Ongoing EPA efforts to evaluate modeled NO_y budgets

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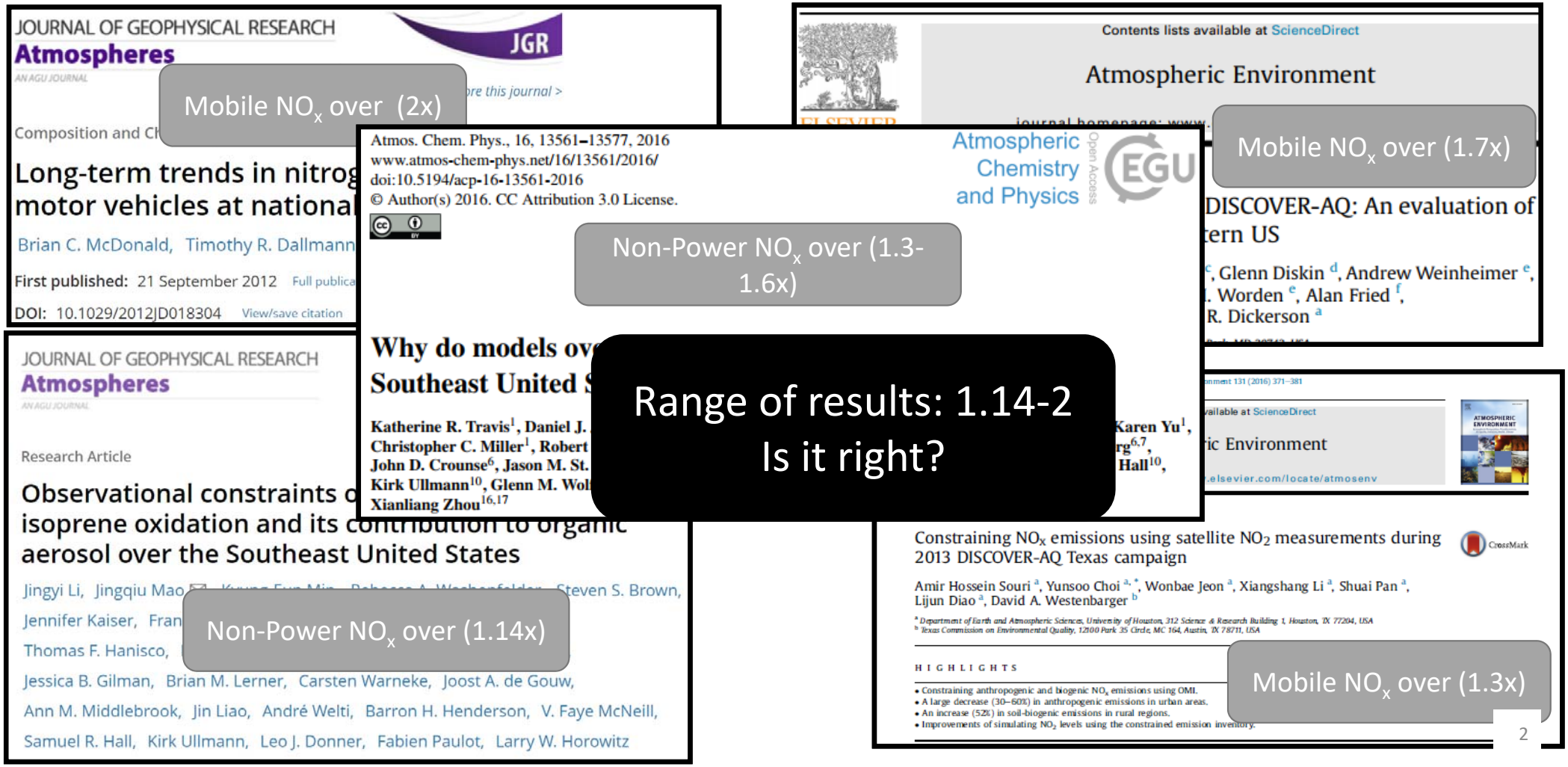
Literature consistent regarding reported high bias

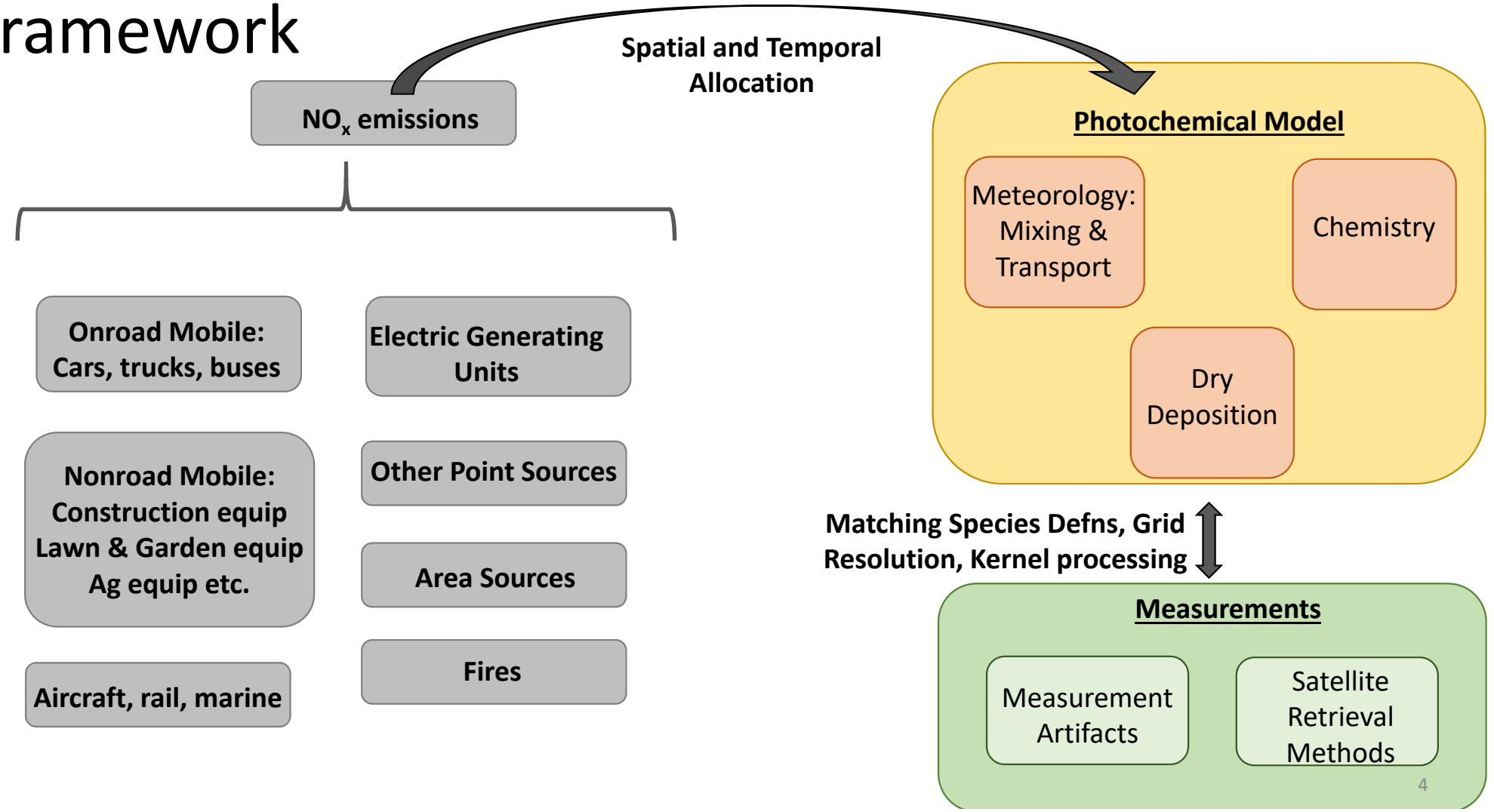


Coordinated efforts within the US EPA and across Federal Agencies

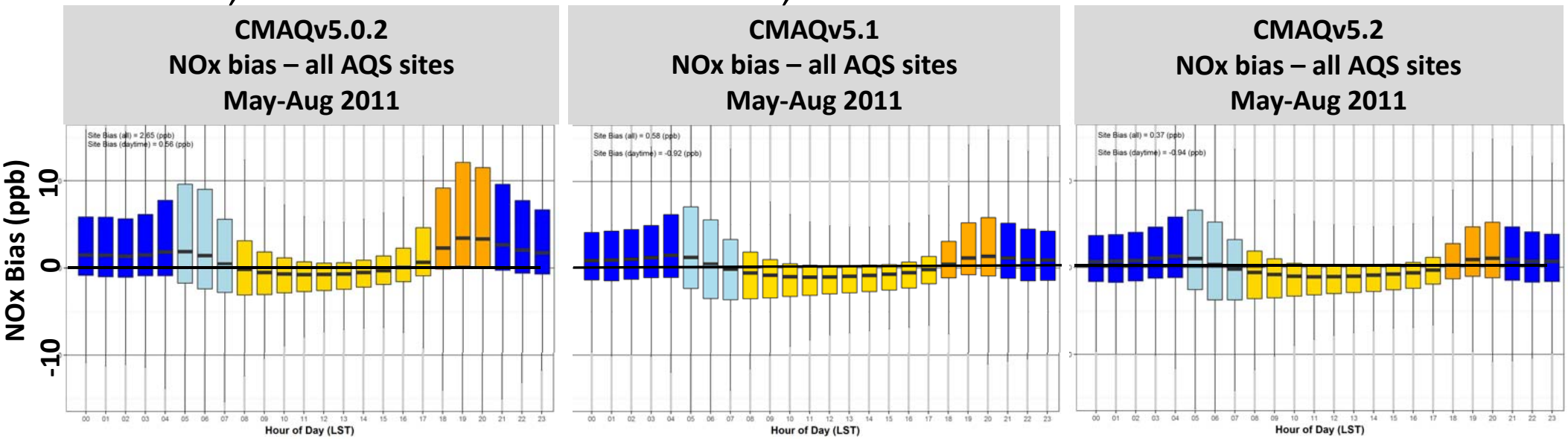
- Cross-Office NO_x Evaluation Work
  - OAQPS, OTAQ, ORD
  - Diverse perspectives, systematic and continual review
  - Targeting research to address community questions.

- Technical discussions on Emissions and Atmospheric Modeling (TEAM)
  - Cross-agency coordination
  - Point of contact: Barron Henderson, Greg Frost (NOAA) and Barry Lefer (NASA)
  - 3 Webinars have been held; 2017 sessions at IEIC, CMAS, AGU

Model Evaluation Framework



Past, Present, and… Future?

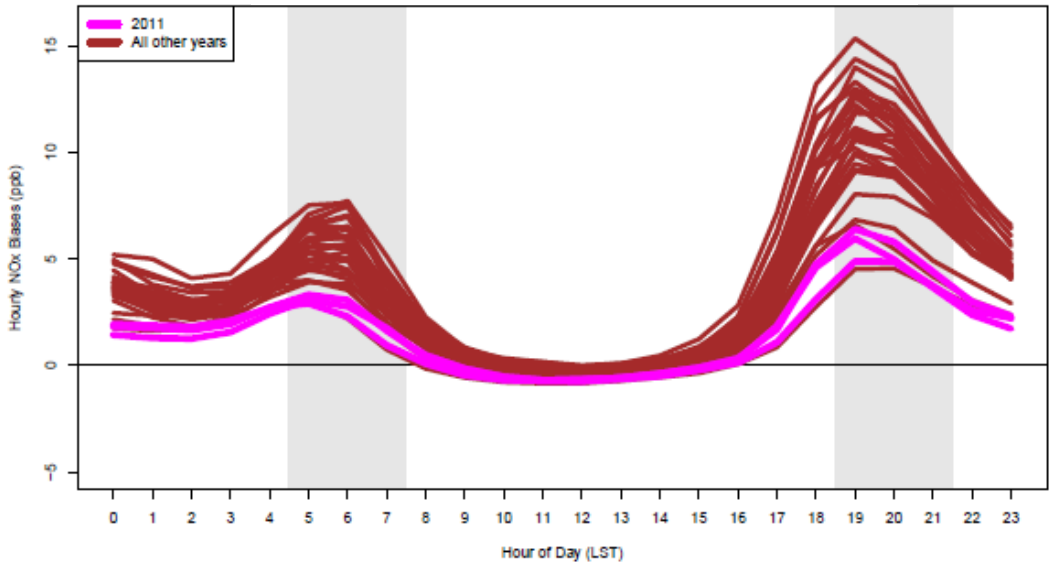


- NO_x is generally **unbiased** or **under-predicted** during **daytime** but is **over-predicted** in **morning** and **evening** transition hours and at **night**
- NO_x biases decrease with each CMAQ version update: v5.0.2 → v5.1 → v5.2
  - CMAQv5.1 has improved characterization of mixing in morning/evening transitions and at night
  - NO_2 decreases across much of the US from CMAQv5.1 to CMAQv5.2 due to multiple model updates
- Can we leverage this to identify error source?

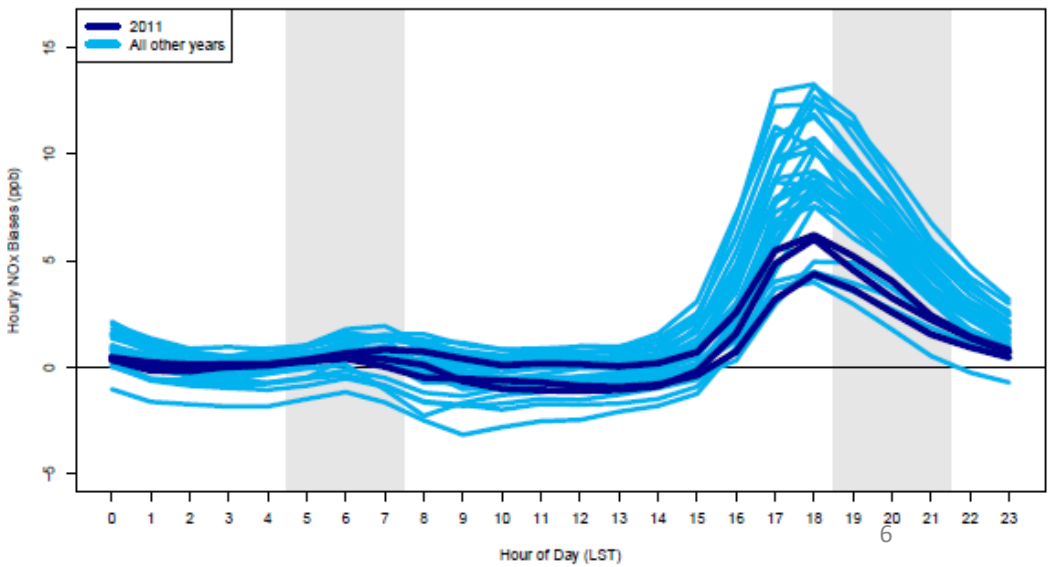
Hypothesis: Model bias is due to some unique feature of **summer** 2011 platform

- 2002 – 2012 CMAQv5.0.2 simulations evaluated at 250 AQS sites across the country.
- Prominent summertime morning NO_x bias is absent in wintertime comparisons.
- This is consistent with seasonal NO_x bias plots in supplement to Appel et al. (2017) CMAQv5.1 model evaluation paper

Summer:

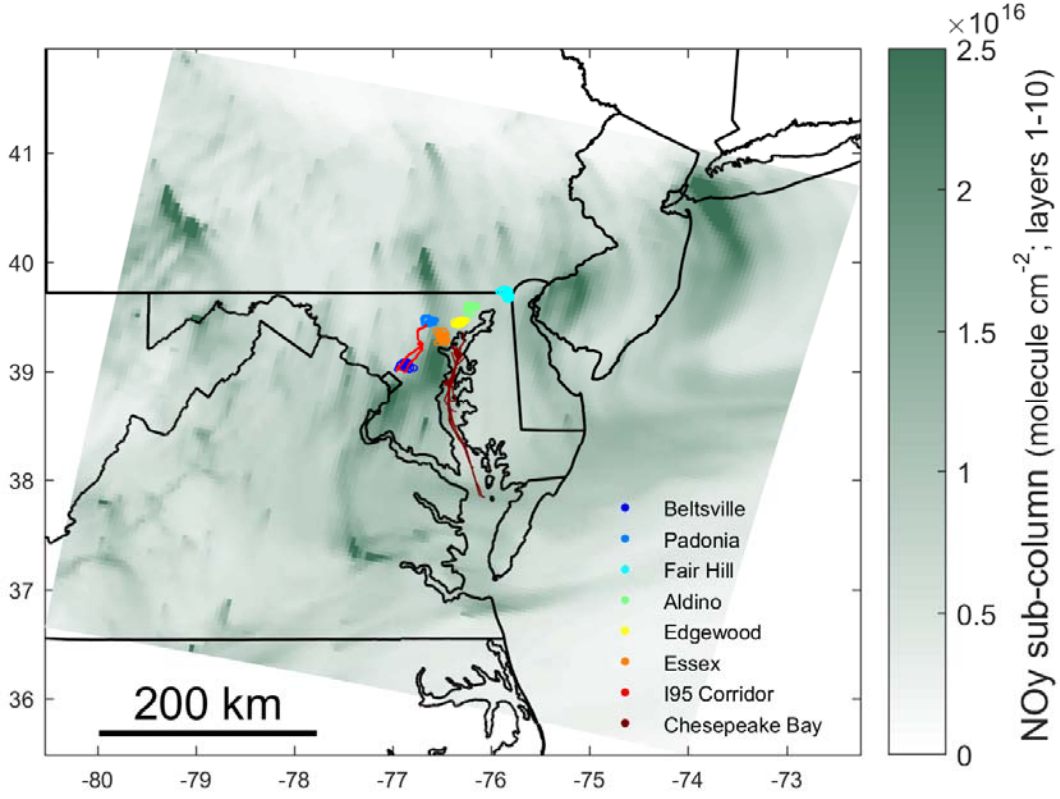


Winter:



Case Study: 2011 DISCOVER-AQ Baltimore Field Campaign

- NASA P-3B aircraft took ambient measurements in the Baltimore-D.C. area on 14 days during July 2011
- Measurements of NO_y species as well as total NO_y are useful for model evaluation
  - NO, NO_2 and NO_y: NCAR four-channel chemiluminescence
  - ANs, PNs, HNO_3: TD-LIF instrument
    - Second NO_2 measurement from LIF
- Previous researchers have used this dataset to conclude that U.S. EPA's onroad mobile NO_x emissions are too high by a factor of 2



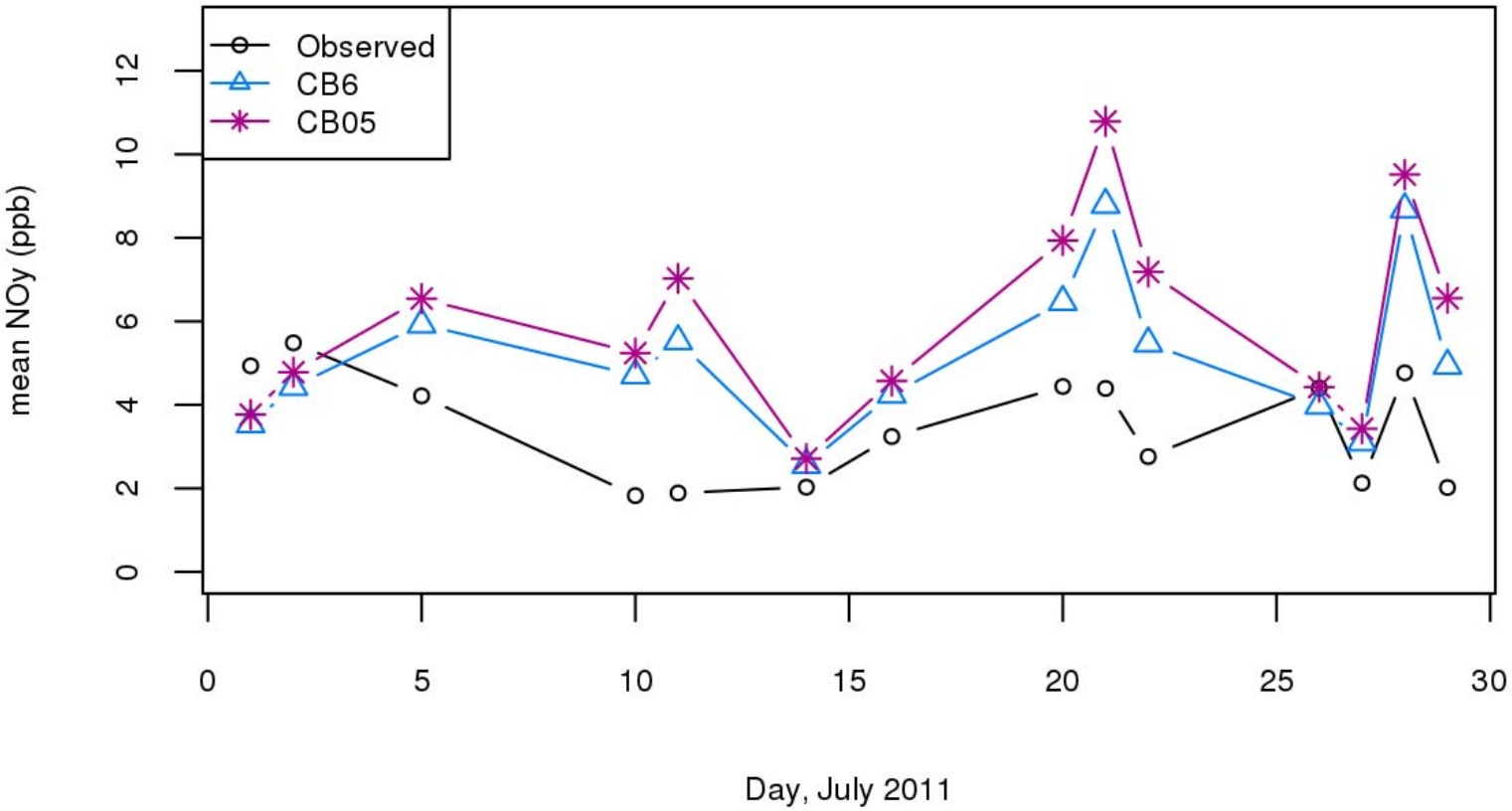
NO_y treatment in CB05 and CB6 chemical mechanisms evaluated

- These are two version of the CB condensed chemical mechanism which is commonly used in regulatory modeling
- The main difference between mechanisms is in their treatment of alkyl nitrates
  - CB05tucl
    - 1 specie
    - Low reactivity
    - Low solubility
    - Can form HNO_3 and NO_2
    - Mostly terminal
  - CB6
    - 3 species
    - Can form HNO_3, other alkyl nitrates, and NO_2
    - Can participate in heterogeneous chemistry
    - More alkyl nitrate removal than CB05
    - Temperature and pressure dependent yields of ANs
- Both mechanisms have 3 PAN species with similar formation/decay rates
- Both mechanisms have similar treatment of deposition and chemical loss of HNO_3 although CB6 AN chemistry leads to more formation of HNO_3
- Changes to VOC and peroxy radical chemistry impacts NO_y directly via PAN and indirectly through OH availability

CMAQ-Observation Comparison with aircraft measurements taken within the PBL

<u>Impact of Chemical Mechanisms on Model NOy Performance:</u>

- CB05 NO_y NMB : 76%
- CB6 NO_y NMB : 51%



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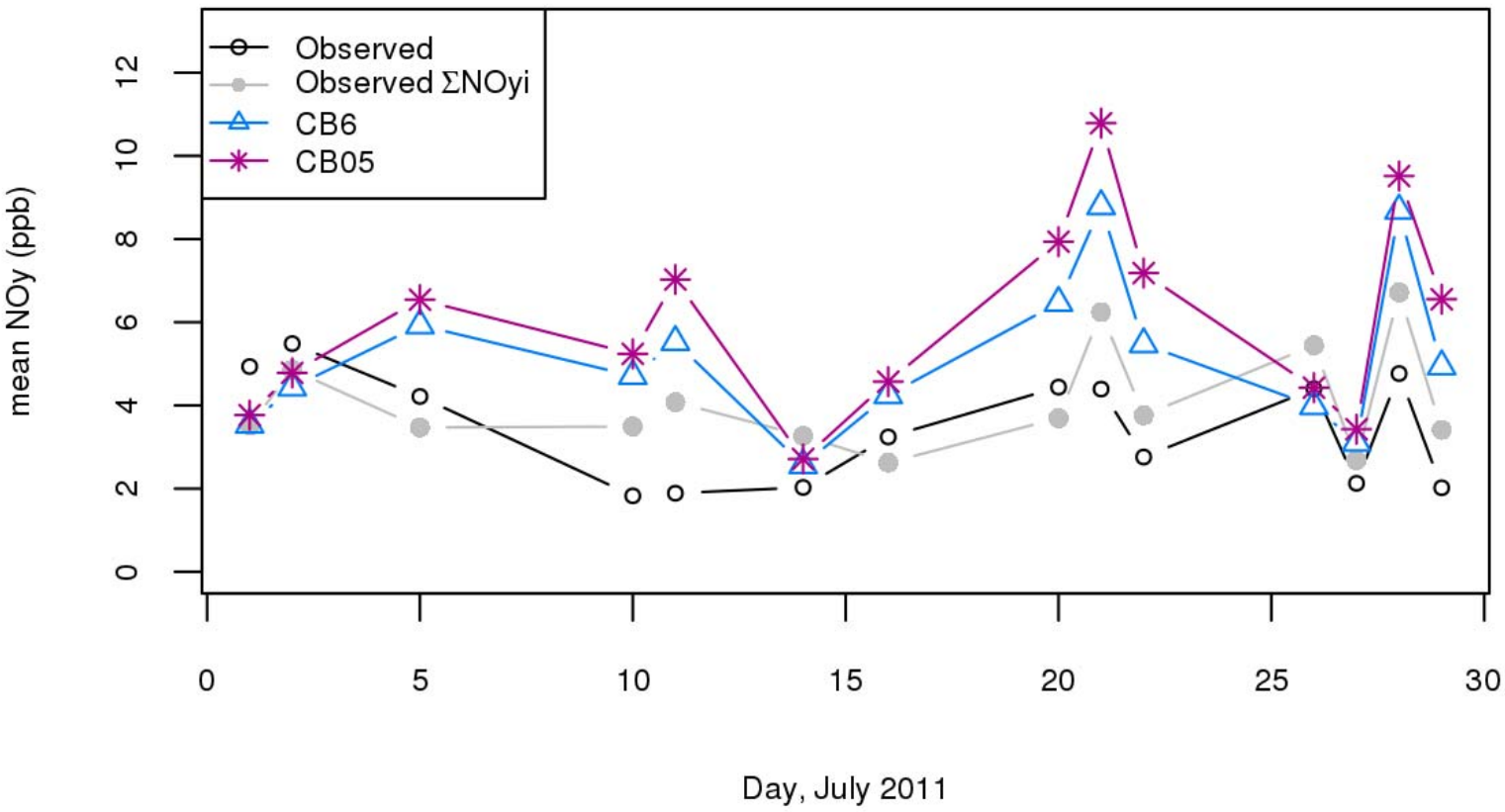
<u>Impact of Observational Uncertainty:</u>

- CB05 NOy NMB compared to Observed $\sum NO_{yi}$: 49%
- CB6 NOy NMB compared to Observed $\sum NO_{yi}$: 28%



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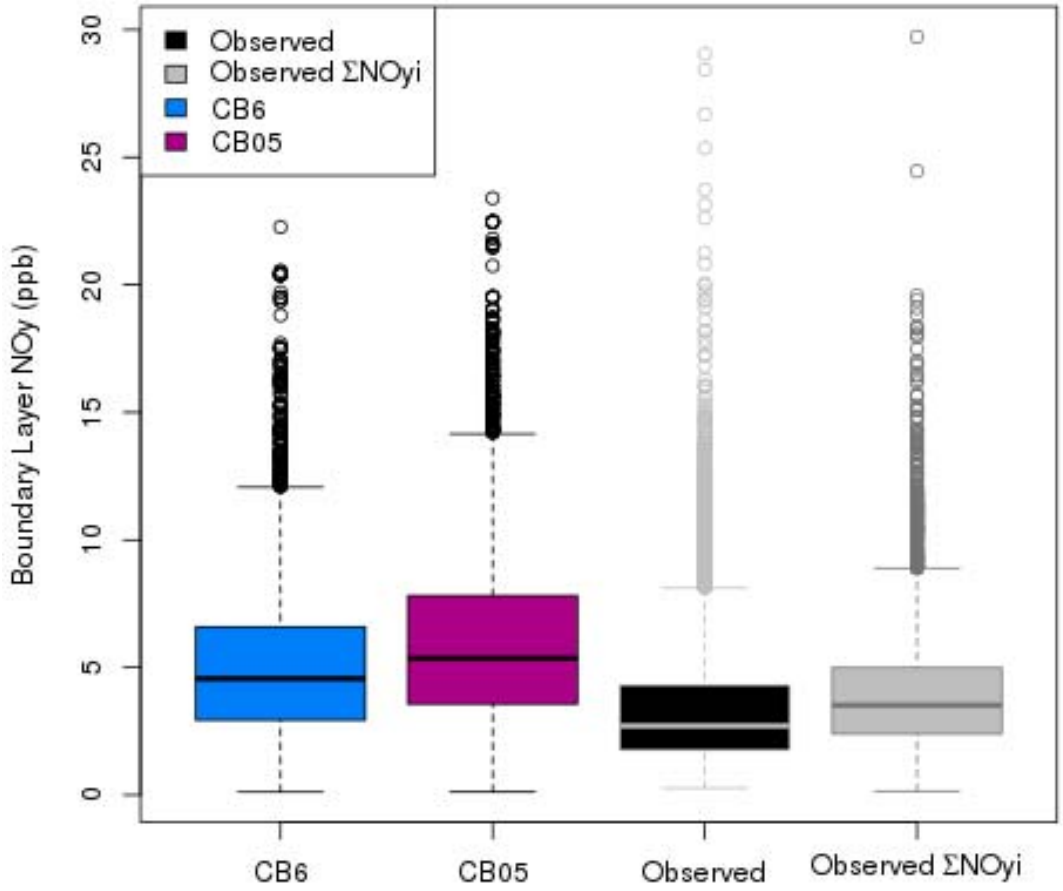
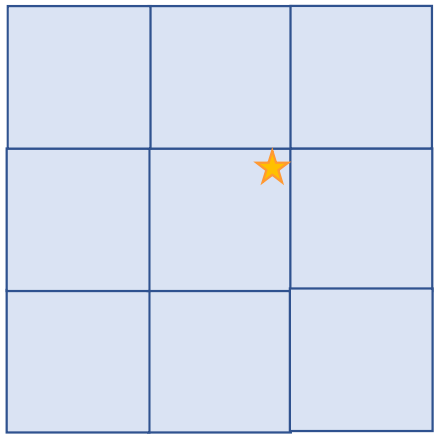
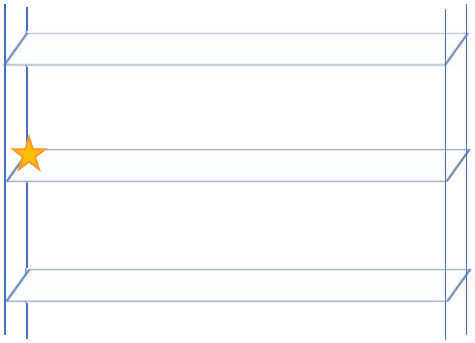


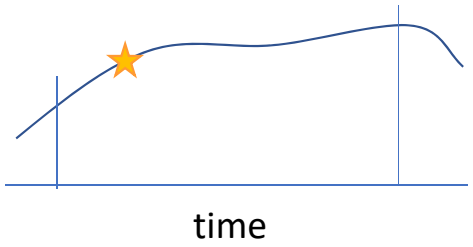
Further Challenges with spatial & temporal matching between model and measurements additionally impacts calculated bias



Horizontal sampling:
12 or 4km grid box averages versus point in space



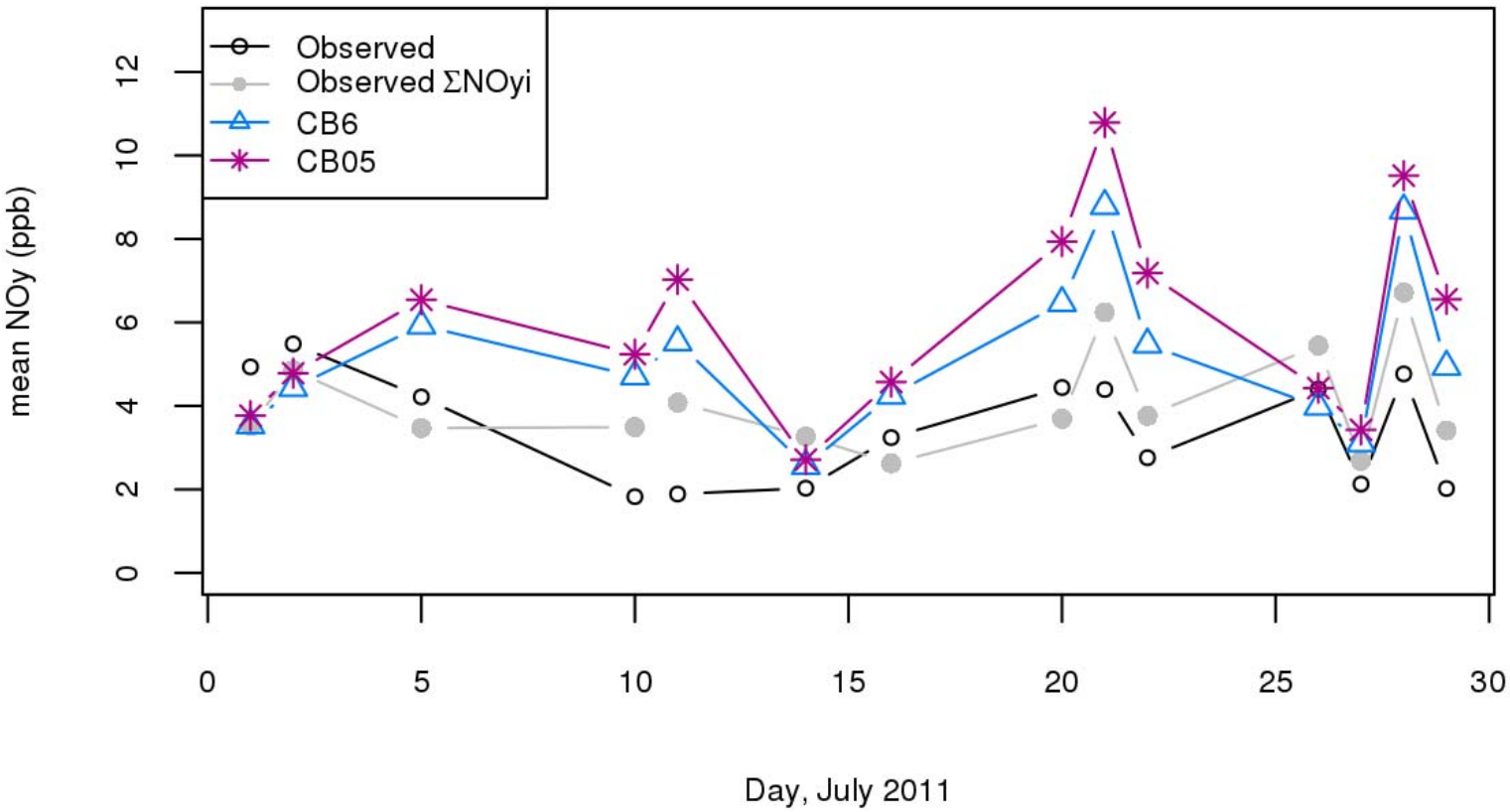
Vertical sampling:
Vertically mixed layers versus point in space



Temporal sampling:
Hourly model values versus 15 second measurements

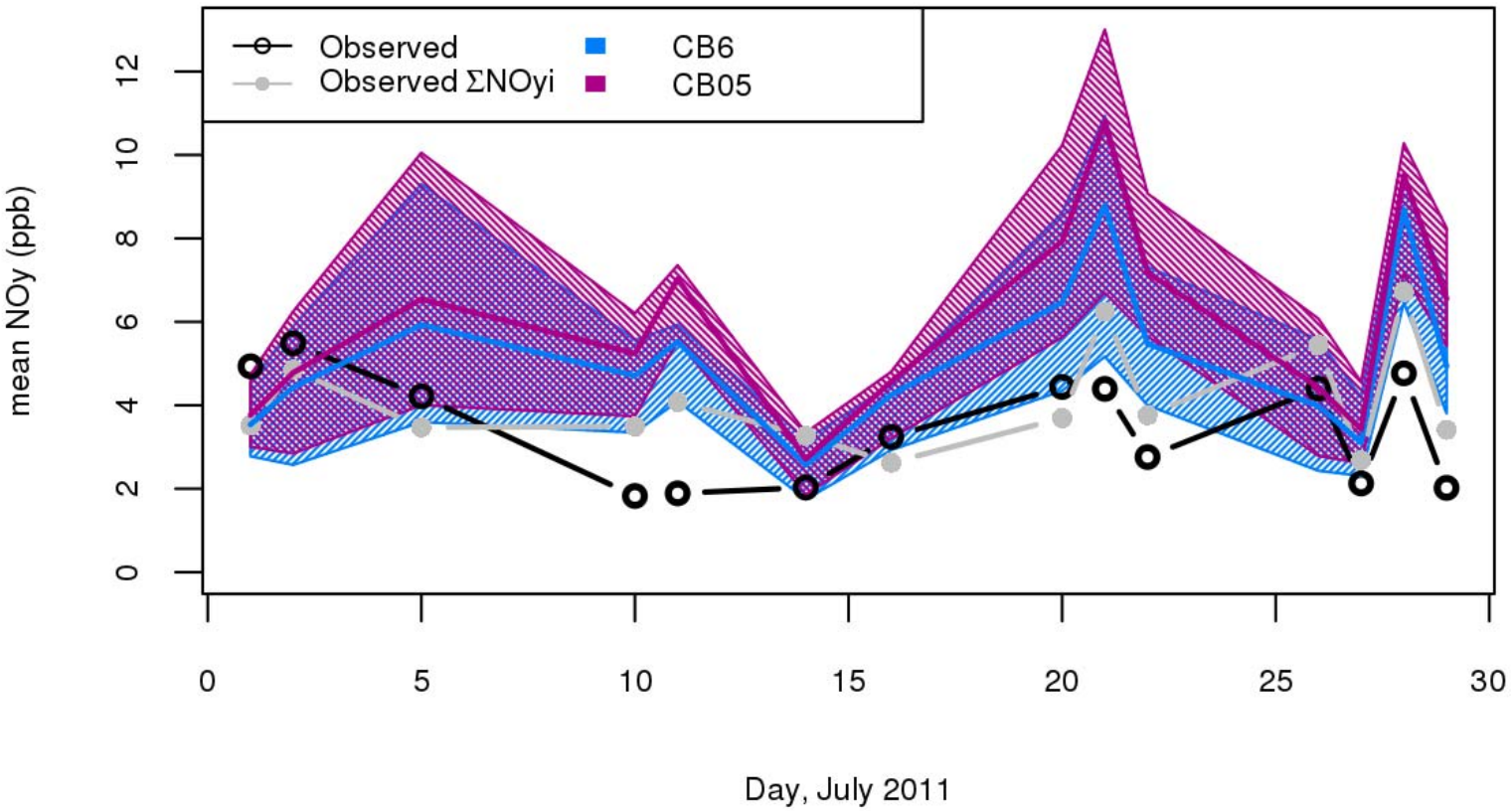
CMAQ-Observation Comparison with aircraft measurements taken within the PBL

Model values represent matching measurement location to grid cell (horizontal and vertical) and measurement time to closest hour

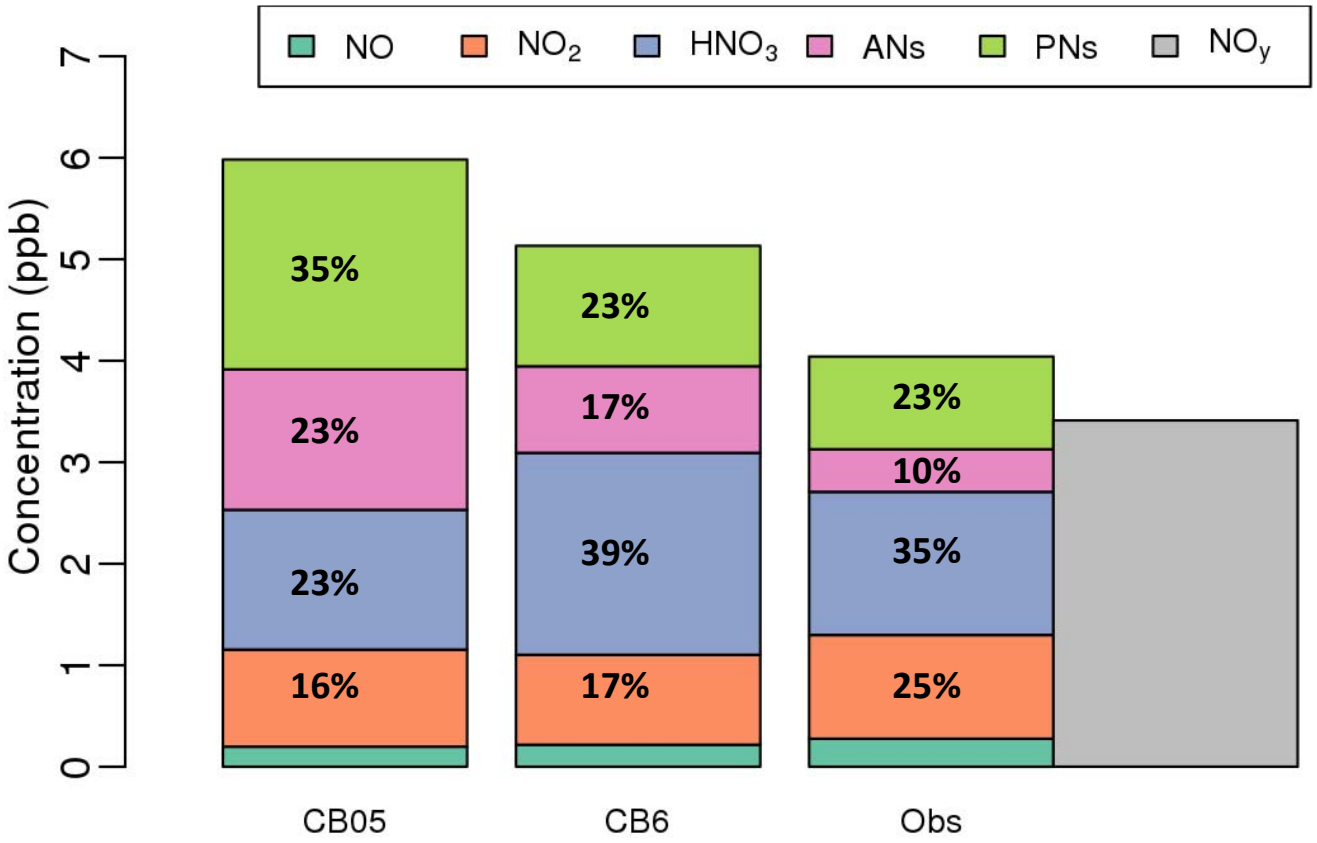


CMAQ-Observation Comparison with aircraft measurements taken within the PBL

Shading represents range of model values if you sample +/- 1 grid cell in each direction and +/- 1 hour



Comparison of NO_y species with BL Measurements from all flight days

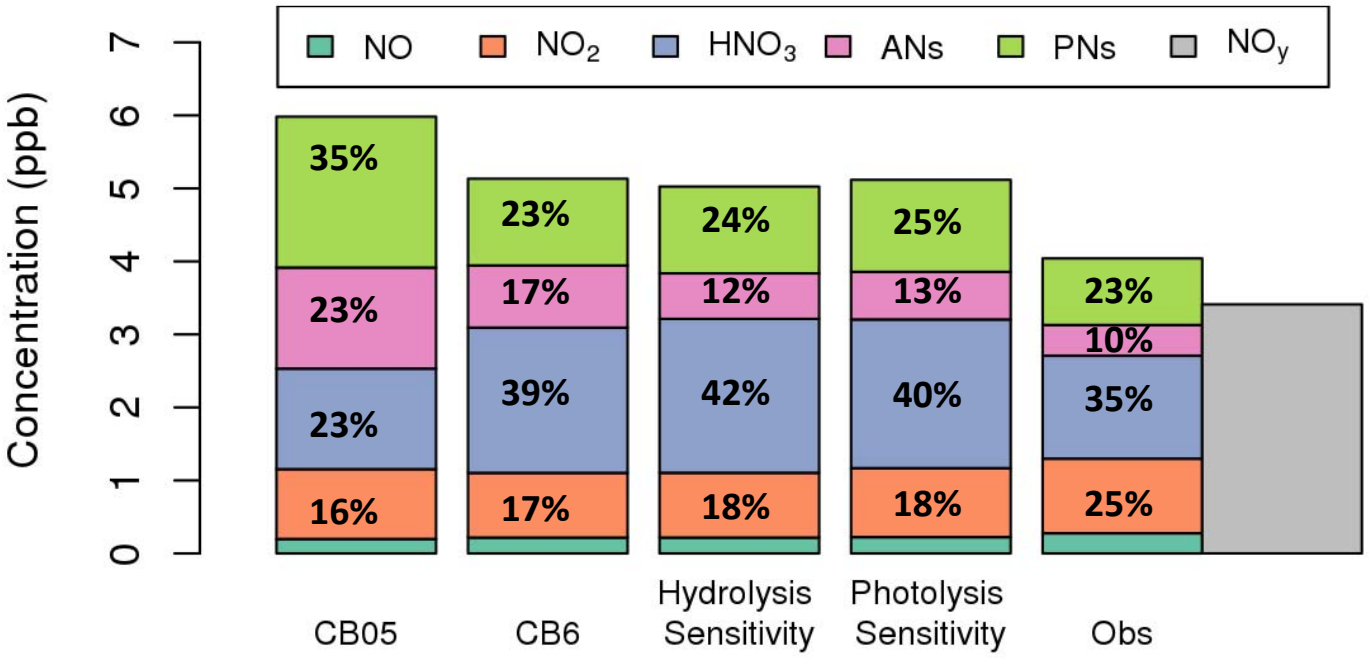


- Both mechanism simulations overpredict NO_y
  - CB6 is an improvement over CB05
- NOx performance is pretty good in both model simulations
  - NO_2 fraction is higher in observations than modeled
- NO_z species are overestimated in all model simulations
  - CB6 has reduced ANs and PNs leading to better agreement with observations
  - CB6 has increased HNO_3 leading to overprediction compared to observations

Impacts of Chemical Mechanism version plus Additional Chemical Mechanism Sensitivities on NO_y Speciation

- Remember key update from CB05 to CB6 was the inclusion of two additional AN species with hydrolysis pathway to terminate NO_x
- 2 Key remaining uncertainties in the NO_y chemistry include:
  - Alkyl nitrate mechanism species hydrolysis lifetimes
  - Alkyl nitrate photolysis pathways and product yields, solubilities, and vapor pressure
- Additional chemical mechanism sensitivities were performed starting with the CB6 chemical mechanism
  - Hydrolysis: changed the hydrolysis lifetime of NTR2 from 6 hours to 2 hours
  - Photolysis: introduce NTR2 photolysis reaction with NO_2 products

Comparison of NO_y species with BL Measurements from all flight days



- Additional sensitivities don't change total NO_y much – slight reduction (improvement) compared to CB6
- Additional loss pathways for ANs leads to slightly lower AN concentrations and reduction in model overprediction
- Some ANs shifted to HNO_3 making HNO_3 overprediction worse
- Most efficient chemical mechanism changes for reducing total NO_y would shift to shorter lifetime species (HNO_3). Any additional shifts towards HNO_3 will further exacerbate HNO_3 overprediction

Conclusions

- Model bias should be reported in the context of measurement uncertainties, including measurement disagreement

- Time/space pairing should be consistent with expected meteorological skill

- NO_y composition is sensitive to current condensed chemical mechanism formulation for alkyl nitrate chemistry
  - CB mechanism ***NO_x*** is relatively ***unbiased*** and ***insensitive***.
  - CB mechanism ***ANs, PNs and HNO_3*** are ***biased*** and ***sensitive***.
  - Updated mechanisms reduce NO_y bias (15% concentration change), but create biased HNO_3

- Outstanding questions:
  - Are emissions the only remaining uncertainty?
  - What role do remaining condensed mechanism uncertainties play?
  - What role do uncertainties in deposition and atmospheric mixing play?

Questions?

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Important Sources of NOx in the 2011 NEI