

Ongoing EPA efforts to evaluate modeled NO_y budgets

Heather Simon, Barron Henderson, Deborah Luecken, Kristen Foley

Literature consistent regarding reported high bias

JOURNAL OF GEOPHYSICAL RESEARCH
Atmospheres
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Mobile NO_x over (2x)

Long-term trends in nitrogen dioxide from motor vehicles at national scale

Brian C. McDonald, Timothy R. Dallmann

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Atmospheric Environment

Mobile NO_x over (1.7x)

DISCOVER-AQ: An evaluation of nitrogen dioxide levels in the eastern US

Glenn Diskin^d, Andrew Weinheimer^e, J. Worden^e, Alan Fried^f, R. Dickerson^a

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Research Article

Observational constraints on isoprene oxidation and its contribution to organic aerosol over the Southeast United States

Jingyi Li, Jingqiu Mao¹, Kwang Eun Min², Barbara A. Weckwerth³, Steven S. Brown⁴, Jennifer Kaiser⁵, Fran⁶, Thomas F. Hanisco⁷, Jessica B. Gilman⁸, Brian M. Lerner⁹, Carsten Warneke¹⁰, Joost A. de Gouw¹¹, Ann M. Middlebrook¹², Jin Liao¹³, André Welti¹⁴, Barron H. Henderson¹⁵, V. Faye McNeill¹⁶, Samuel R. Hall¹⁷, Kirk Ullmann¹⁸, Leo J. Donner¹⁹, Fabien Paulot²⁰, Larry W. Horowitz²¹

Non-Power NO_x over (1.14x)

Atmos. Chem. Phys., 16, 13561–13577, 2016
www.atmos-chem-phys.net/16/13561/2016/
doi:10.5194/acp-16-13561-2016
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Non-Power NO_x over (1.3–1.6x)

Range of results: 1.14–2
Is it right?

Atmospheric Chemistry and Physics
Open Access
EGU

Constraining NO_x emissions using satellite NO₂ measurements during 2013 DISCOVER-AQ Texas campaign

Amir Hossein Souri^a, Yunsoo Choi^{a,*}, Wonbae Jeon^a, Xiangshang Li^a, Shuai Pan^a, Lijun Diao^a, David A. Westenbarger^b

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^b Texas Commission on Environmental Quality, 1200 Park 35 Circle, MC 164, Austin, TX 78711, USA

Mobile NO_x over (1.3x)

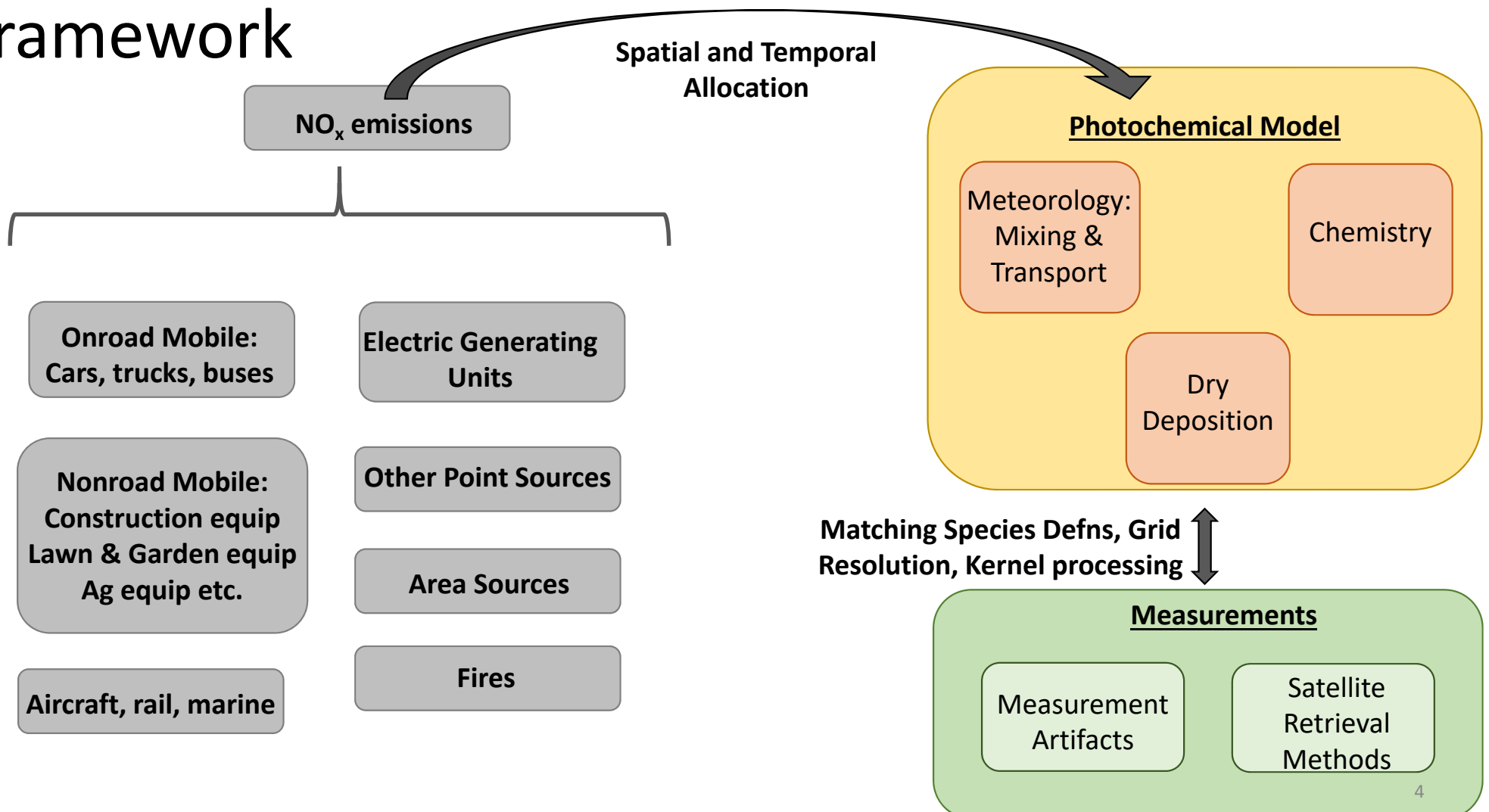
HIGHLIGHTS

- Constraining anthropogenic and biogenic NO_x emissions using OMI.
- A large decrease (30–60%) in anthropogenic emissions in urban areas.
- An increase (52%) in soil-biogenic emissions in rural regions.
- Improvements of simulating NO₂ levels using the constrained emission inventory.

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

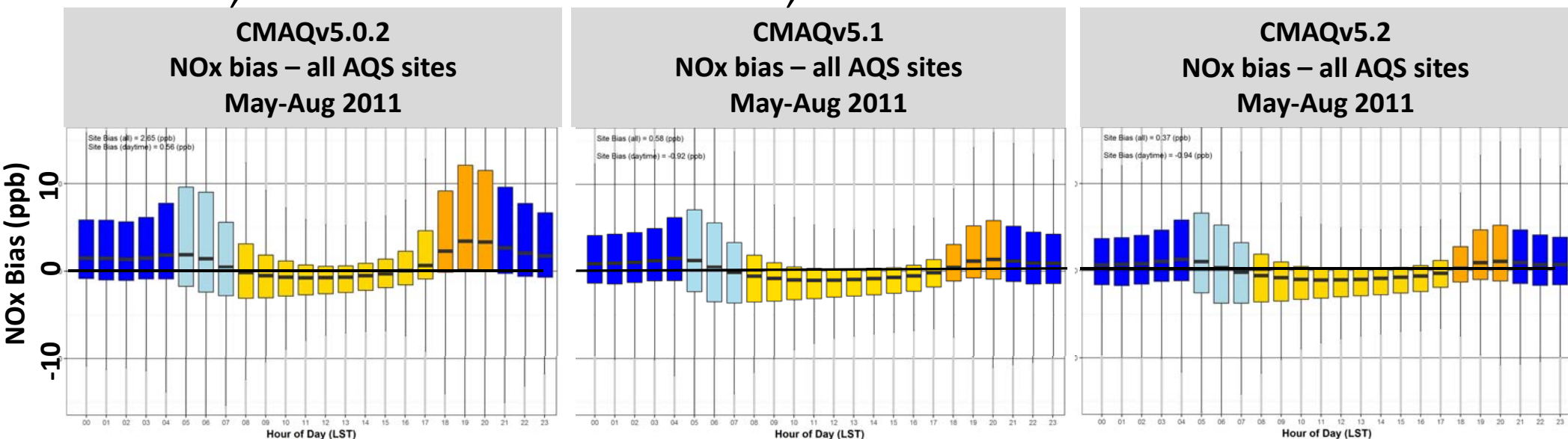
Model Evaluation Framework



Past,

Present, and...

Future?



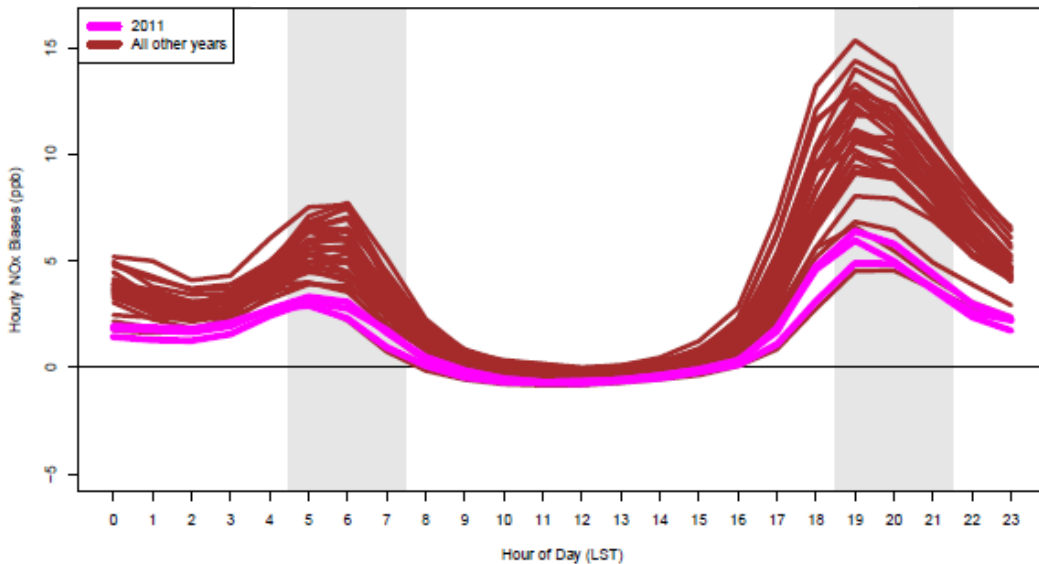
- NO_x is generally **unbiased** or **under-predicted** during **daytime** but is **over-predicted** in **morning** and **evening** transition hours and at **night**
- NO_x biases decrease with each CMAQ version update: v5.0.2 → v5.1 → v5.2
 - CMAQv5.1 has improved characterization of mixing in morning/evening transitions and at night
 - NO₂ 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

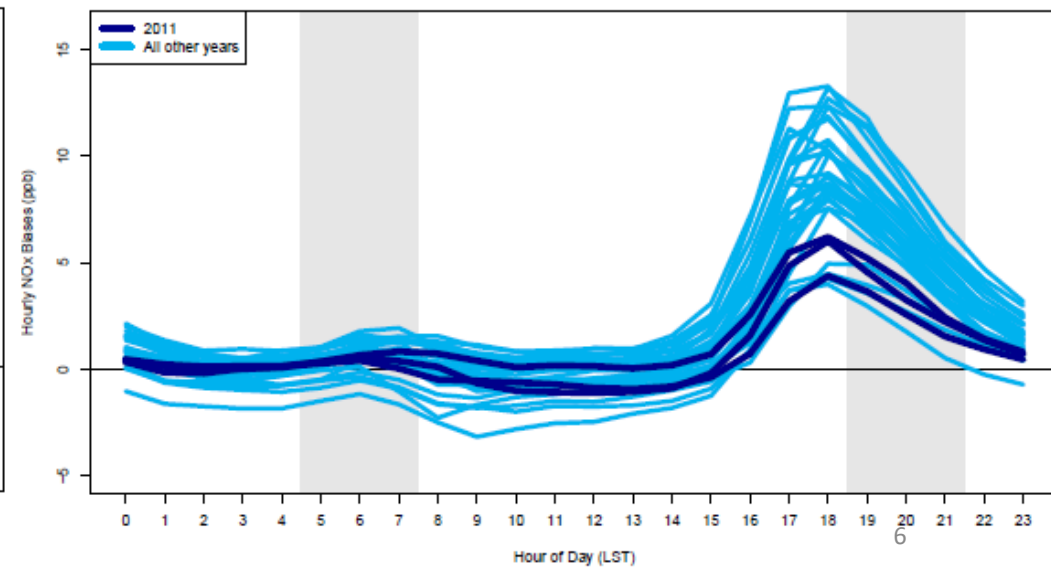
Summer:

CMAQv5.0.2: Monthly Median NO_x Bias by Hour
Site = All Sites | Period = Jun,Jul,Aug 2002-2012



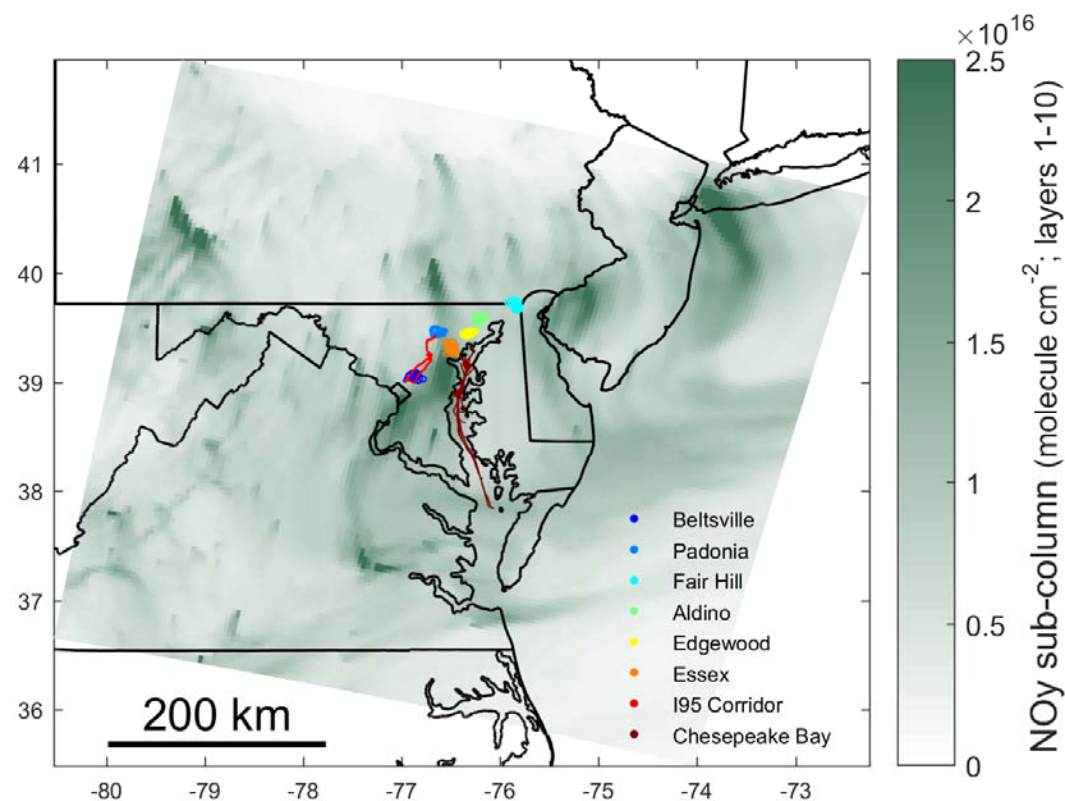
Winter:

CMAQv5.0.2: Monthly Median NO_x Bias by Hour
Site = All Sites | Period = Jan, Feb, Dec 2002-2012



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, PN_s, 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



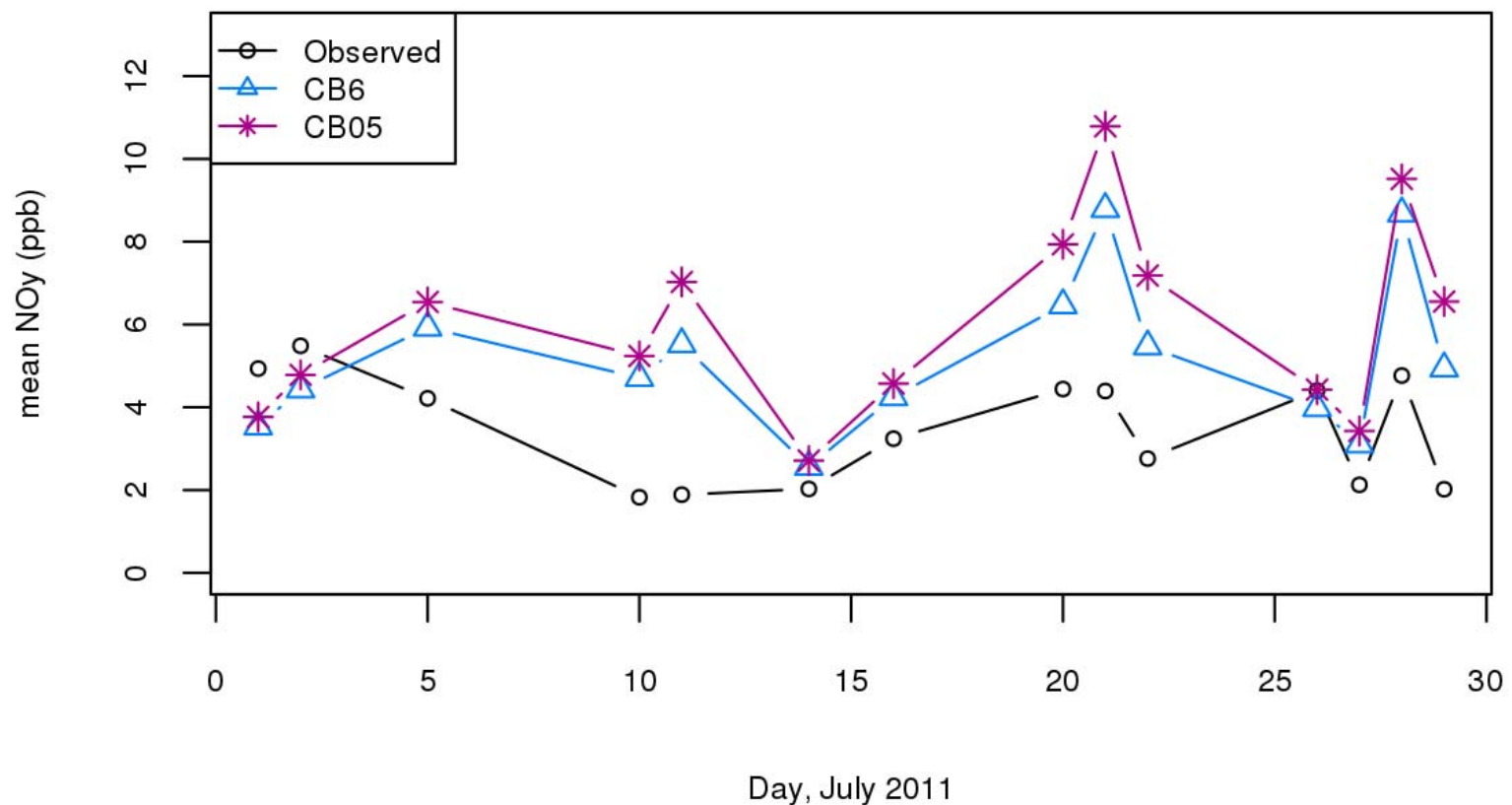
NO_y treatment in CB05 and CB6 chemical mechanisms evaluated

- These are two versions 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 HNO₃ and NO₂
 - Mostly terminal
 - CB6
 - 3 species
 - Can form HNO₃, other alkyl nitrates, and NO₂
 - 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 HNO₃ although CB6 AN chemistry leads to more formation of HNO₃
- 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

Impact of Chemical Mechanisms on Model NO_y Performance:

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



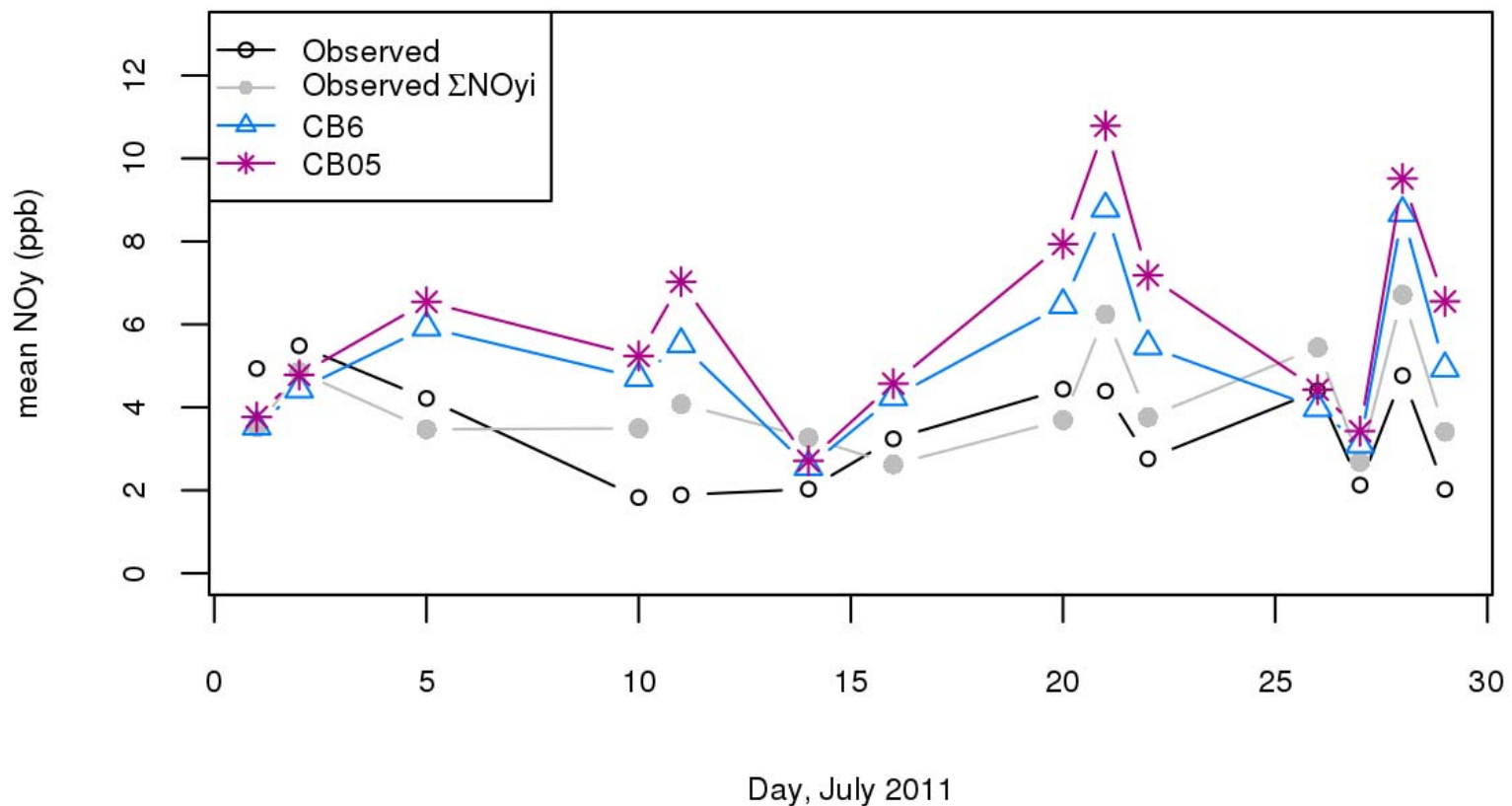
CMAQ-Observation Comparison with aircraft measurements taken within the PBL

Impact of Chemical Mechanisms on Model NO_y Performance:

- CB05 NO_y NMB : 76%
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Impact of Observational Uncertainty:

- CB05 NO_y NMB compared to Observed ΣNO_{yi} : 49%
- CB6 NO_y NMB compared to Observed ΣNO_{yi} : 28%



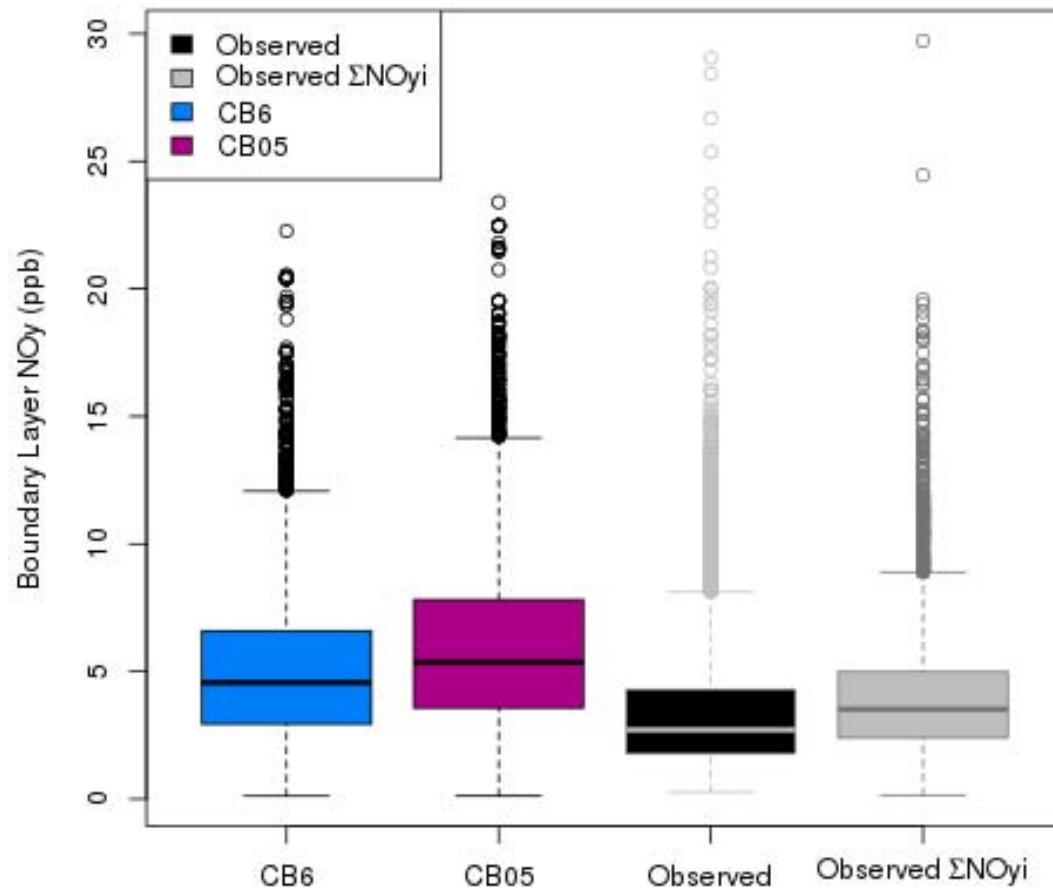
CMAQ-Observation Comparison with aircraft measurements taken within the PBL

Impact of Chemical Mechanisms on Model NO_y Performance:

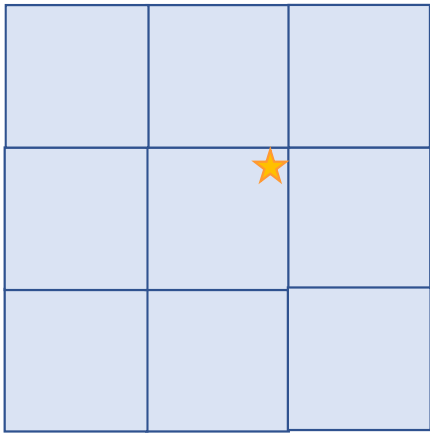
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Impact of Observational Uncertainty:

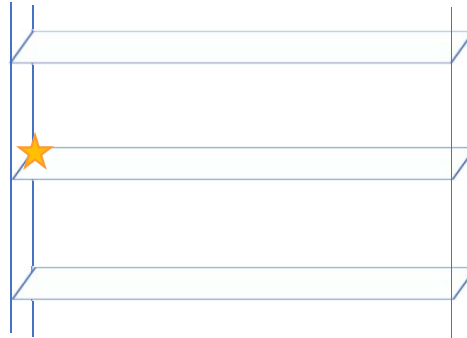
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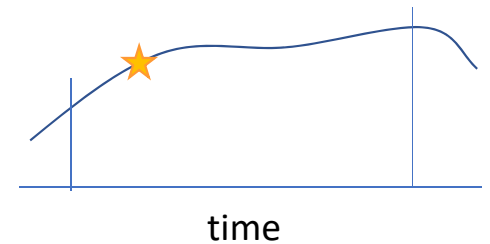
Further Challenges with spatial & temporal matching between model and measurements additionally impacts calculated bias



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

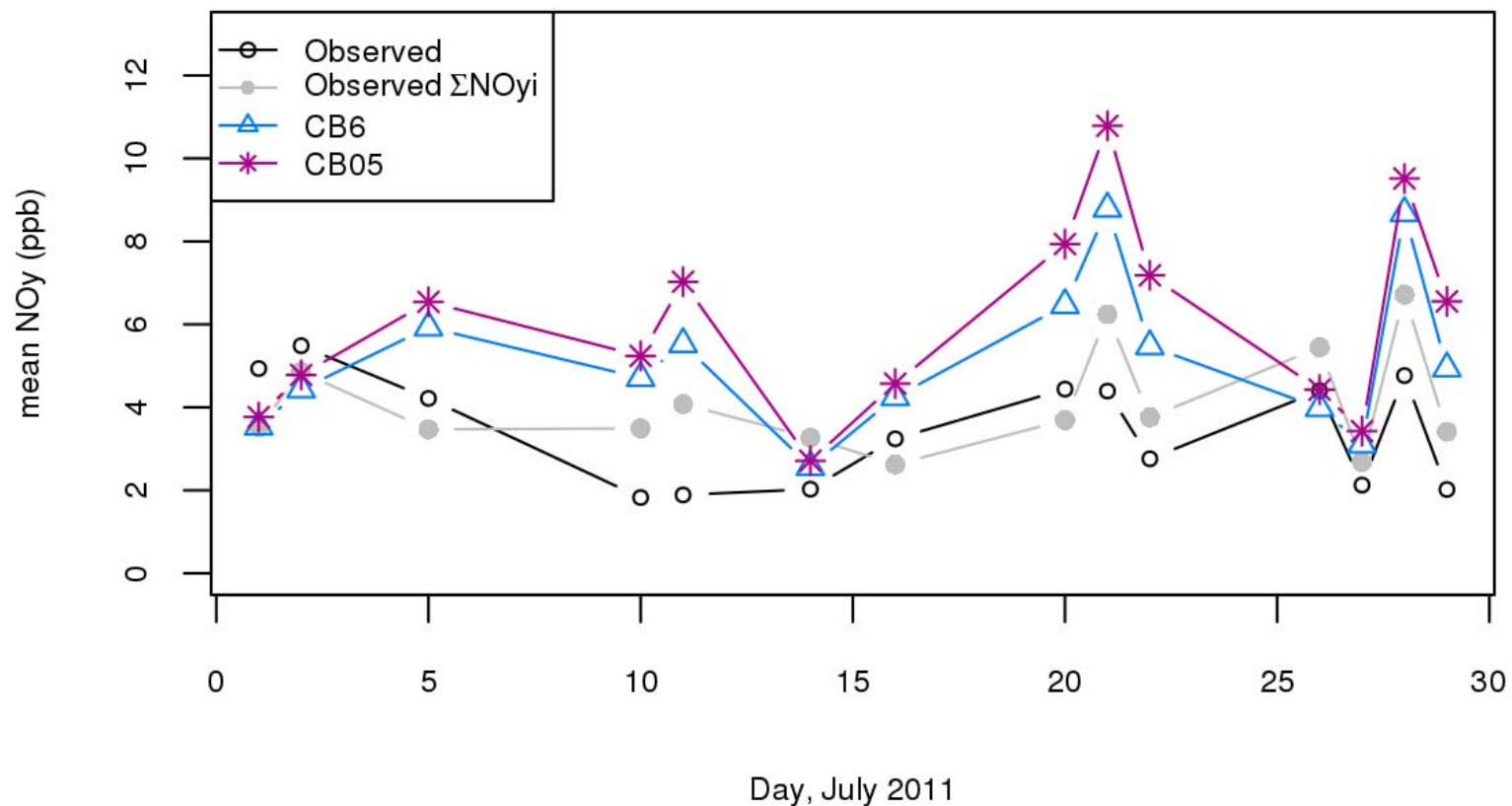


Vertical sampling:
Vertically mixed layers versus
point in space



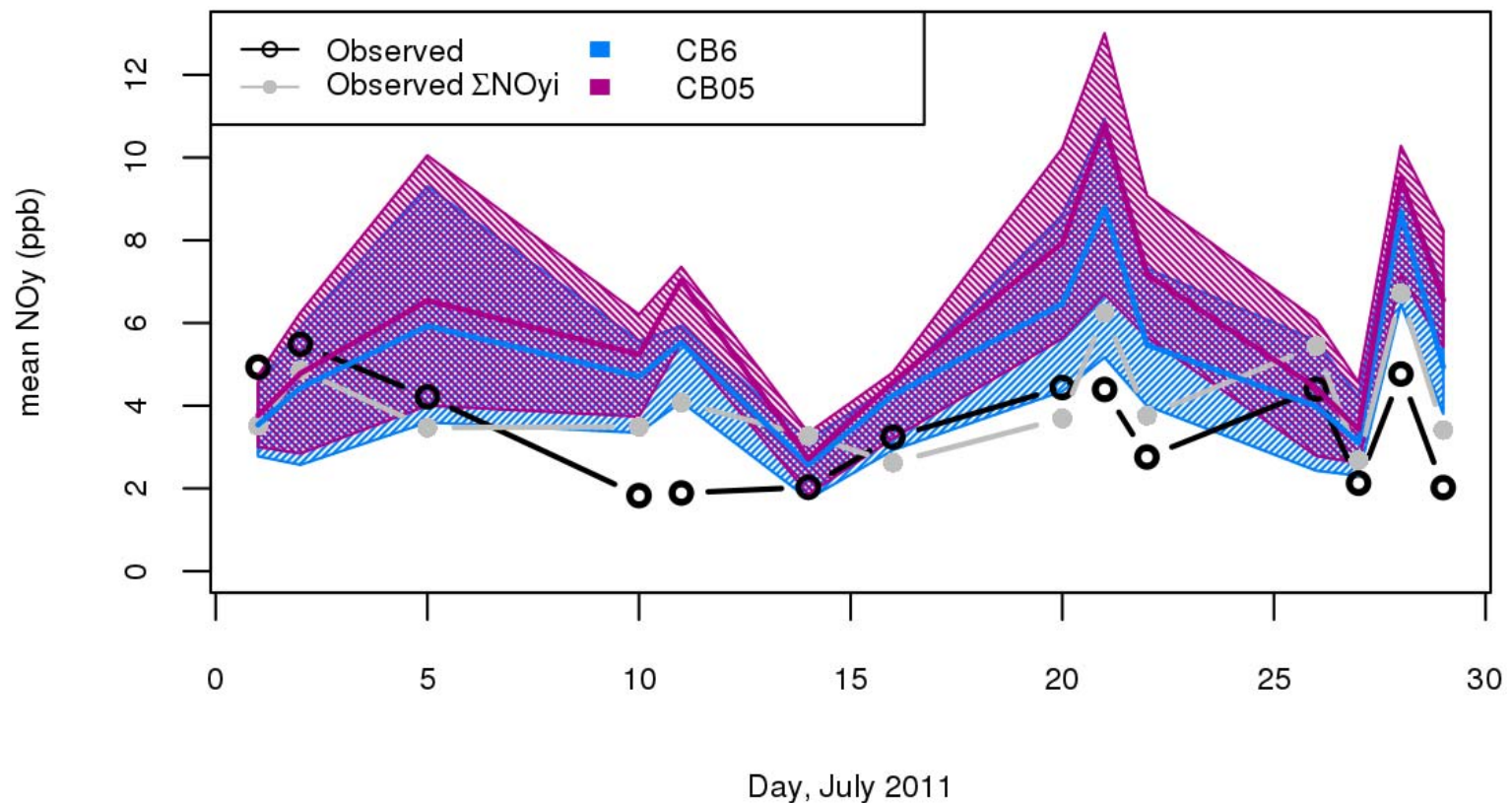
Temporal sampling:
Hourly model values versus
15 second measurements

CMAQ-Observation Comparison with aircraft measurements taken within the PBL



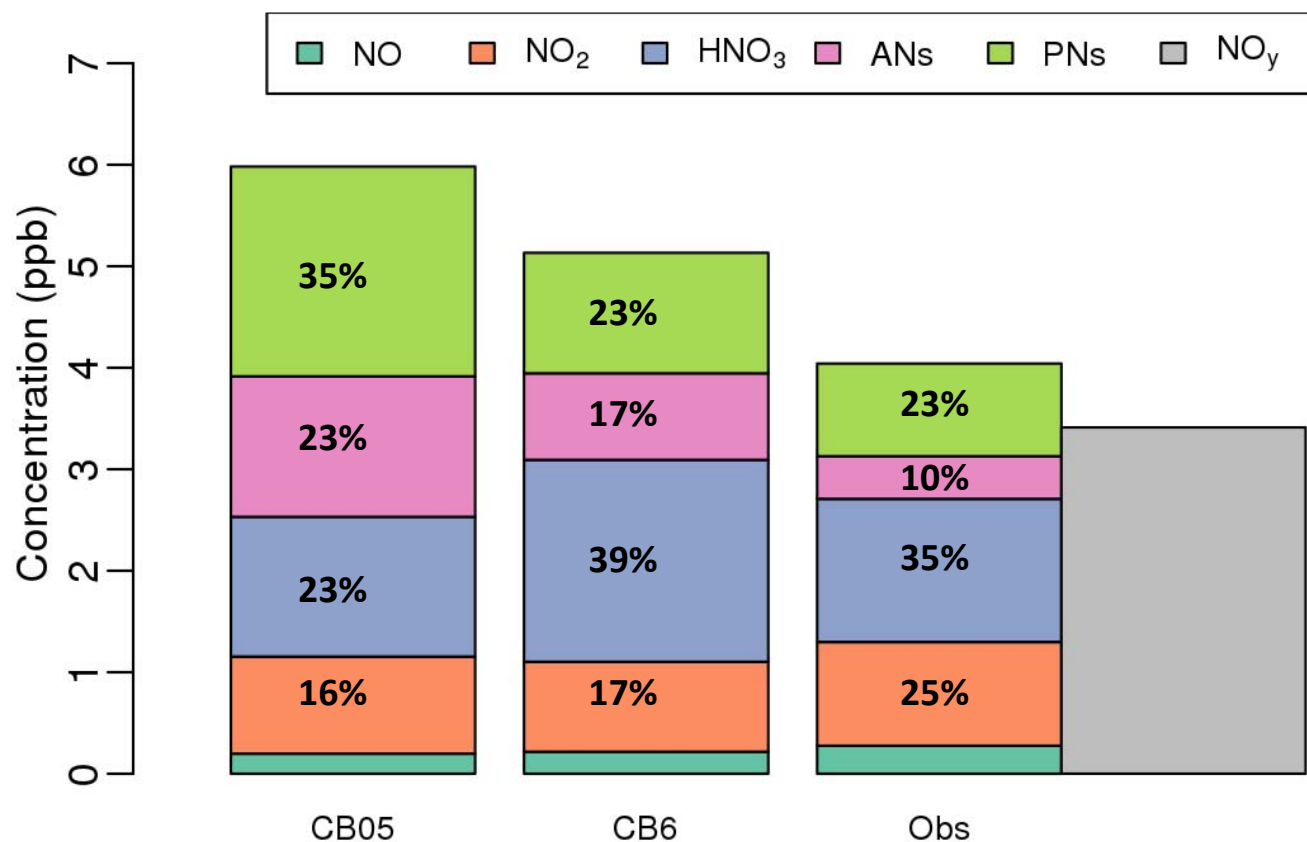
Model values represent matching measurement location to grid cell (horizontal and vertical) and measurement time to closest hour

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

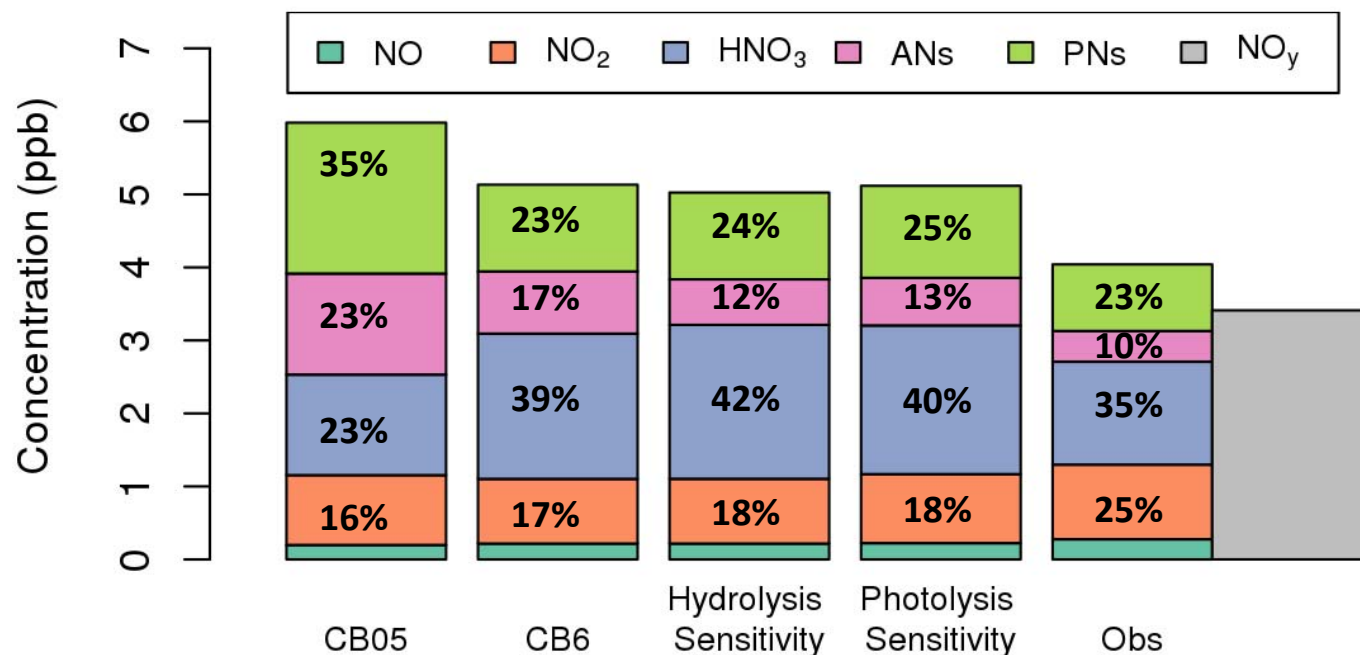


- Both mechanism simulations overpredict NO_y
 - CB6 is an improvement over CB05
- NO_x performance is pretty good in both model simulations
 - NO₂ fraction is higher in observations than modeled
- NO_z species are overestimated in all model simulations
 - CB6 has reduced ANs and PNs leading to better agreement with observations
 - CB6 has increased HNO₃ 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 NO₂ 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?

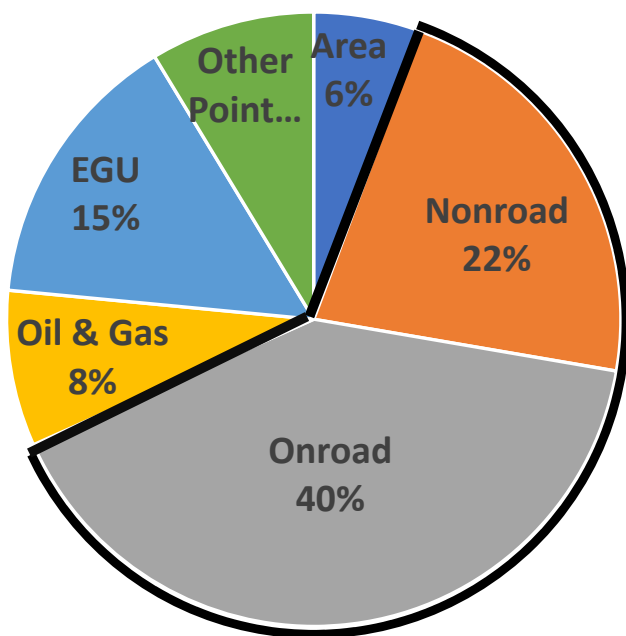
Questions?

Disclaimer:

The views expressed in this presentation are those of the authors and do not necessarily reflect the views or policies of the U.S. EPA, Office of Research and Development.

Important Sources of NOx in the 2011 NEI

NOx Emissions in the 2011 NEI (tons)



Breakout of NOx emissions from onroad and nonroad mobile source sectors

