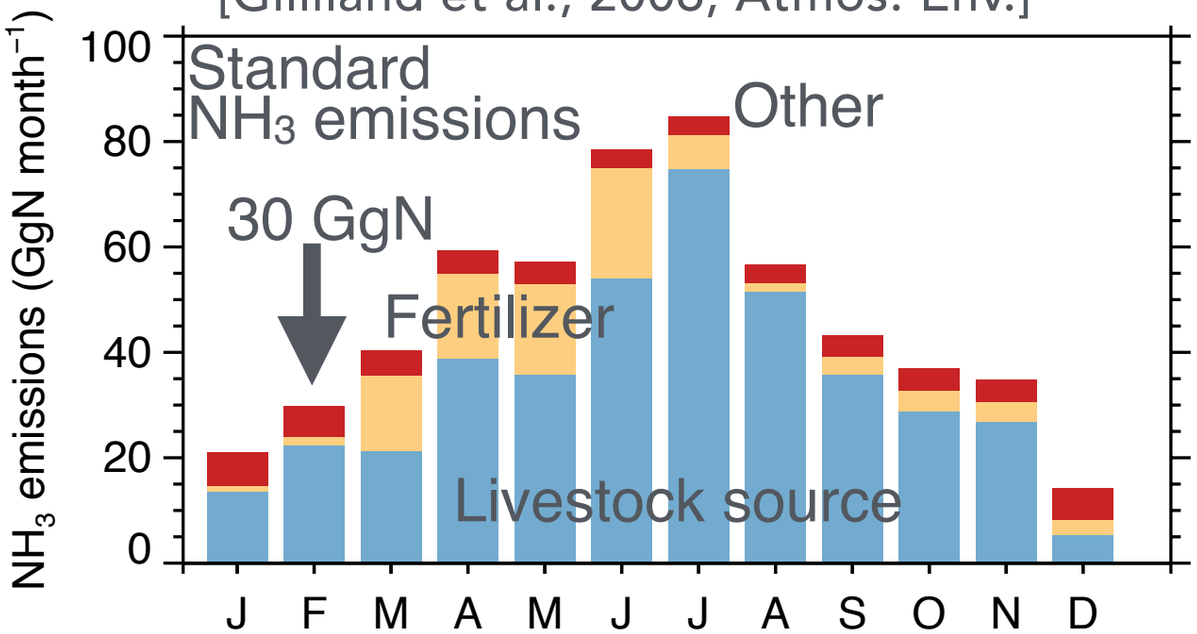
$SO_2+SO_4^{2-}$ and $NO_y+NO_3^-$ within 20% of the observations

$NH_3+NH_4^+$ overestimated by a factor of 2

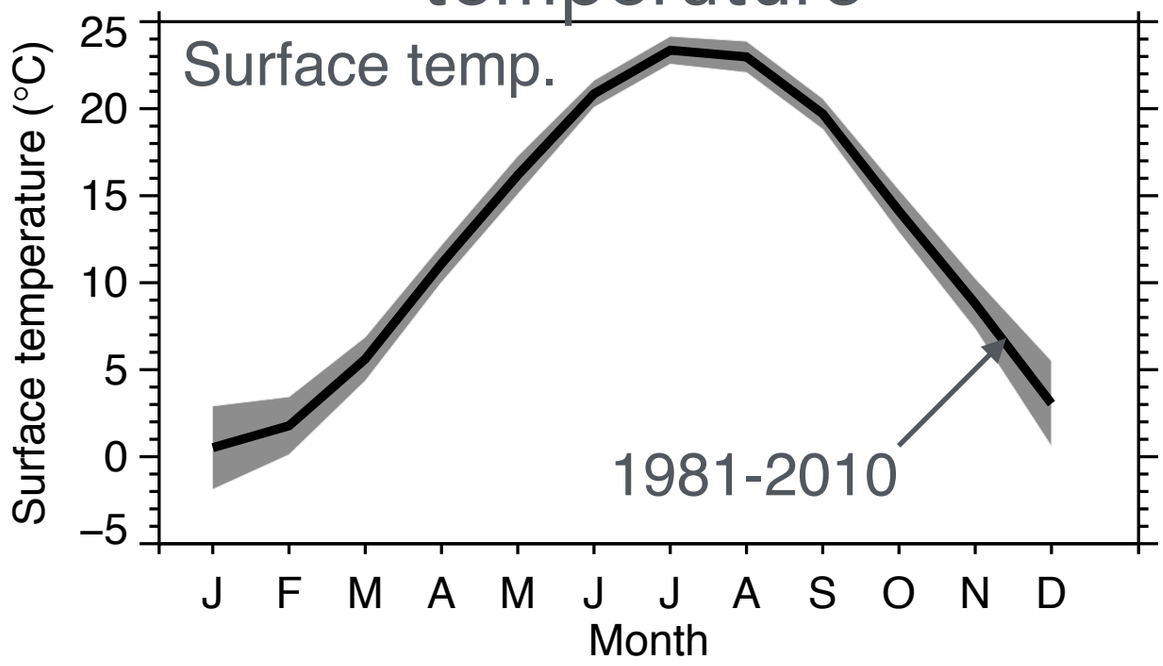
Seasonality of NH_3 emissions

Standard seasonal NH_3 emissions

[Gilliland et al., 2006, Atmos. Env.]



Eastern U.S. surface temperature



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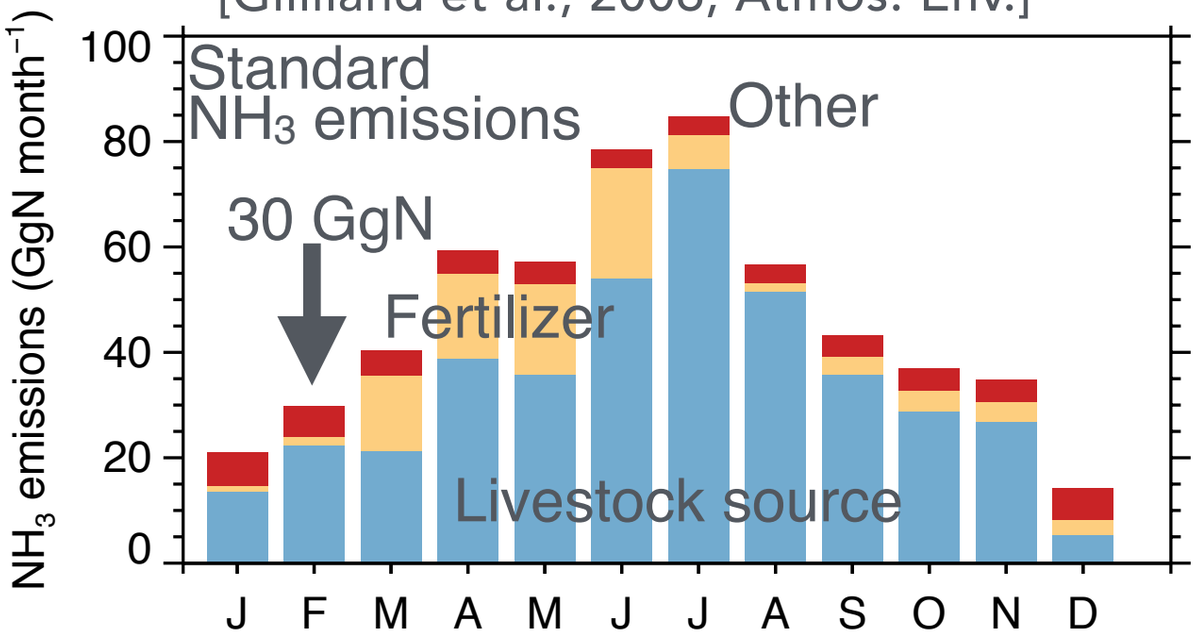

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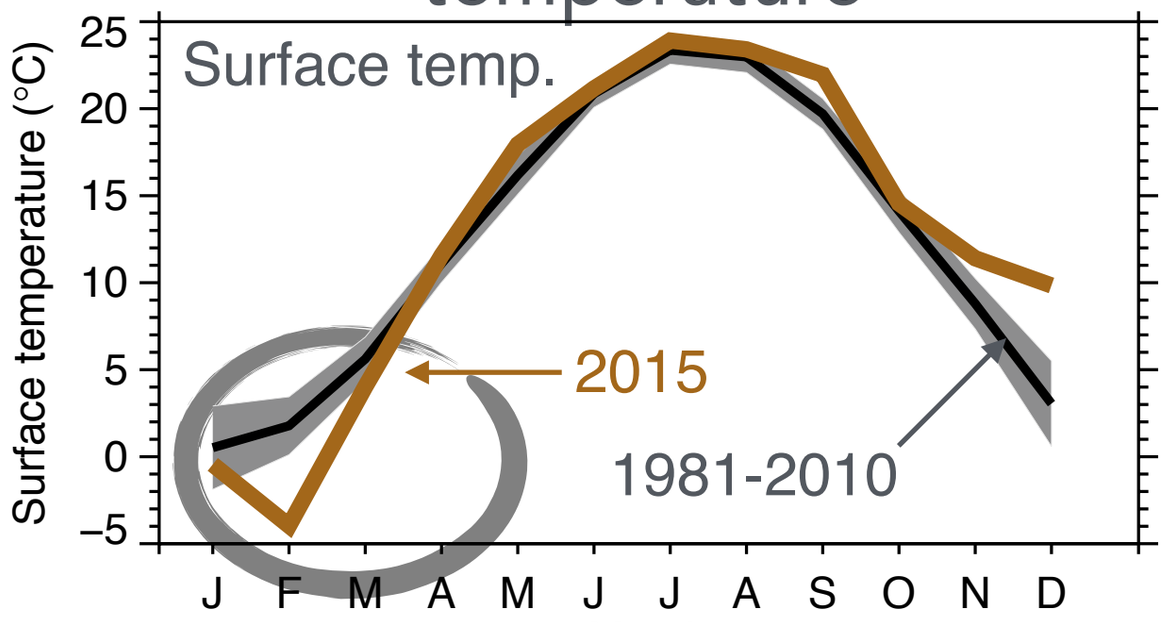
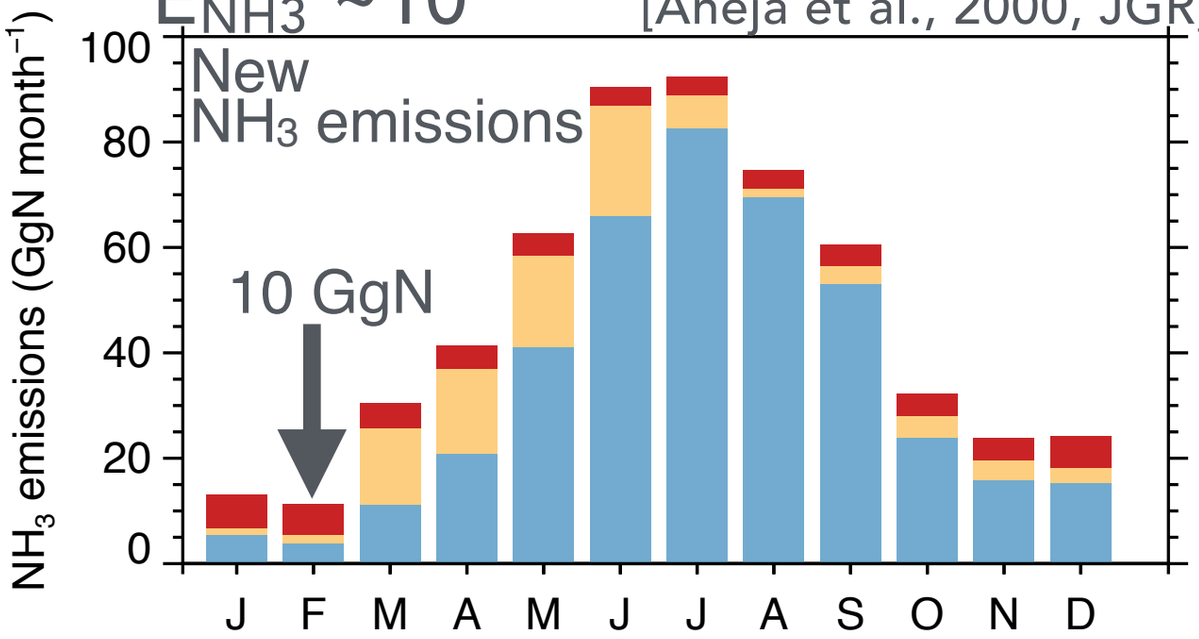
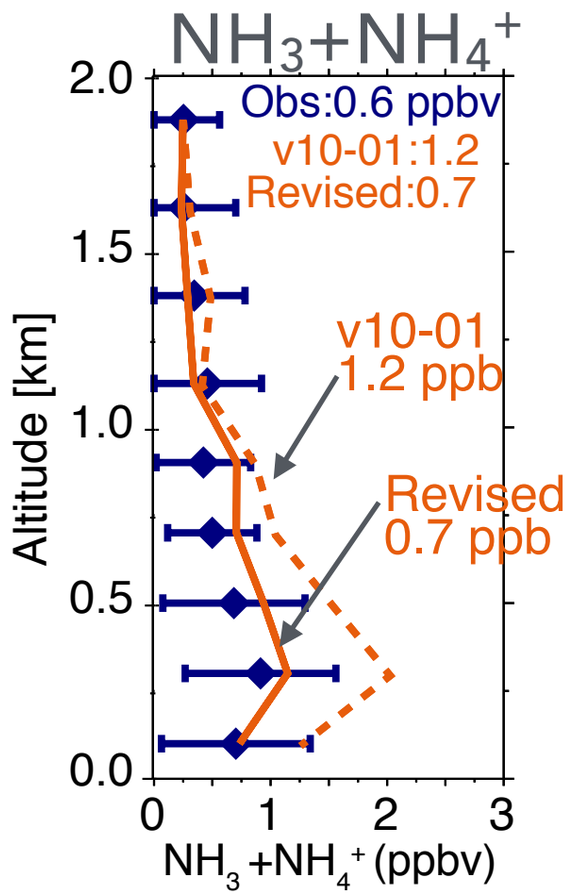


Recalculated livestock emissions

$E_{NH3} \sim 10^{0.48*T}$ [Aneja et al., 2000, JGR]

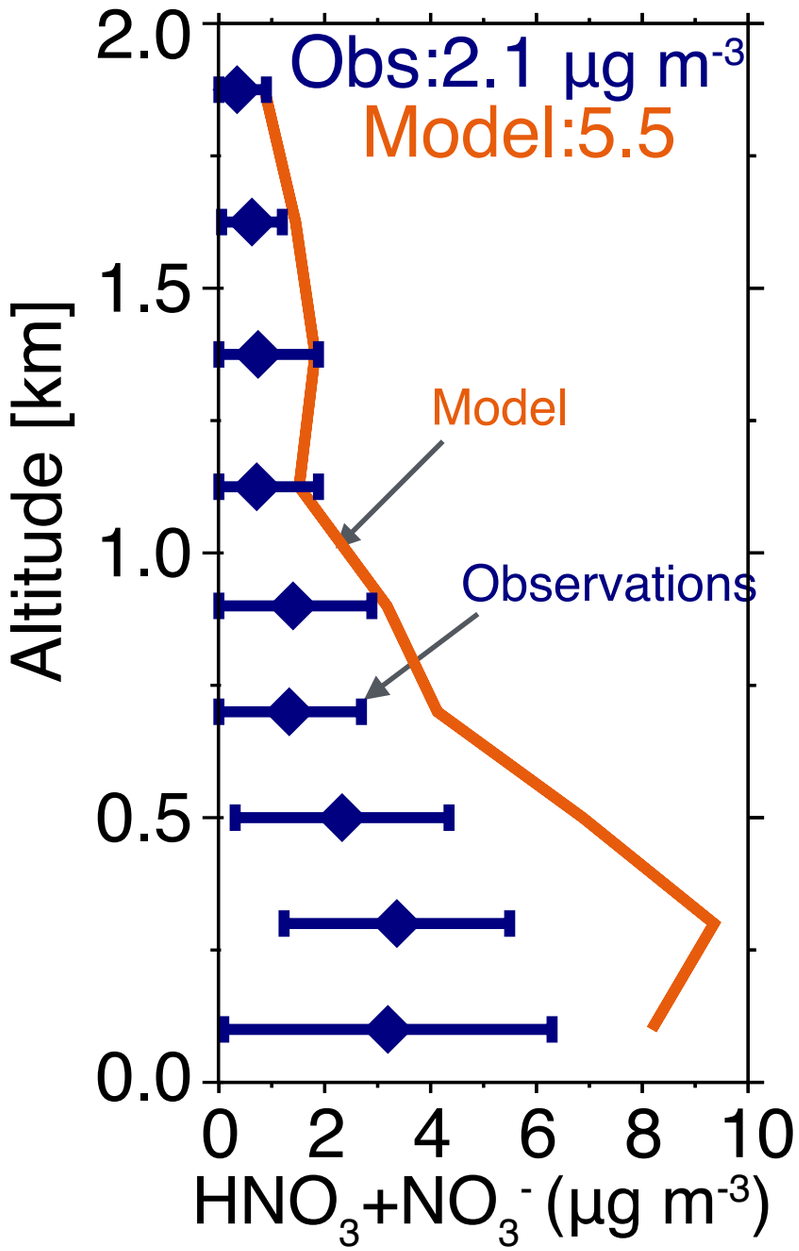




$NH_3+NH_4^+$ overestimate reduced to <20% with year-specific emissions

Model overestimate of total nitrate

Total nitrate (HNO_3+NO_3^-)

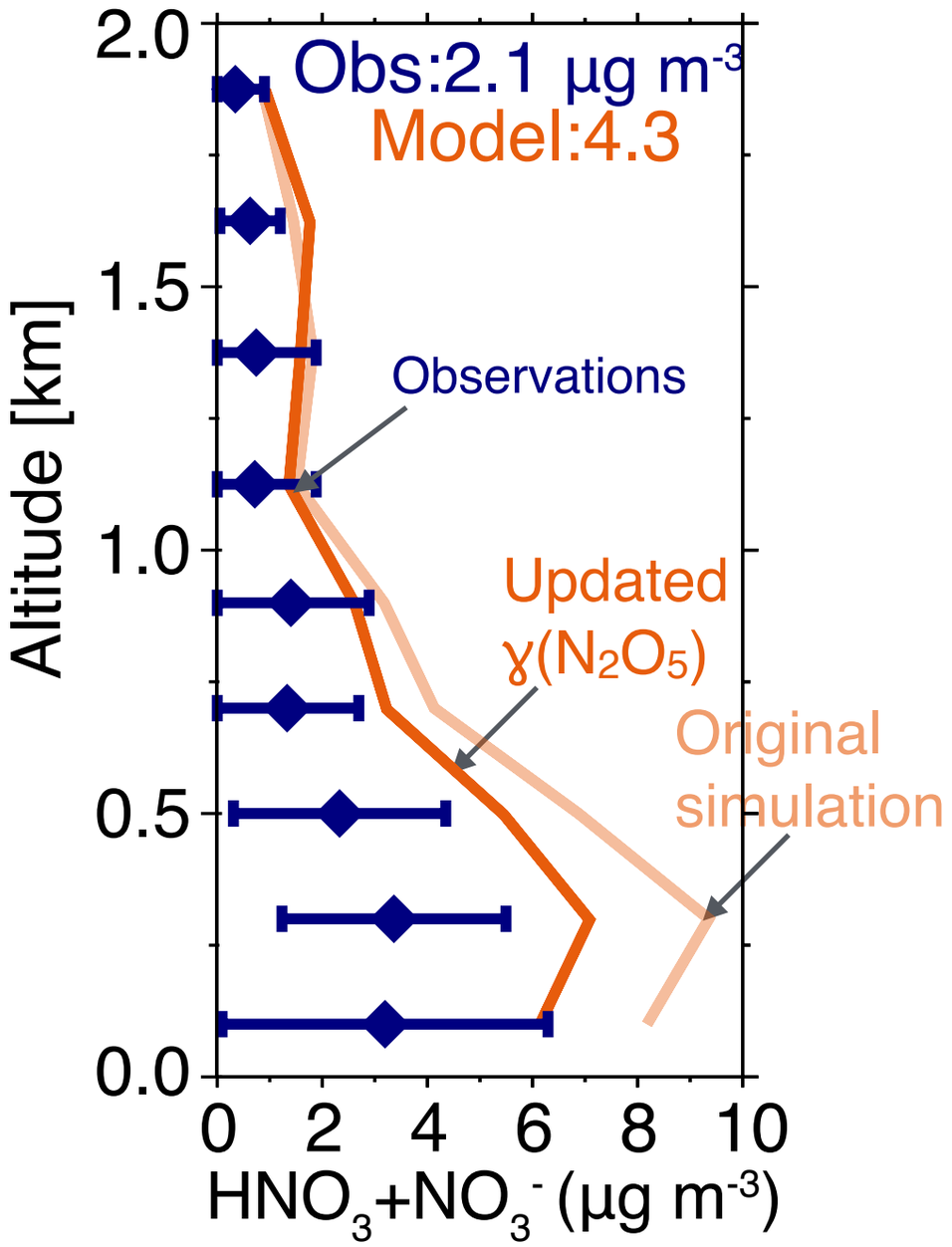


- Nitrate overestimate noted in previous studies.
  [Heald et al., 2012,ACP; Zhang et al., 2012, ACP]
- Faster production and/or slower loss?

2.5 times overestimate in original modeled HNO_3+NO_3^-.

Total nitrate production too fast

Total nitrate (HNO_3+NO_3^-)



N_2O_5 hydrolysis:

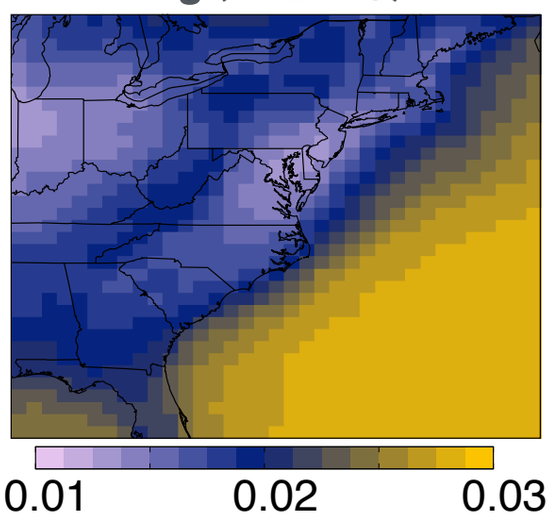
Original $\gamma(N_2O_5)$~0.02
[Evans and Jacob, 2005,GRL]

Update $\gamma(N_2O_5)$ to lab studies
[Bertram and Thornton,2009,ACP;
Badger et al.,2006,ACP]

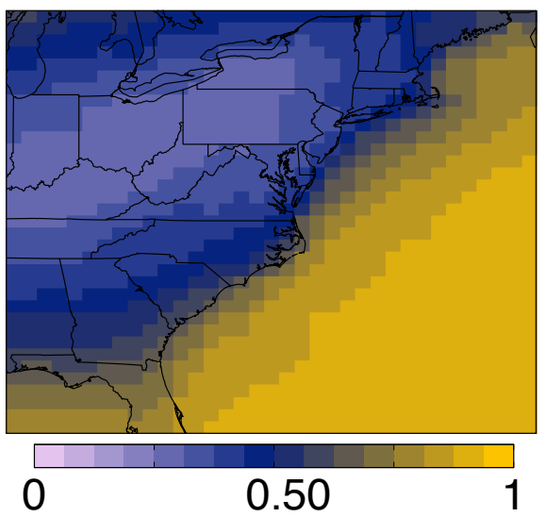
$$N_2O_5 + H_2O_{(l)} / Cl^-_{(aq)} \xrightarrow{\gamma} \Phi ClNO_2 + (2-\Phi)HNO_3$$

$\gamma(N_2O_5), \Phi(ClNO_2) \sim f(H_2O, NO_3^-, Cl^-)$

$\gamma(N_2O_5)$



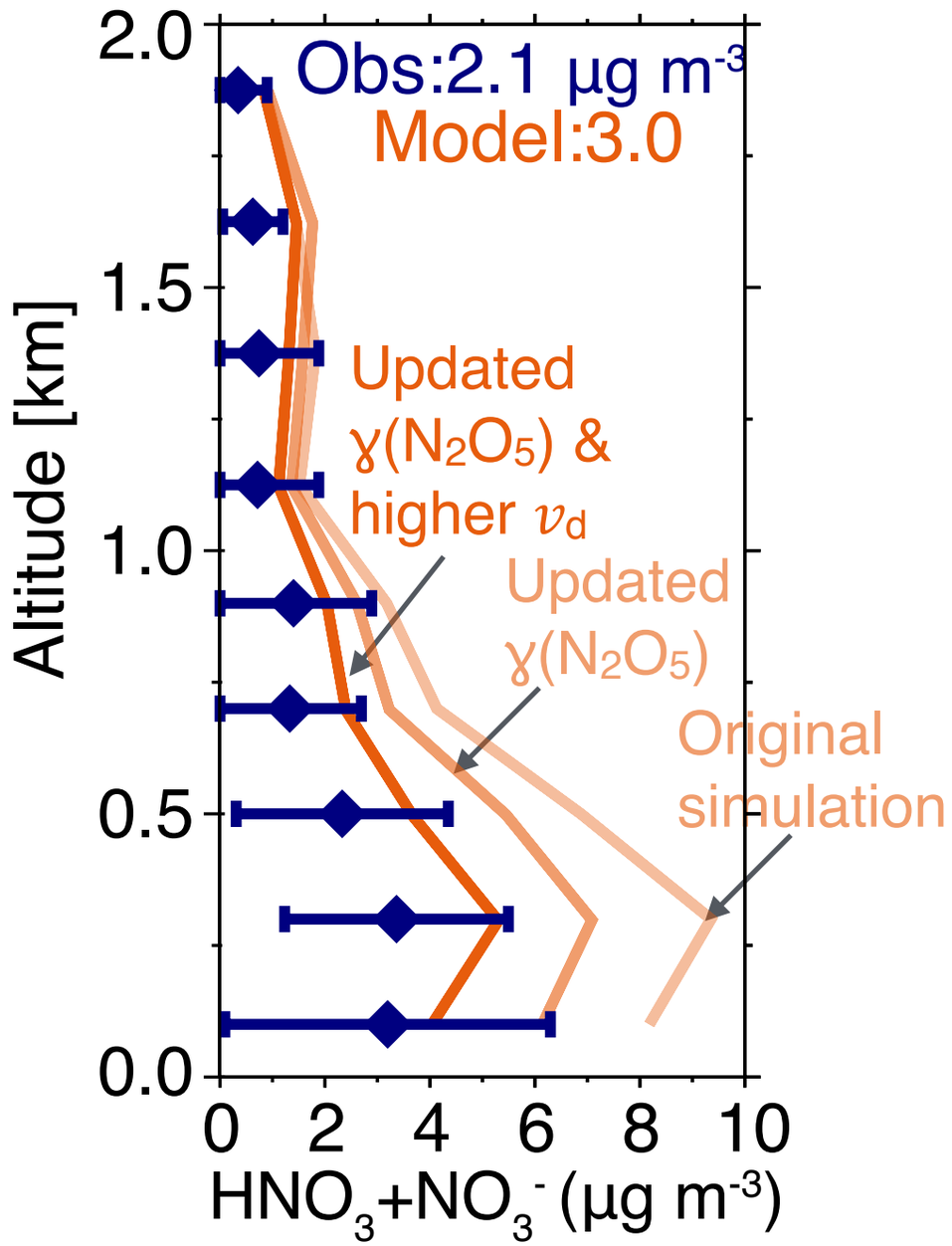
$\Phi(ClNO_2)$



Updated $\gamma(N_2O_5)$ reduces overestimate in HNO_3+NO_3^-.

HNO_3 deposition too slow

Total nitrate (HNO_3+NO_3^-)



HNO_3 dry deposition:

Original surface resistance (Rc) high over snow
[Johansson and Granat,1986, Atmos. Env.]

Set Rc = 0
[Wesely and Hicks,2000,Atmos Env; Björkman et al.,2013,Tellus]

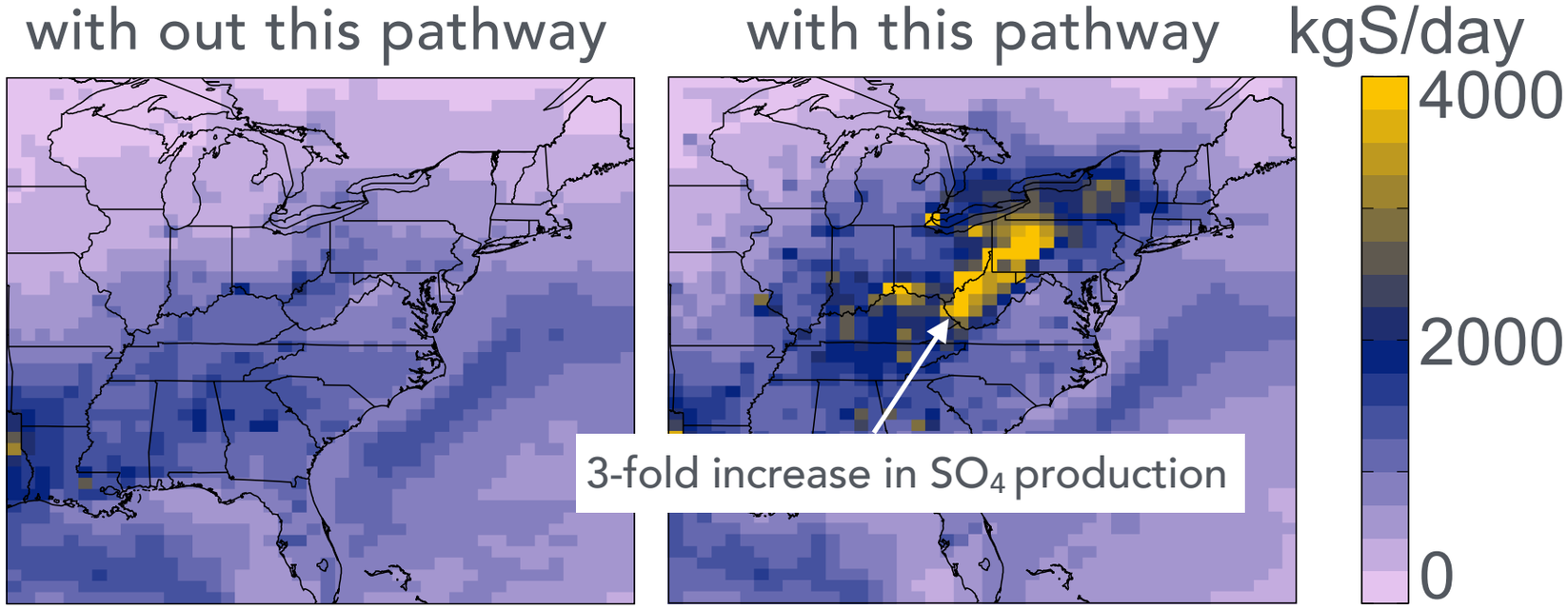
Revised v_d ~1-4 cm s^{-1}

Updated $\gamma(N_2O_5)$ & higher v_d decreases overestimate to <50%.

Fe^{3+}/Mn^{2+} catalyzed sulfate production

$$SO_2 + O_{2(aq)} \xrightarrow{Fe^{3+} / Mn^{2+}} SO_4^{2-}$$

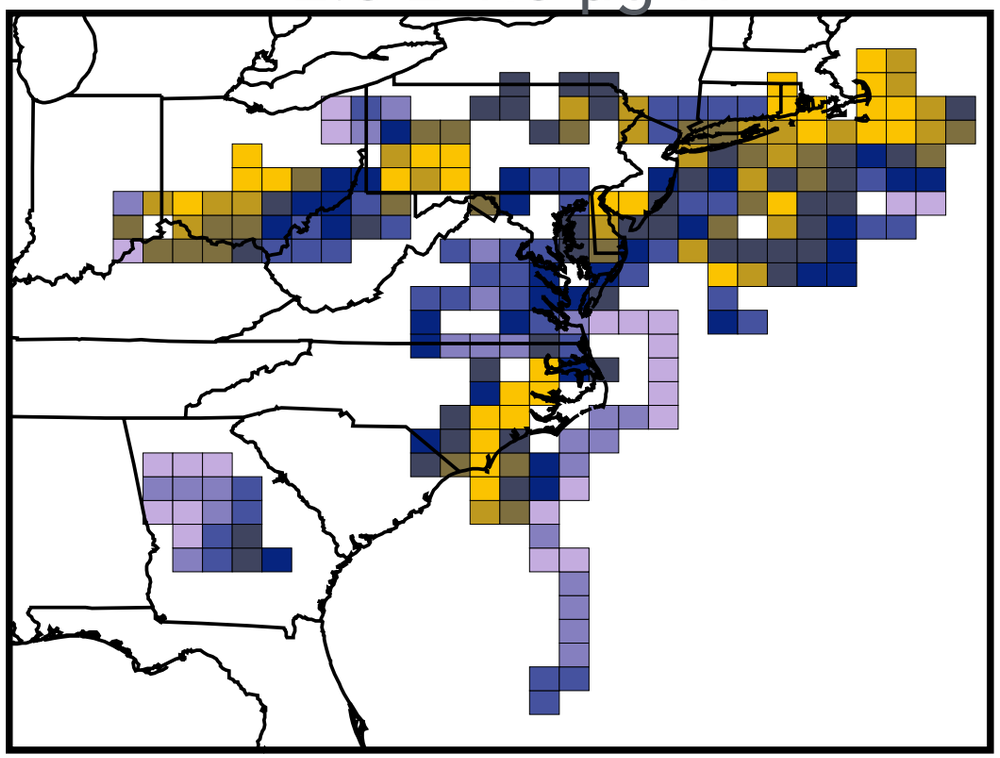
Sulfate production (below 2 km)



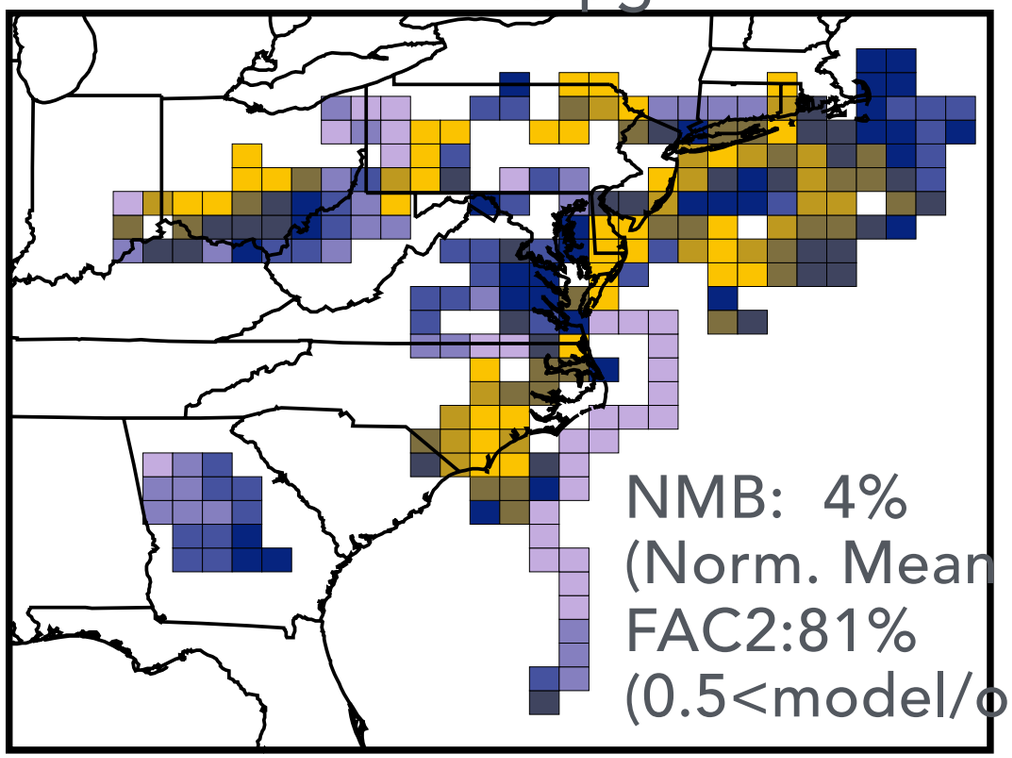
Transition metal catalyzed oxidation is significant during winter

$SO_4^{2-} + NO_3^- + NH_4^+$

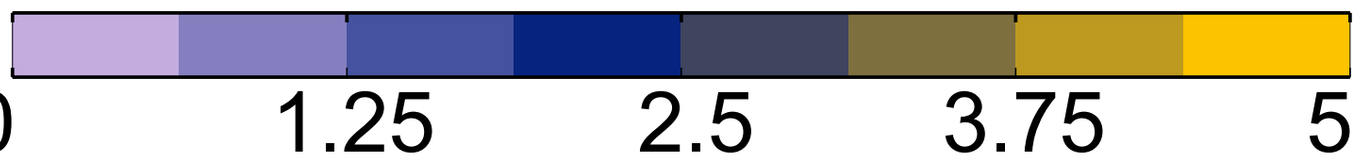
AMS Observations:
2.6 ± 1.5 μg m^{-3}



GEOS-Chem:
2.7 ± 1.9 μg m^{-3}



NMB: 4%
(Norm. Mean Bias)
FAC2:81%
(0.5<model/obs<2)



Total $SO_4^{2-} + NO_3^- + NH_4^+$ in good agreement with observations.

$SO_4^{2-} + NO_3^- + NH_4^+$

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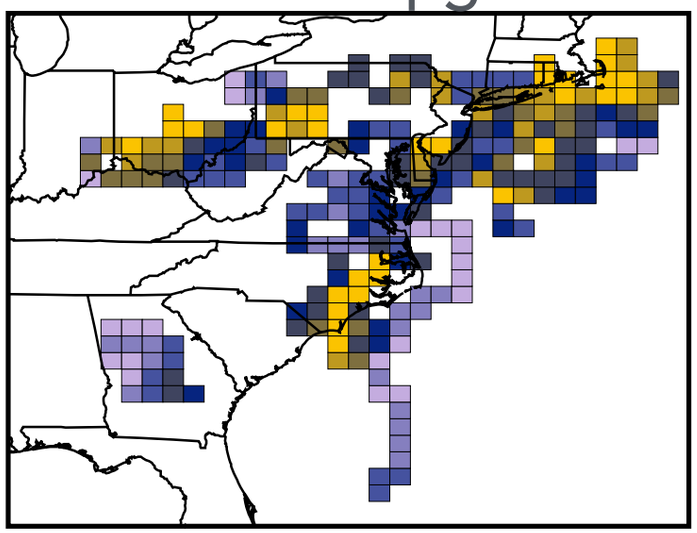

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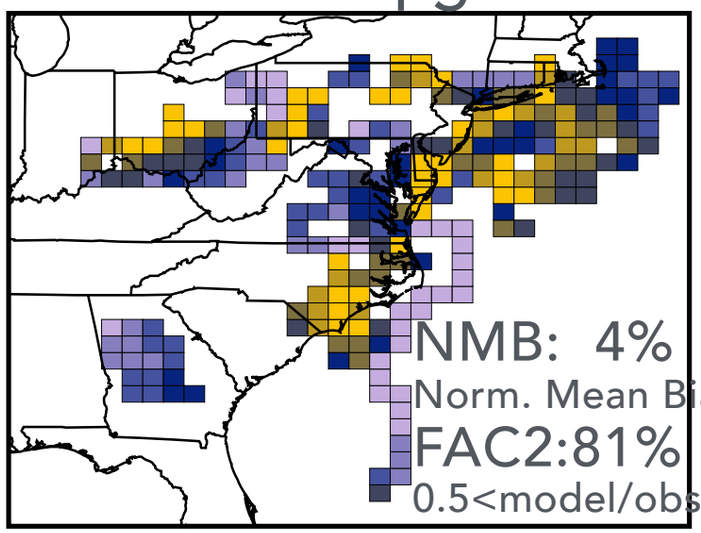

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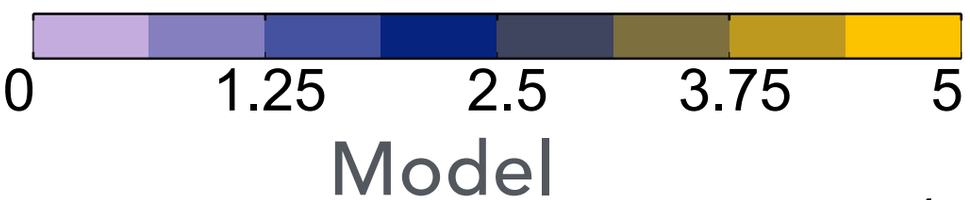
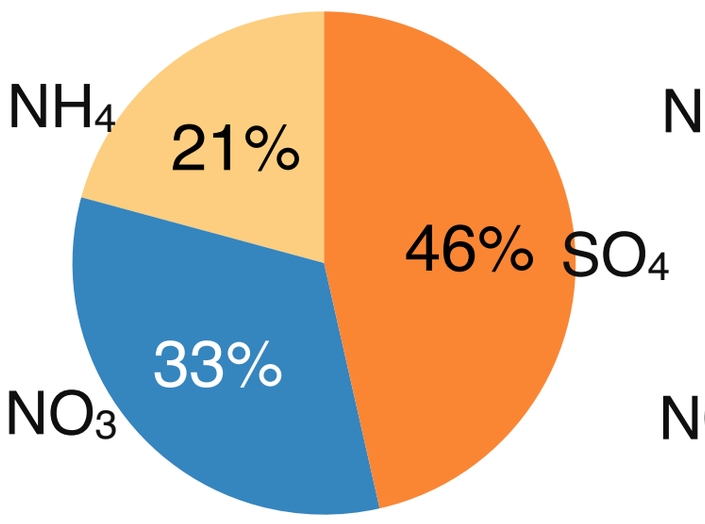
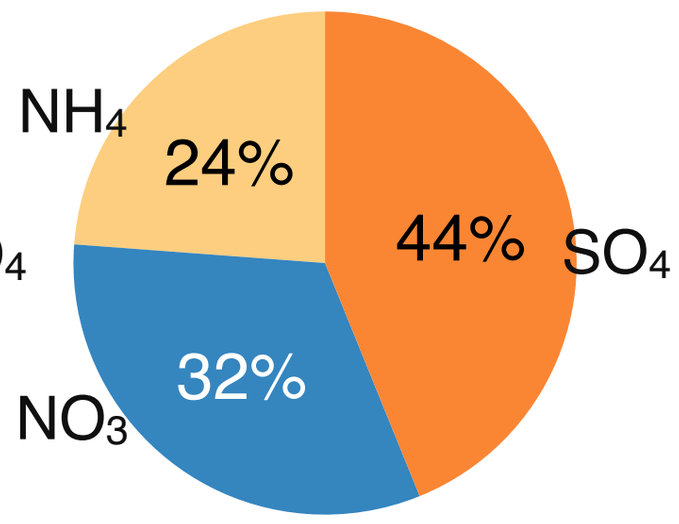


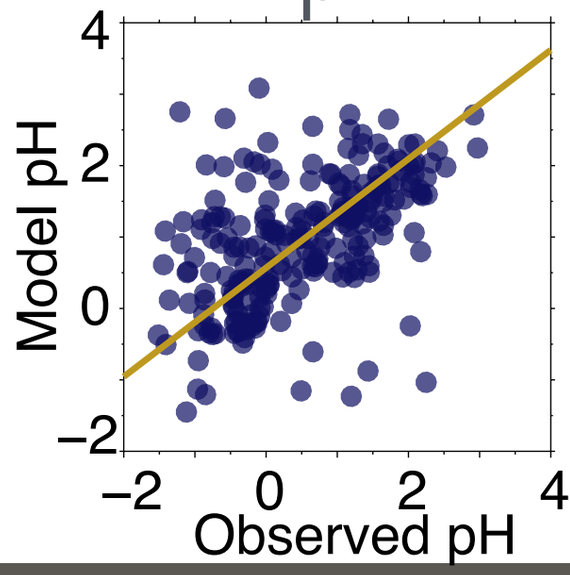
Observed



Model



pH



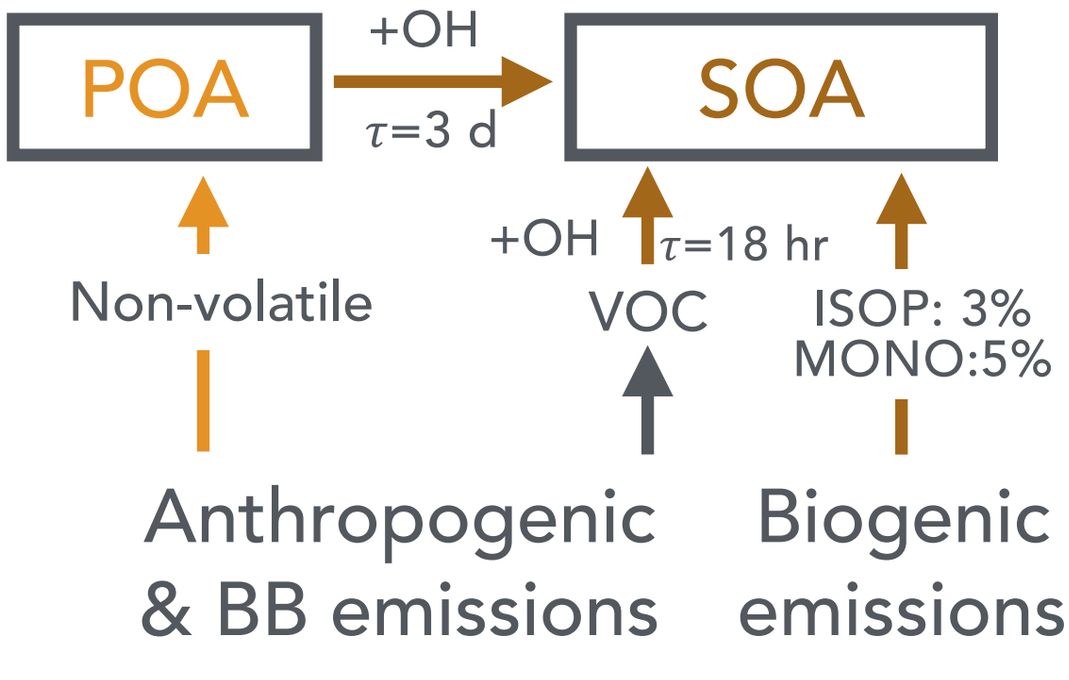
Obs:0.6
[Guo et al., 2016, JGR]

Model:1.0

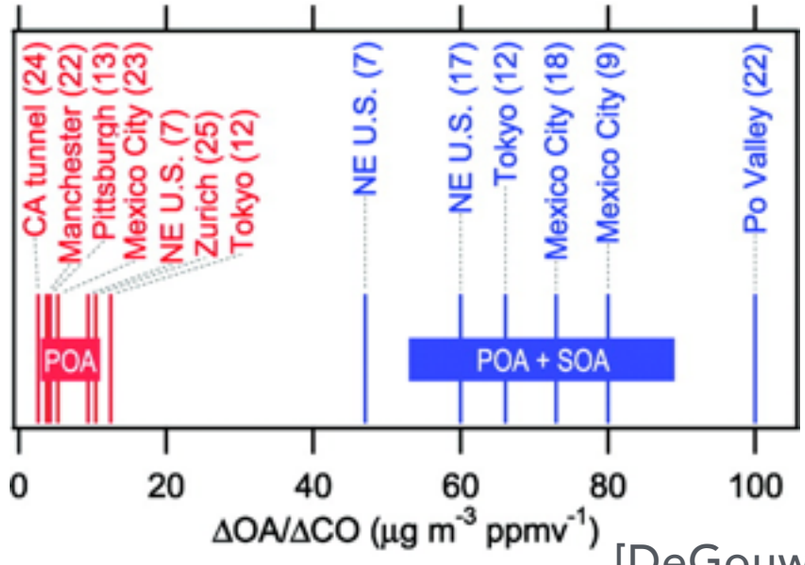
- Total $SO_4^{2-} + NO_3^- + NH_4^+$ in good agreement with observations.
- Aerosol composition well reproduced.
- Highly acidic aerosol, model pH 0.4 units higher.

Simplified SOA formation scheme

[Hodzic & Jimenez, 2011, GMD, Kim et al., 2015, ACP]



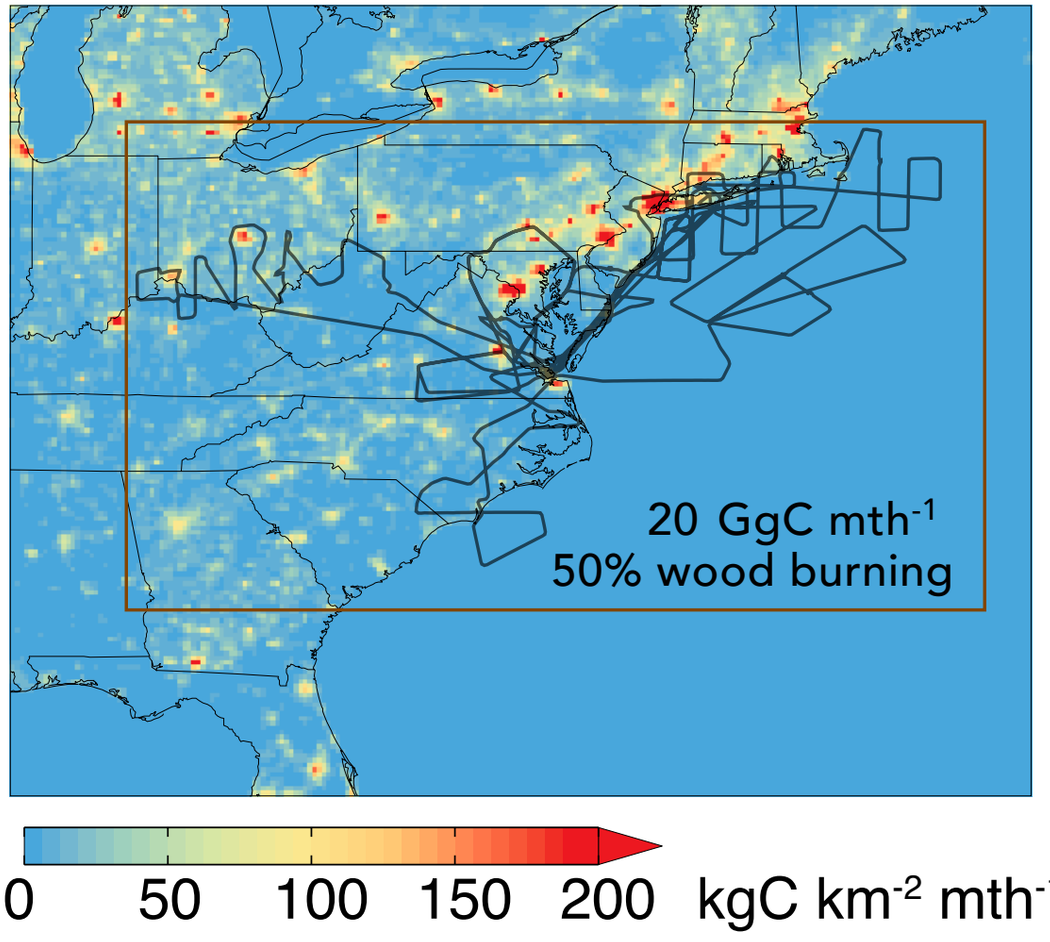
Based on observed SOA evolution in urban areas

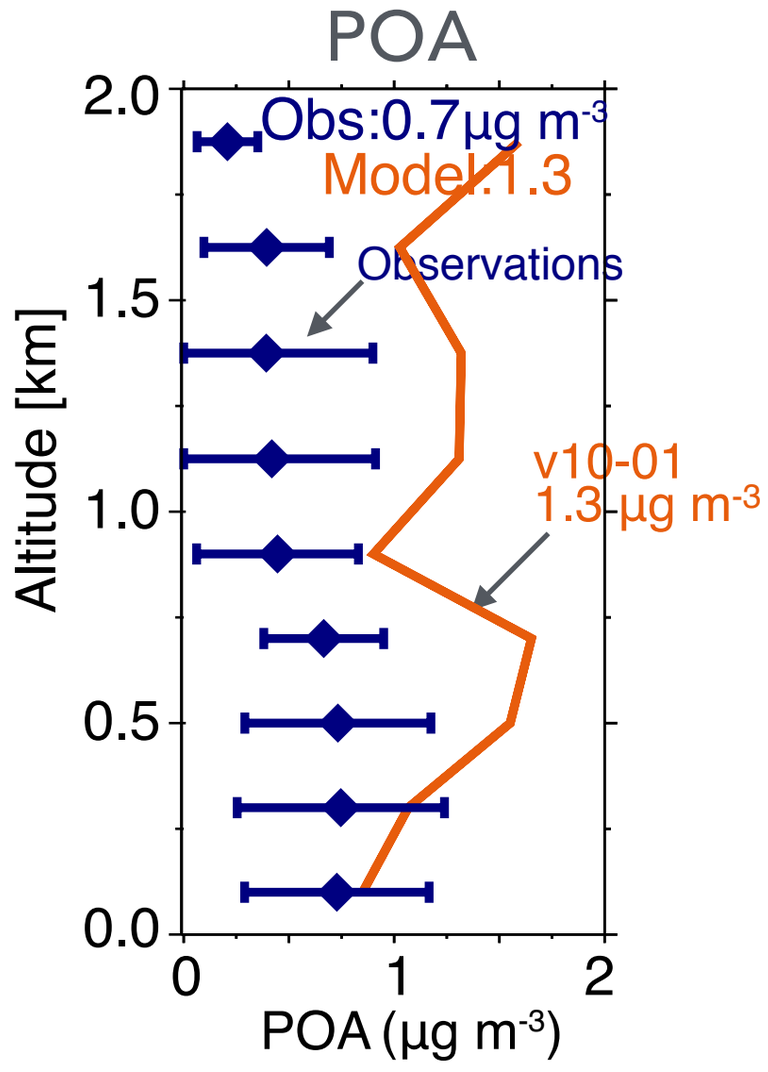


[DeGouw & Jimenez, 2009, ES&T]

Emissions organic carbon aerosols

Emissions: NEI 2011 scaled to 2015



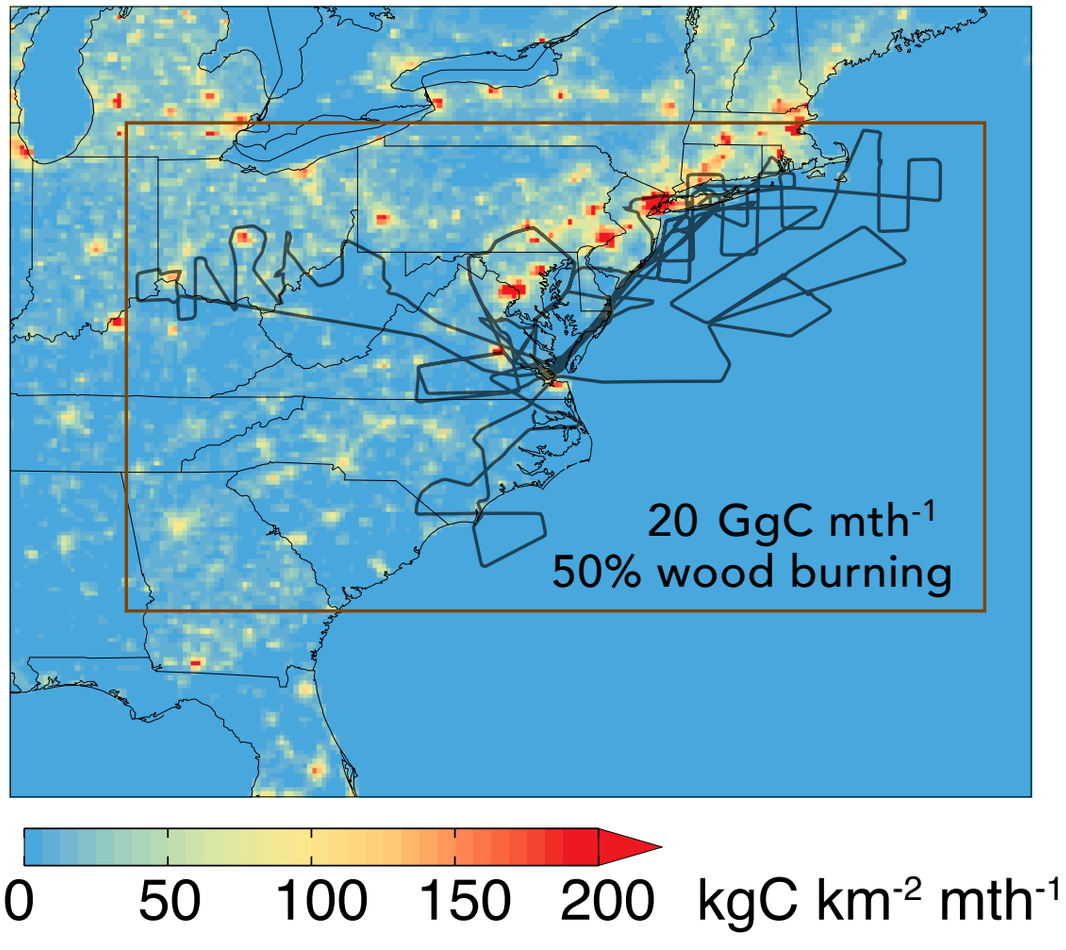


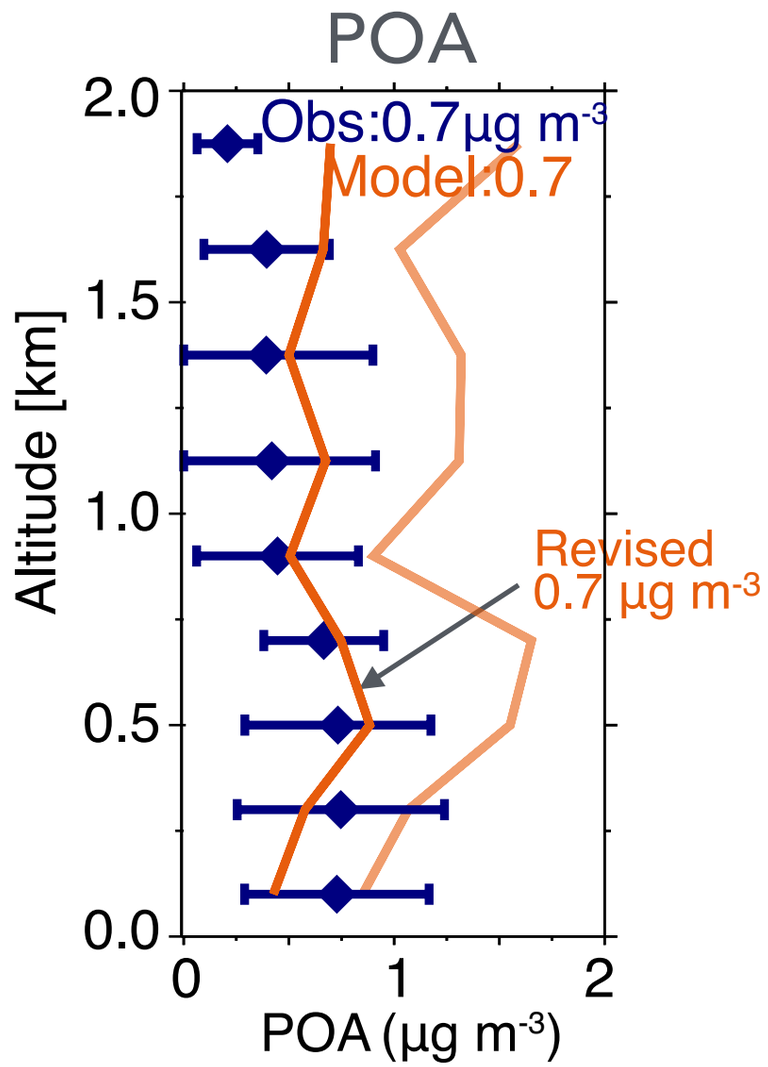
POA overestimated by a factor of 2

Emissions organic carbon aerosols

Emissions: NEI 2011 scaled to 2015

Scale-down OC emissions by 50%.

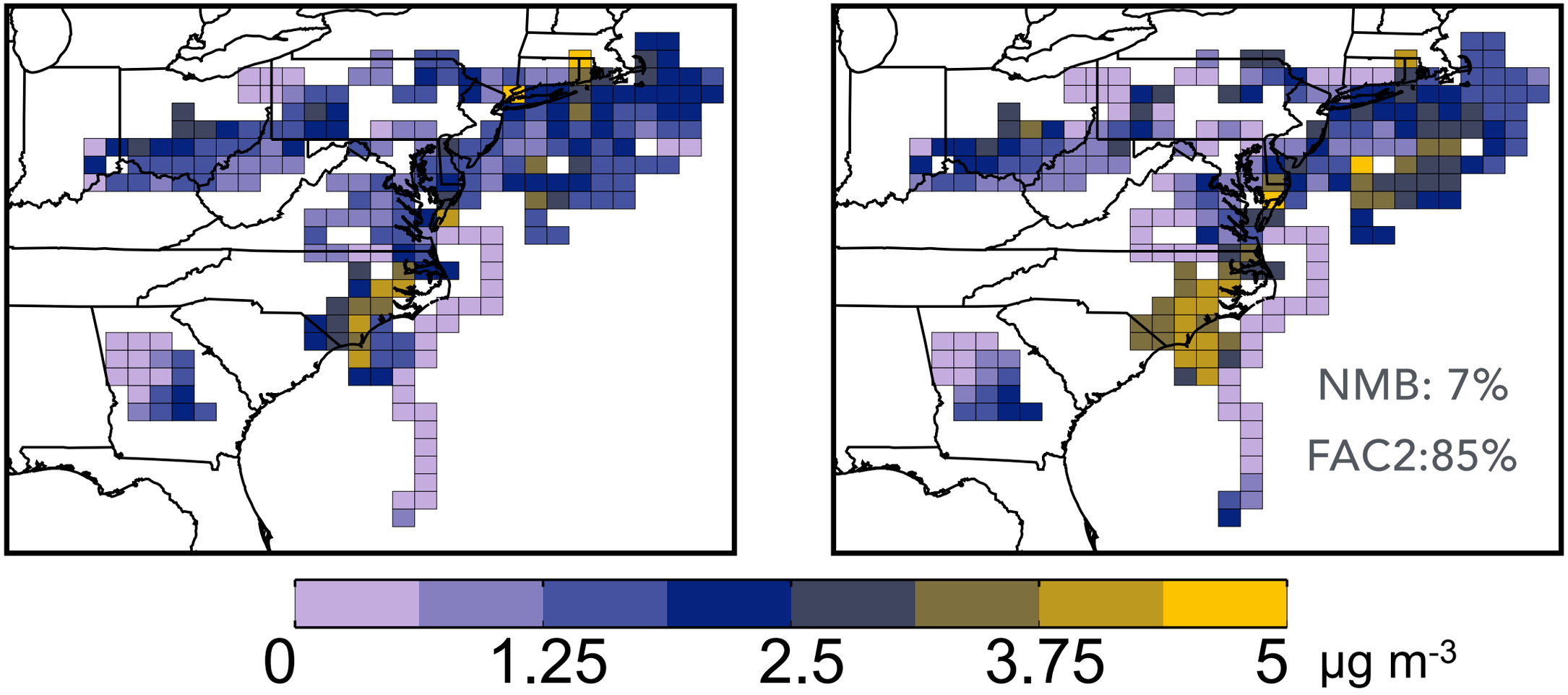




Organic aerosols

AMS Observations:
1.6 ± 1.0 μg m^{-3}

GEOS-Chem:
1.7 ± 1.1 μg m^{-3}



Modeled OA in good agreement with observations.

Organic aerosols

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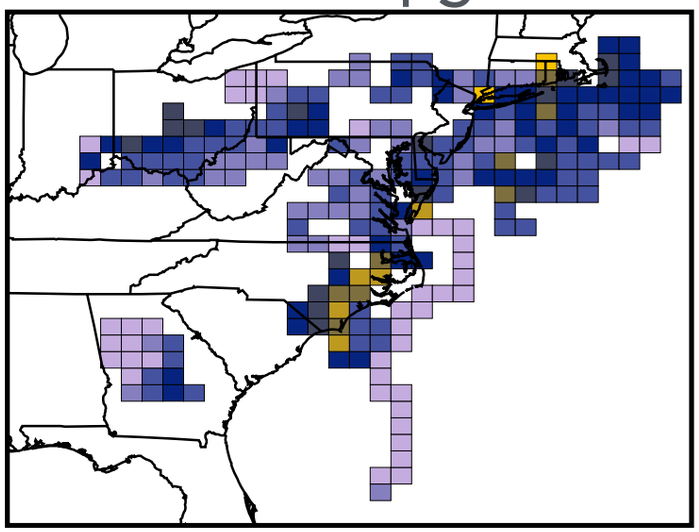

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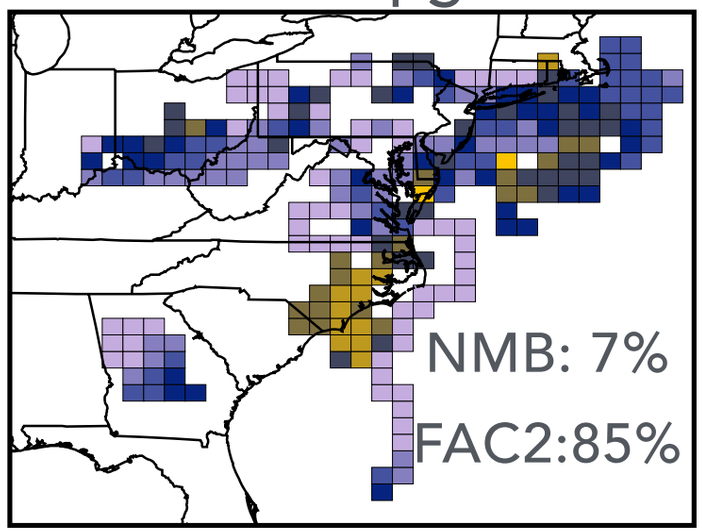
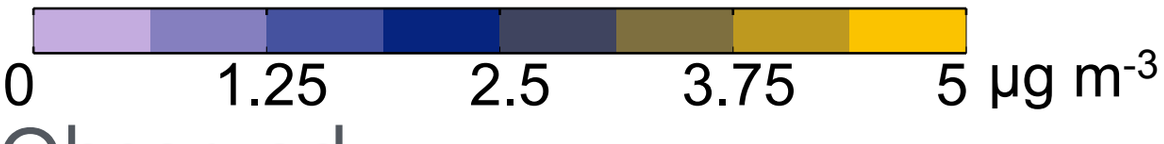
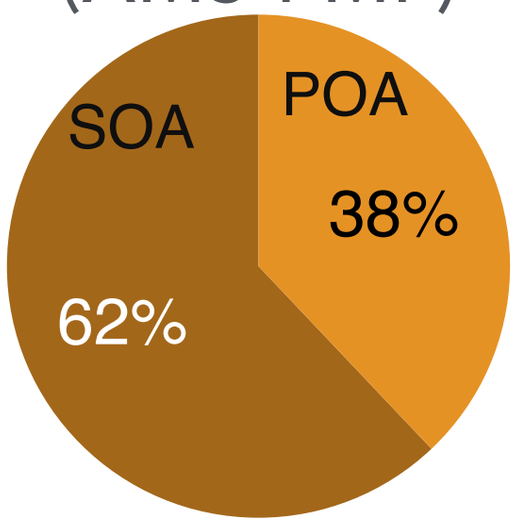
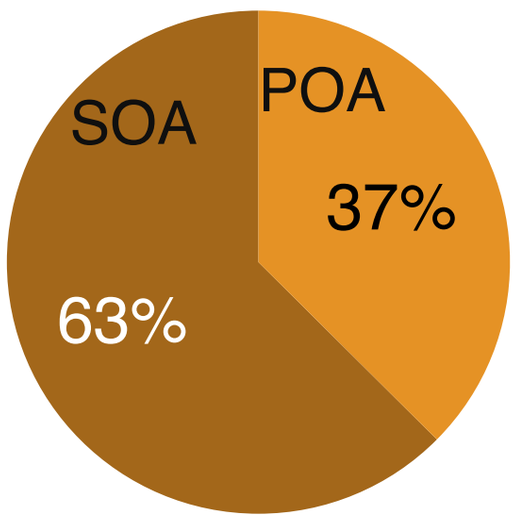




Observed
(AMS-PMF)

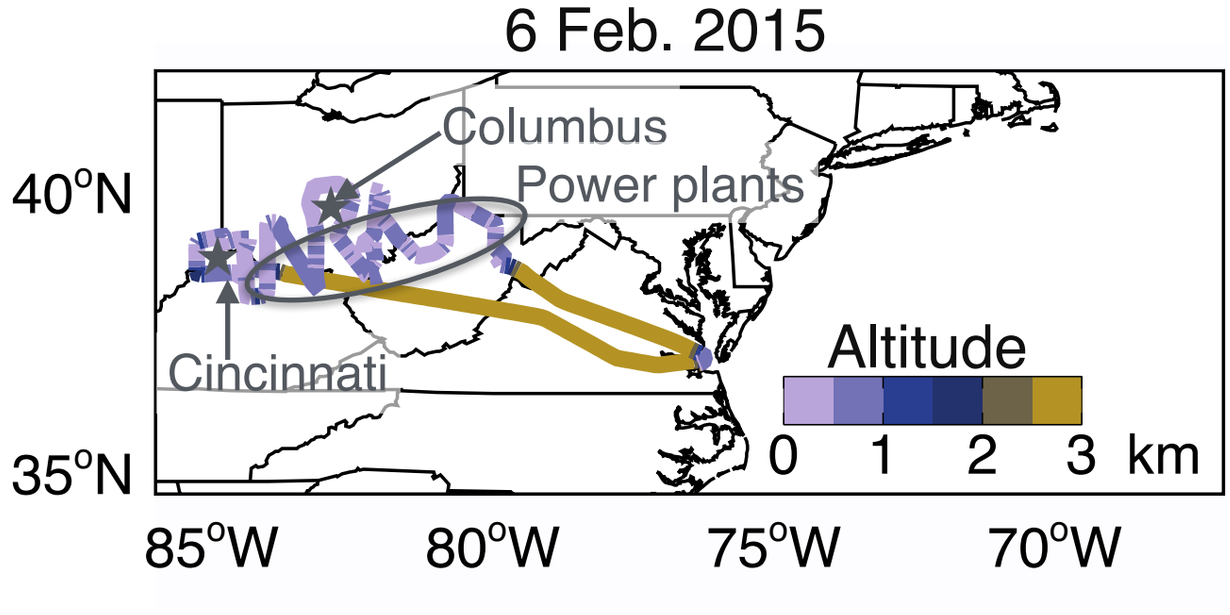


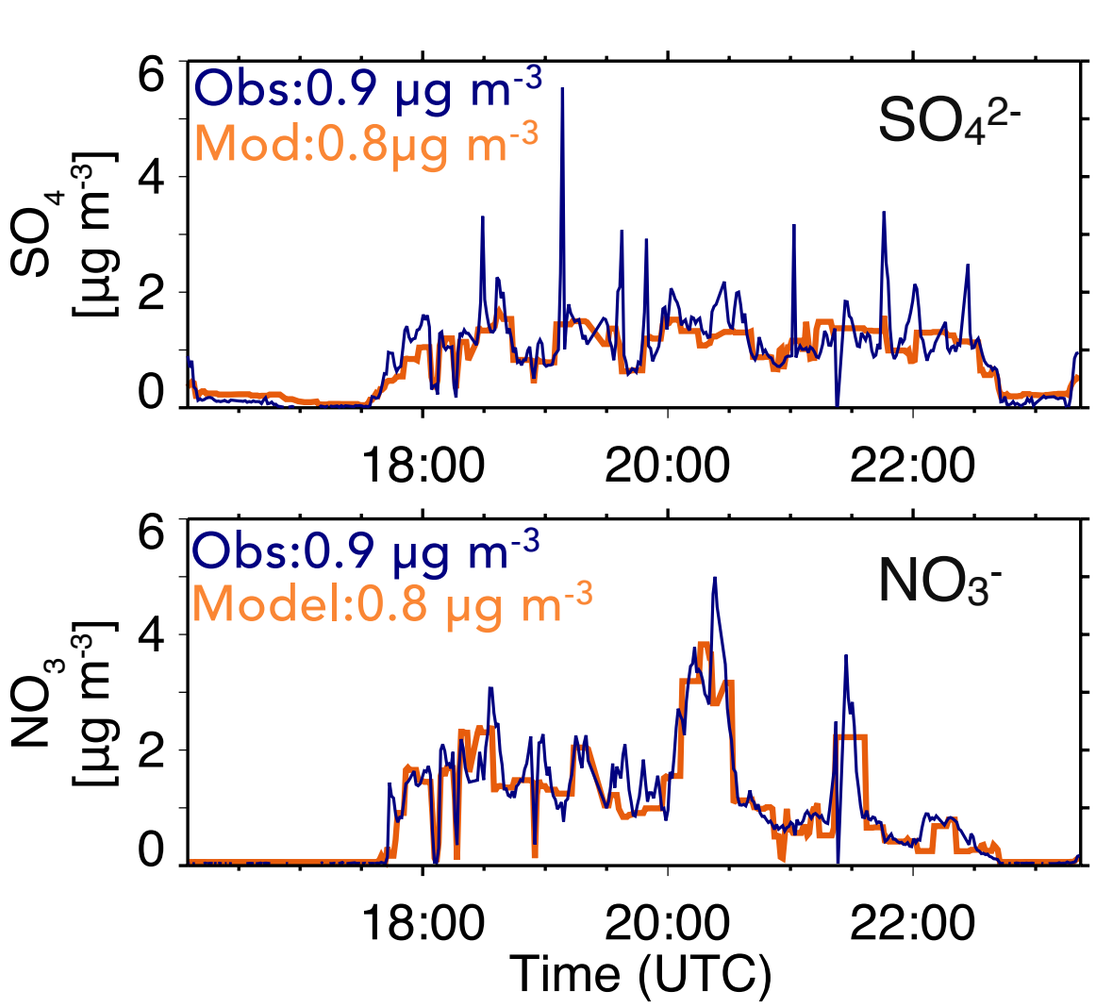
Model

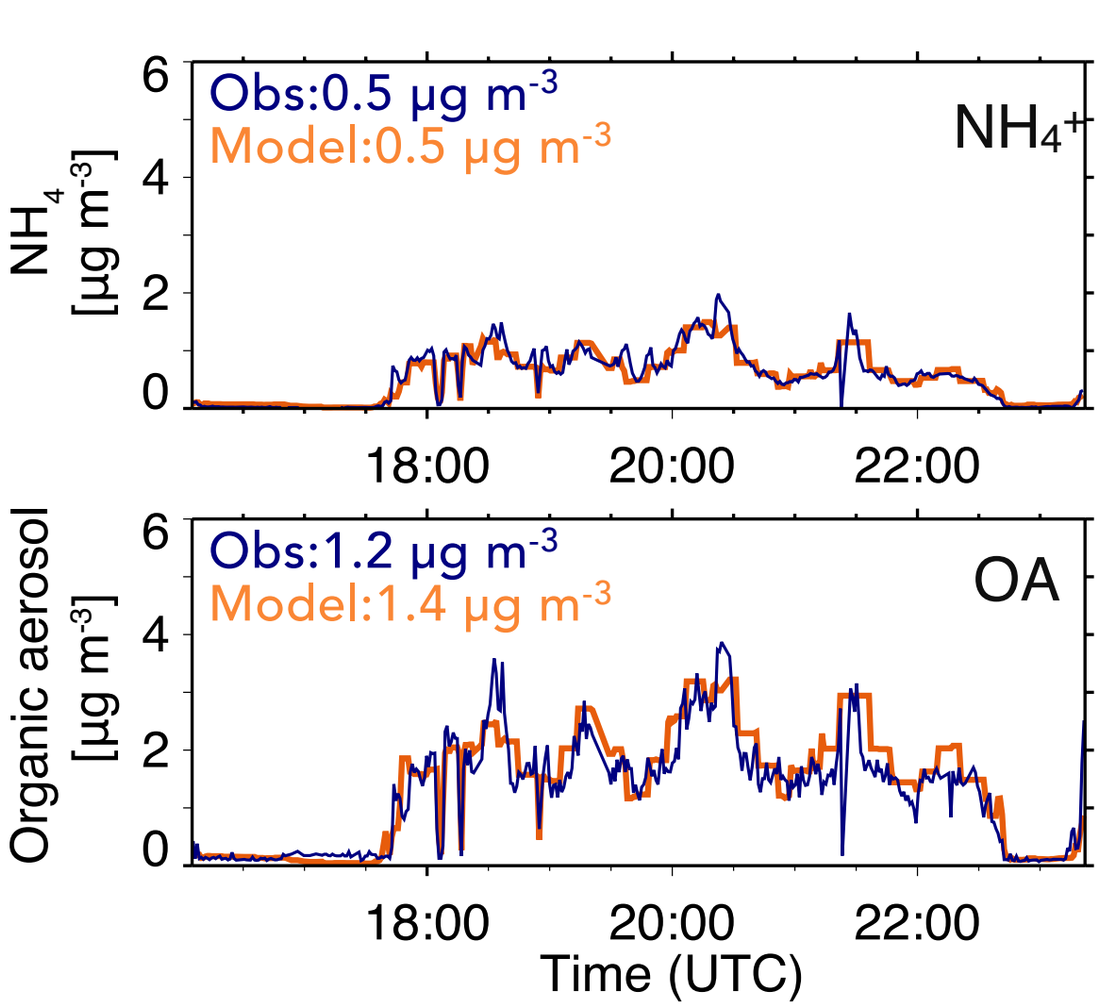


- ✦ Modeled OA in good agreement with observations.
- ✦ Fraction of POA and SOA well simulated.

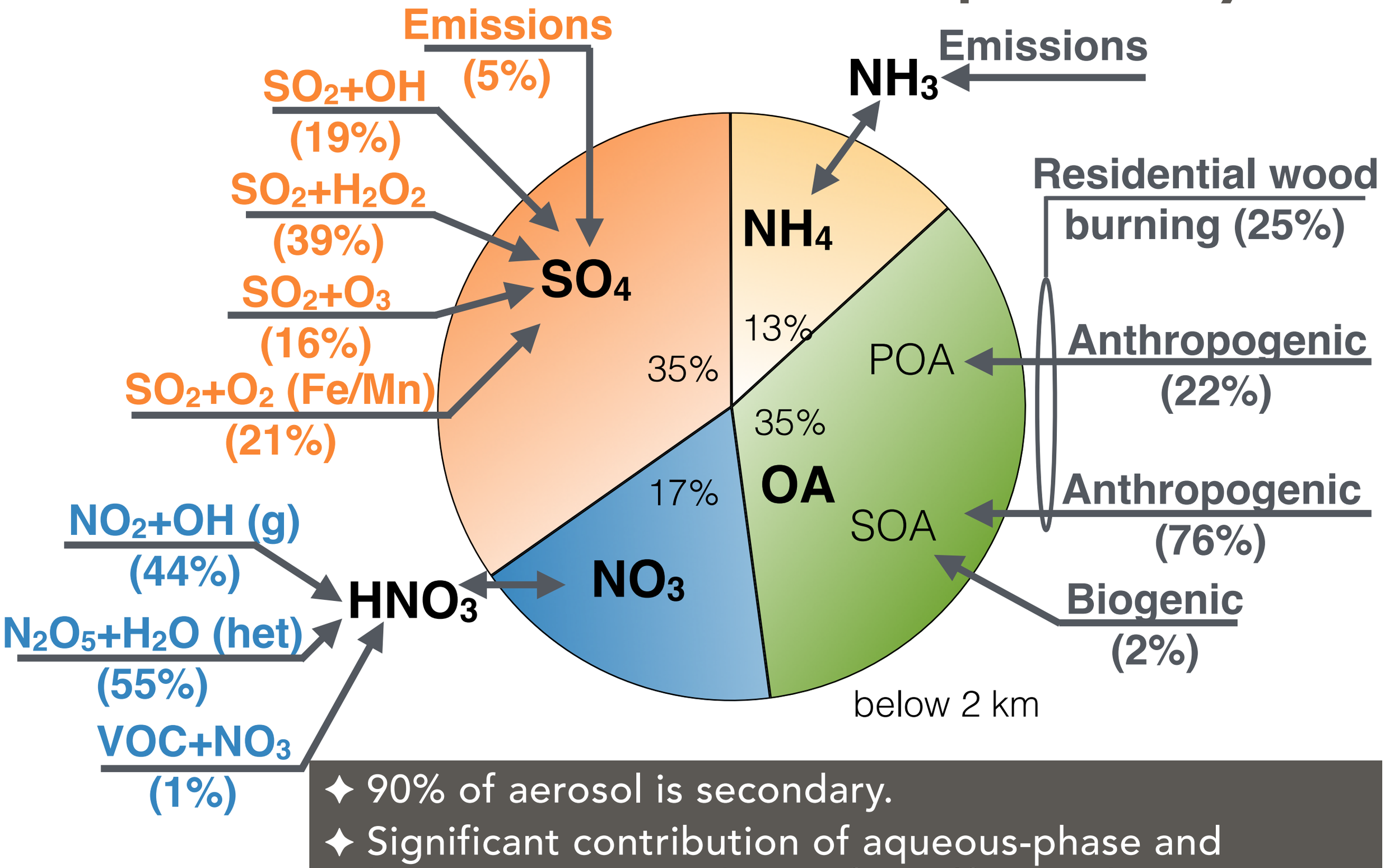
Flight RF-02: Ohio River Valley







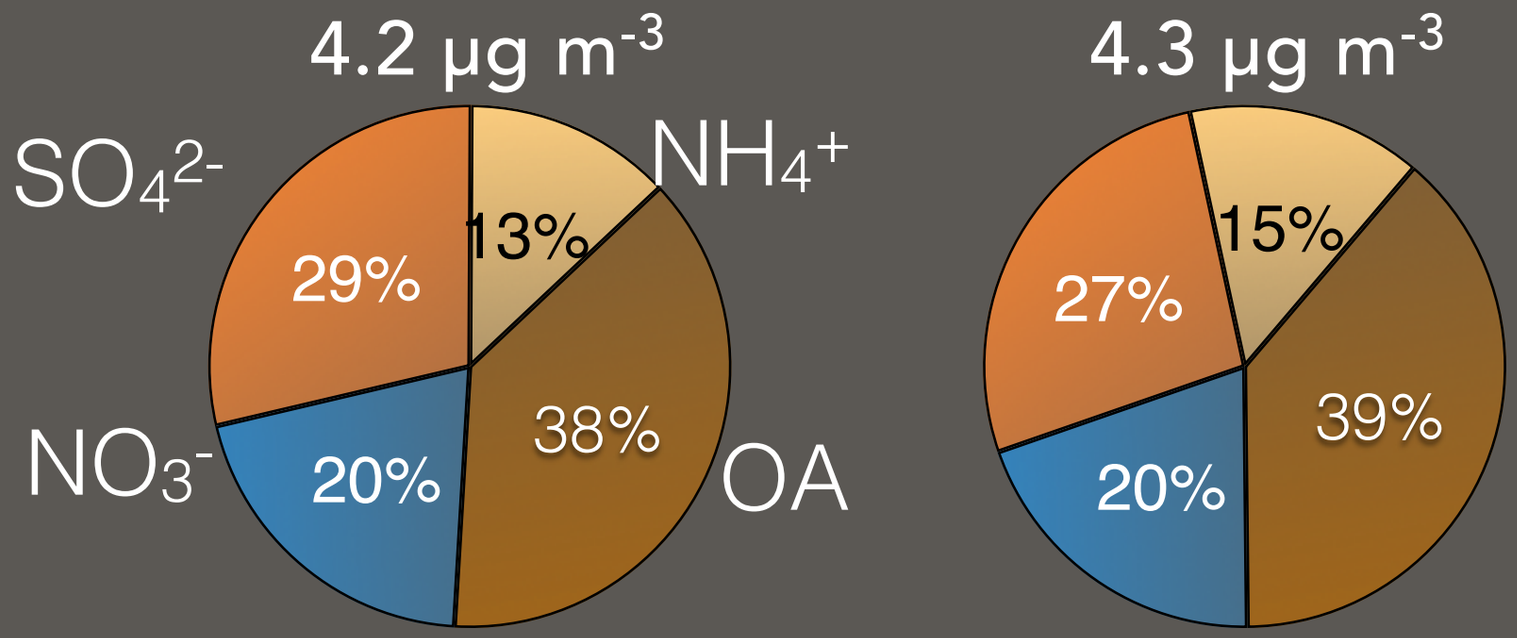
Winter aerosol formation pathways



- 90% of aerosol is secondary.
- Significant contribution of aqueous-phase and heterogeneous pathways for sulfate and nitrate.
- 25% of OA from residential wood burning

Conclusions

Observed and modeled aerosols during the WINTER campaign



Modeled wintertime aerosols sensitive to:

- Temperature dependence of NH_3 emissions.
- Hydrolysis of N_2O_5 & HNO_3 dry deposition.
- Aqueous phase sulfate production.
- POA emissions and urban SOA production.