NOx Chemistry in Action: A Comparison of Methodologies

Emily Tupper, Lead Consultant

Jason Reed, Principal

Ramboll Americas Engineering Solutions, Inc.

September 25, 2025

2025 AWMA RMSS Conference – Denver, CO

Agenda

1. Objective and Methodology
2. Background
3. GRSM NOx Chemistry
4. Overview of MPE
5. Considerations

Objective and Methodology

- Provide background on the NOx chemistry options in AERMOD
- Use existing AERMOD NOx chemistry database to evaluate the sensitivity to in-stack ratios
  - GRSM/PVMRM estimation if in-stack ratio is varied

Model Evaluation Databases - NO_2
README (TXT)(1 KB, 10-31-2023) - Document that explains the NO_2 databases below that contain input and output data for the model evaluation Balko (ZIP)(12 MB, 10-31-2023) - Input/output data for Balko; Terrain, Rural, Downwash, Independent, 4 NO_2 monitors Denver-Julesburg (Supplemental for 2023 TSD) (ZIP) (2 MB, 10-31-2023) - Input/output data for Denver-Julesburg; Terrain, Rural, Downwash, Independent, 12 NO_2 monitors Denver-Julesburg (ZIP)(108 MB, 08-18-2020) - Input/output data for Denver-Julesburg: Flat, Rural, Non-downwash, Independent, 12 NO_2 monitors Empire Abo (ZIP)(14M, 10-31-2023) - Input/output data for Empire Abo; Flat, Rural, Downwash, Independent, 2 NO_2 monitors Pala'au (ZIP)(6 MB, 10-31-2023) - Input/output data for Pala'au; Flat, Rural, Downwash, Inpendent,1 NO_2 monitor

History of NOx Chemistry in AERMOD

1971 — Annual NO_2 standard promulgated

1998 — AERMOD replaces ISC as EPA's preferred Regulatory Model

2005 — AERMOD is incorporated into Appendix W!
- Tier 1 NOx chemistry (100% conversion)
- Tier 2 NOx chemistry (75% conversion)
- Tier 3 NOx chemistry on a case-by-case basis (OLM), PVMRM is still being tested…

2010 — 1-hour NO_2 standard promulgated Use of OLM/PVMRM generally accepted

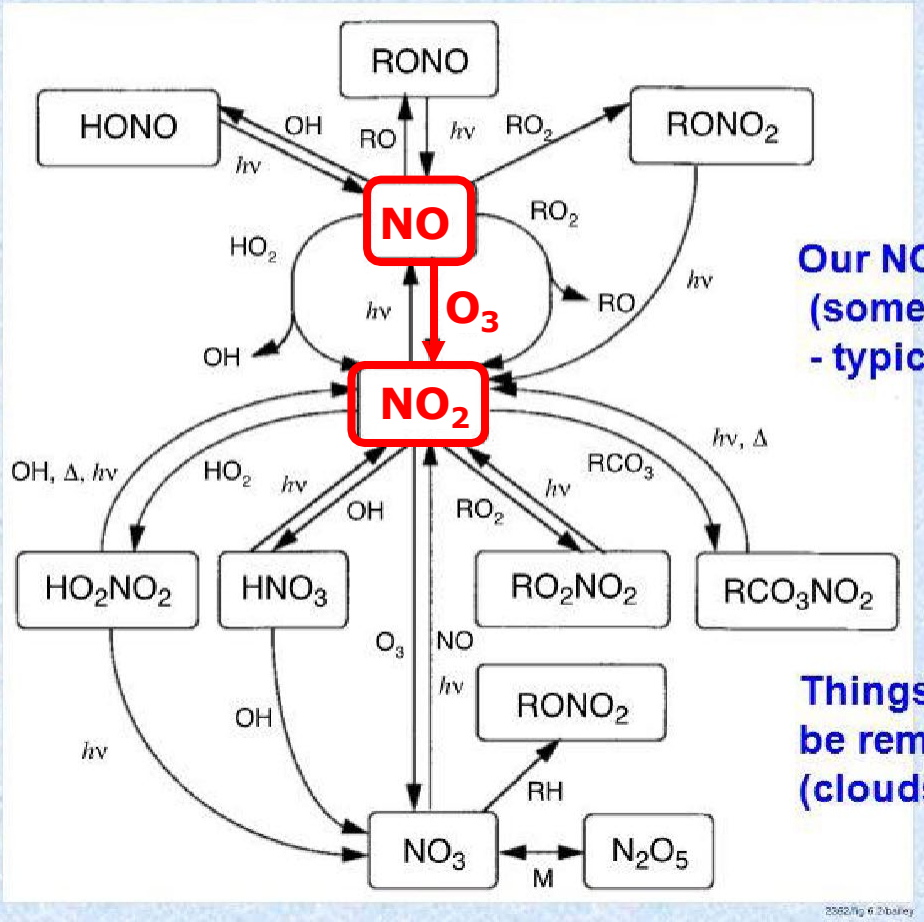
2017
- OLM/PVMRM approved as Tier 3 preferred screening methods
- ARM2 replaces ARM

2024 — Appendix W approved GRSM as another Tier 3 Option!

Big year for AERMOD, yet 2005 Emily was not even thinking about AERMOD!

Why are there NOx Chemistry Options in AERMOD?

NOx chemistry in the troposphere



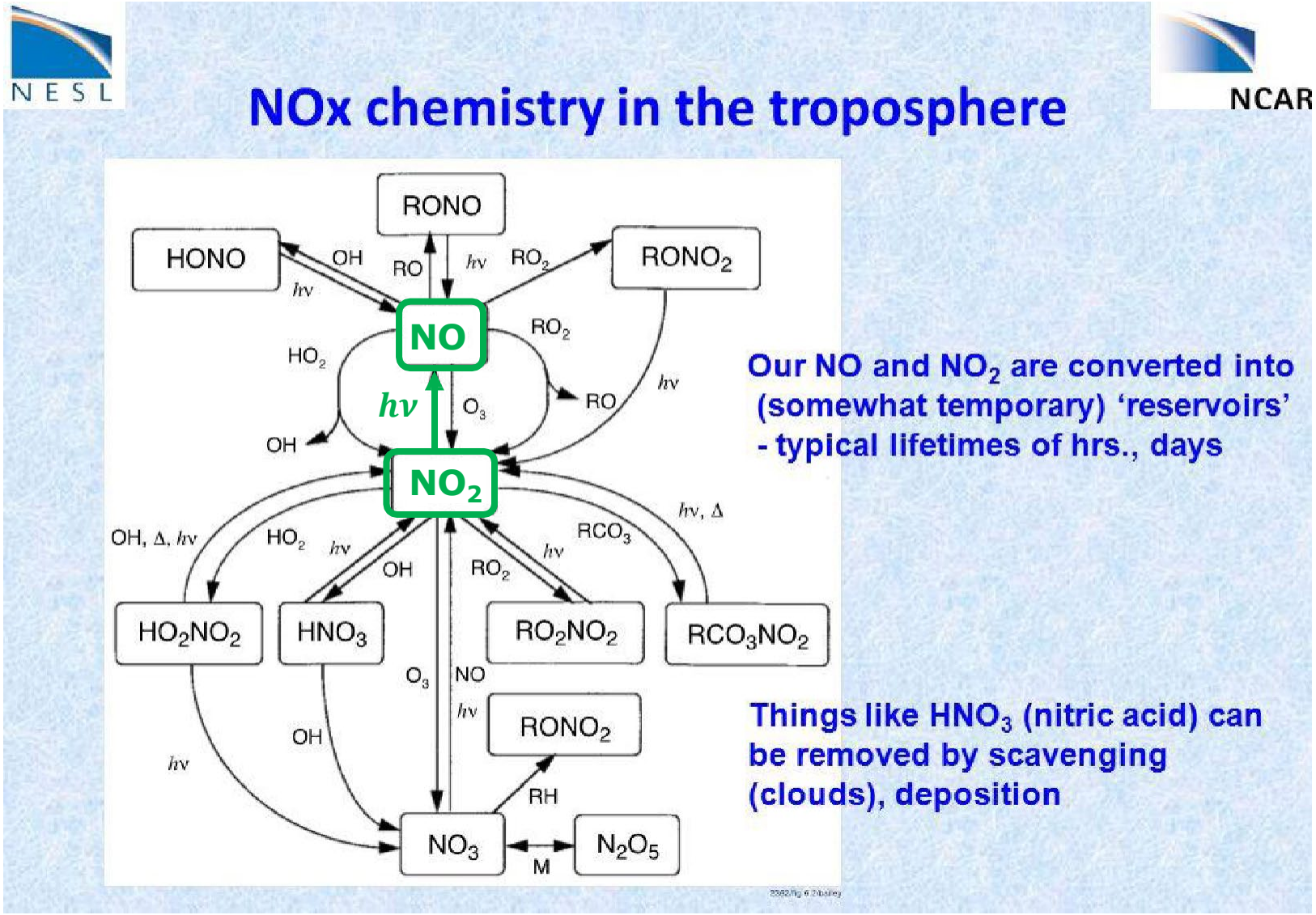
Our NO and NO_2 are converted into (somewhat temporary) 'reservoirs' - typical lifetimes of hrs., days

Things like HNO_3 (nitric acid) can be removed by scavenging (clouds), deposition

"Ozone titration"

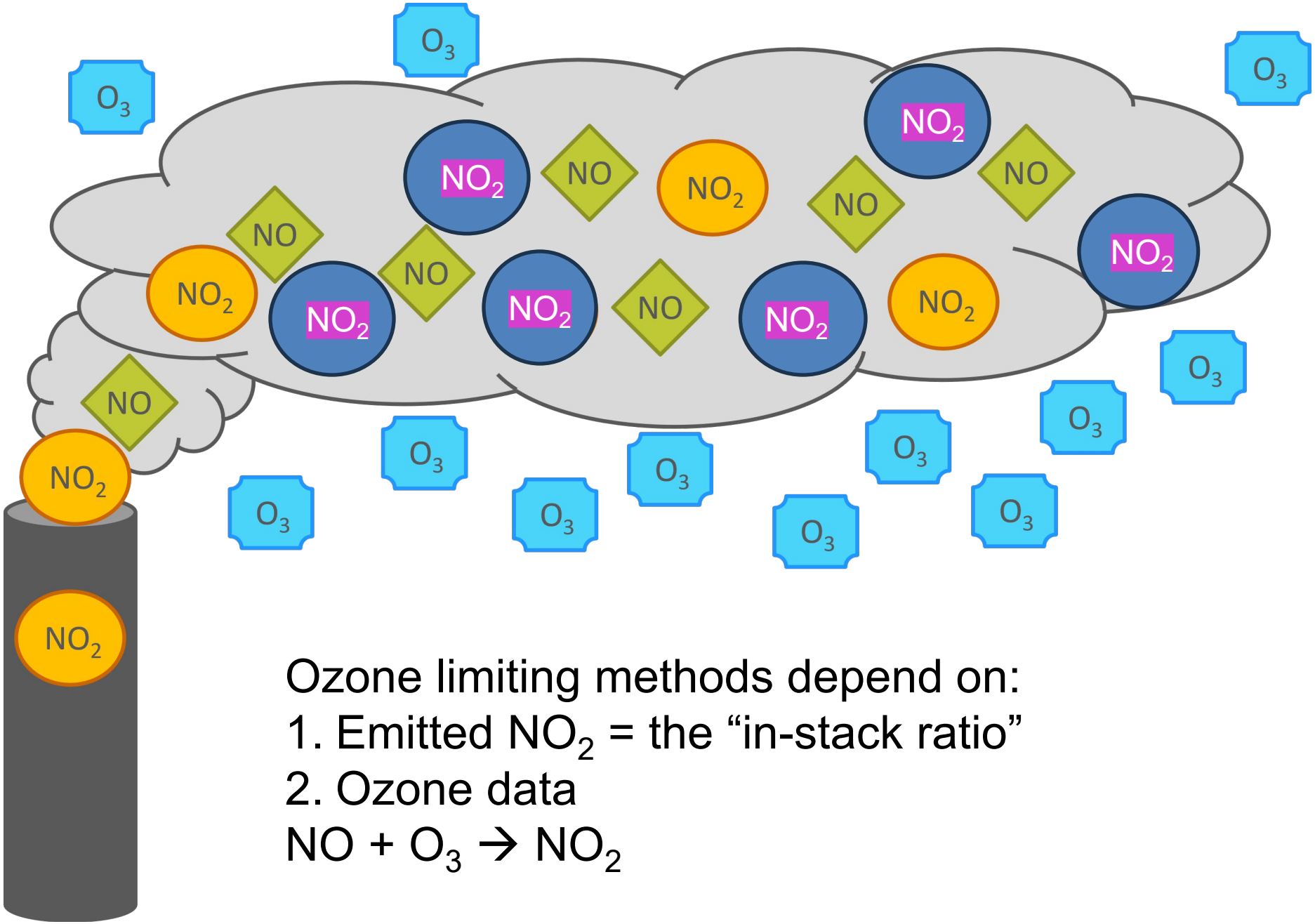
$$NO + O_3 \rightarrow NO_2 + O_2$$

Why are there NOx Chemistry Options in AERMOD?



"NO_2 Photolysis"

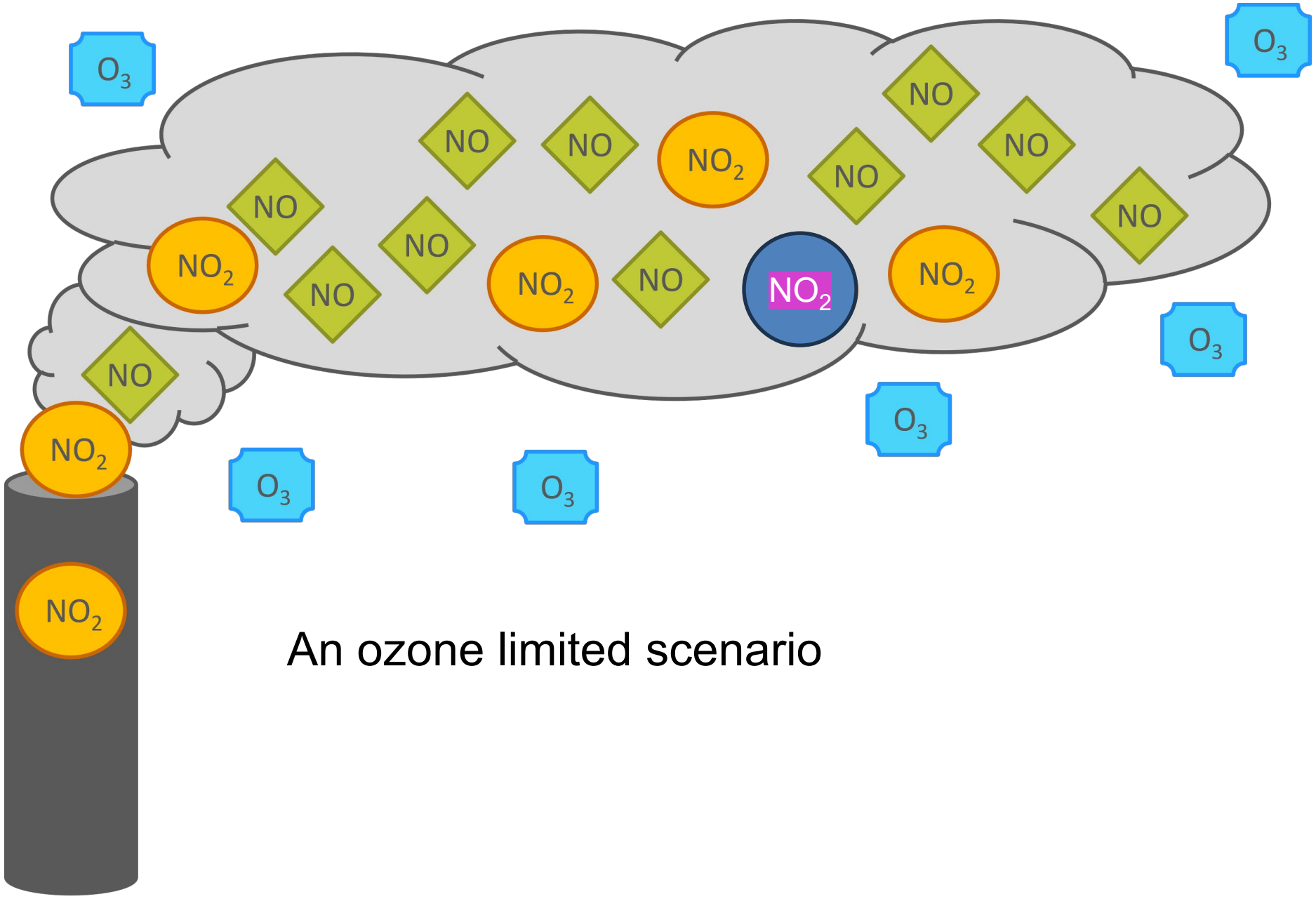
$$NO_2 + h\nu \rightarrow NO + O$$



Ozone limiting methods depend on:

1. Emitted NO_2 = the “in-stack ratio”
2. Ozone data

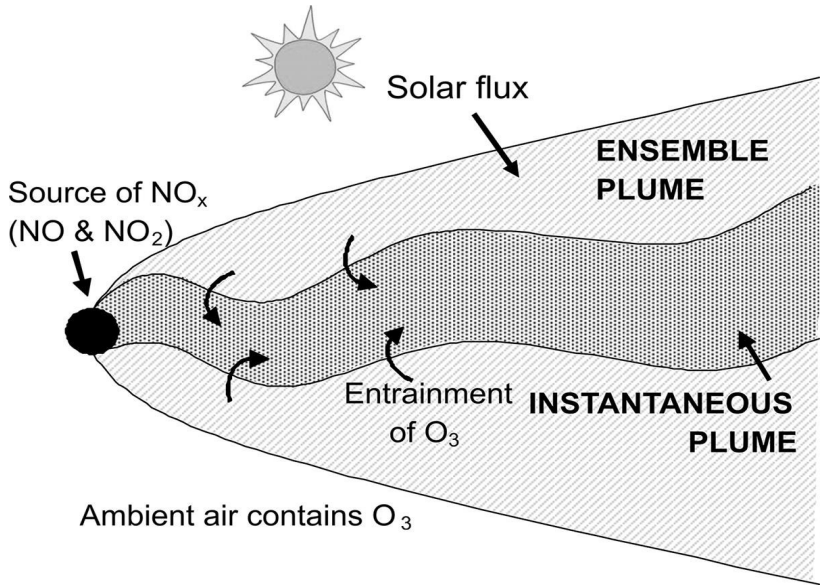
$NO + O_3 \rightarrow NO_2$



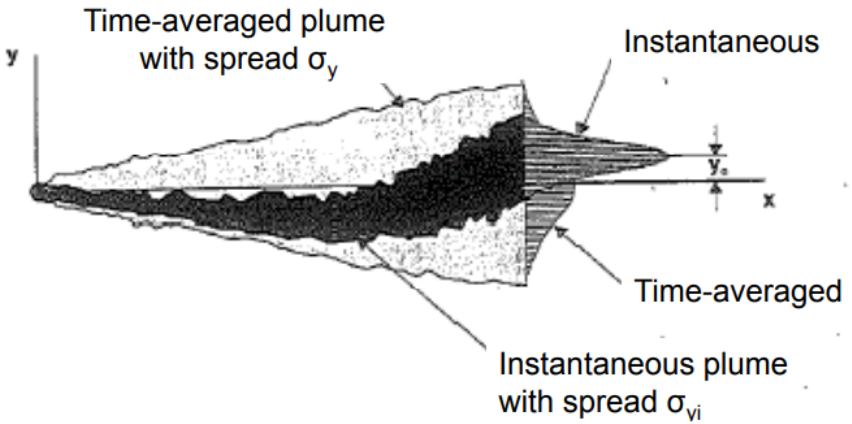
An ozone limited scenario

Differences in Tier 3 Options

Item	OLM (Ozone-Limiting Method) *regulatory*	PVMRM (Plume Volume Molar Ratio Method) *regulatory*	GRSM (Generic Reaction Set Method) *regulatory*
Hourly background	O_3	O_3	O_3, NO_x, NO_2
Method for 'O_3 titration'	100% conversion	100% conversion	Explicit calculation
Method for 'photolysis'	Neglects	Neglects	Explicit calculation
Method for entrainment of O_3 into the plume	Fully entrained into ensemble plume (time-averaged plume)	Limited entrainment (volume-based approach) into *instantaneous* plume	Limited entrainment (cross-sectional area-based approach) into *instantaneous* plume
Main sources of inaccuracy of predicted NO_2	Full entrainment into ensemble plume so upper bound for NO_2	Neglects reaction rates; assumptions relating to entrainment method	Reaction rates; assumptions relating to entrainment method



From: "Theory, Application, and Evaluation of the Generic Reaction Set Method (GRSM) for NO_2 Chemistry" by Jenny Stocker. 2021 (June 21) RSL Workshop



Dr. D. J. Wilson 1995, "Concentration Fluctuations and Averaging Time in Vapor Clouds" (CCPS Concept Book)

GRSM NOx Chemistry

Equation 1 (ozone titration) R1[NO] + [O_3] ➔ NO_2 + O_2 (Eq. 1)
Equation 2 (photolysis) [NO_2] + sunlight (R2) ➔ NO + O_3 (Eq. 2)

Theory:

Entrainment into the instantaneous plume

During the day, GRSM assumes a photostationary state (PSS), which establishes equilibrium between background O_3, NOx, and NO_2

- Eq. 1 = Eq. 2 (equilibrium)
- R1 and R2 are reaction rates (ppb/s) that are function of temperature and solar radiation
- Inputs to GRSM change each hour: NO_2, NOx, ozone, radiation, and temperature

During the night, GRSM operates similar to PVMRM

*simplified overview and dependent on inputs

Model Performance Evaluation (MPE)

Databases:

- Power plant located on the Island of Moloka'i Pala'au, Hawaii (Palaau)
- Gas processing plant in Artesia, New Mexico (Empire Abo)
- Gas compressor station near Balko, Oklahoma (Balko)
- **Oil and gas drill rig in Denver-Julesburg Basin near Platteville, Colorado**

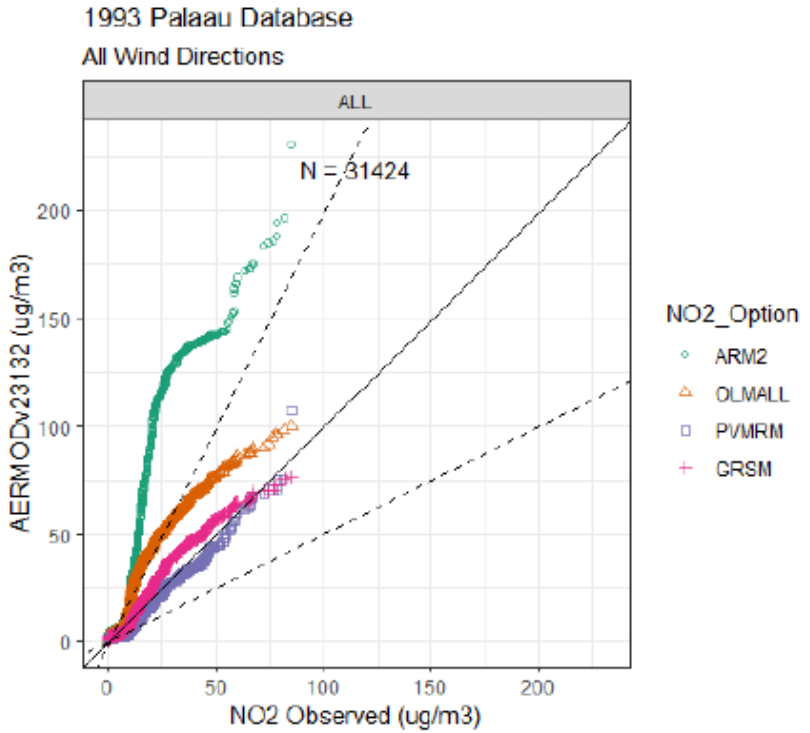


Figure 2 – Pala'au NO_2 Ranked Q-Q Plot

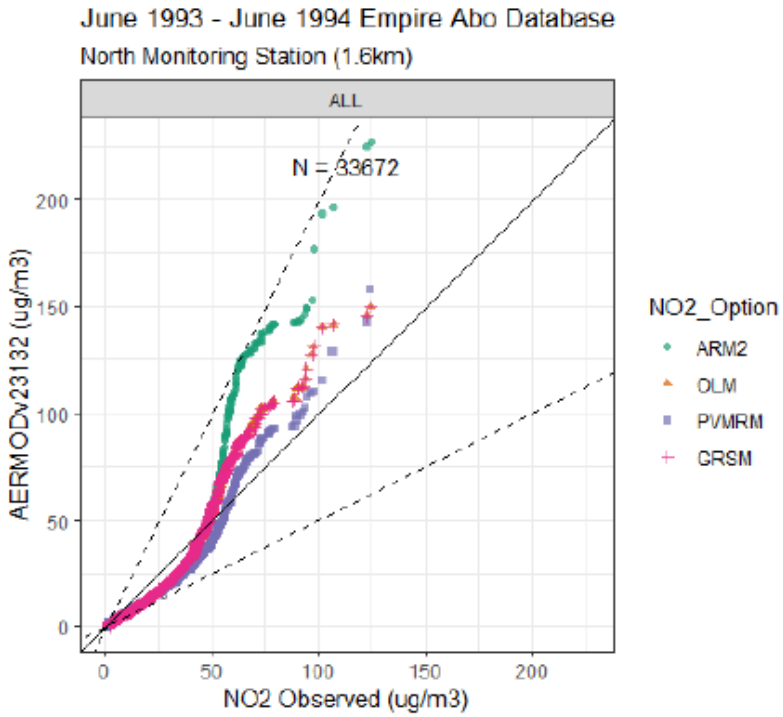
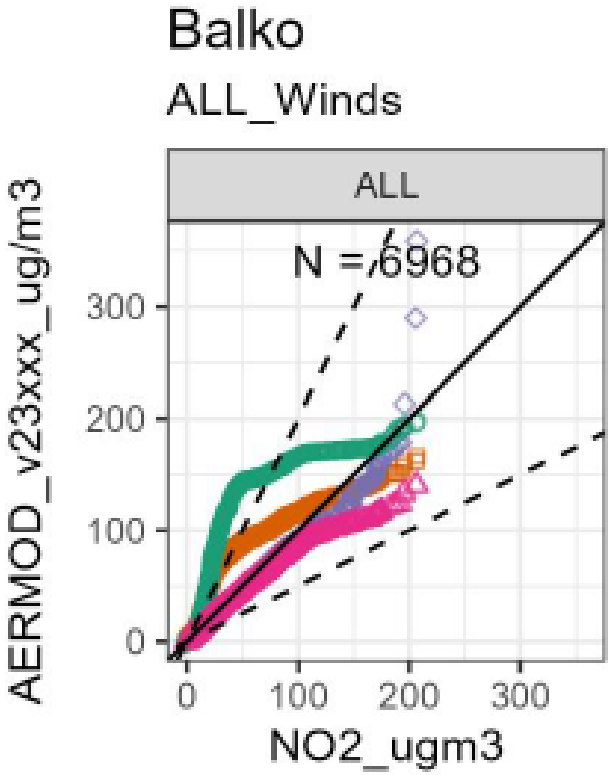
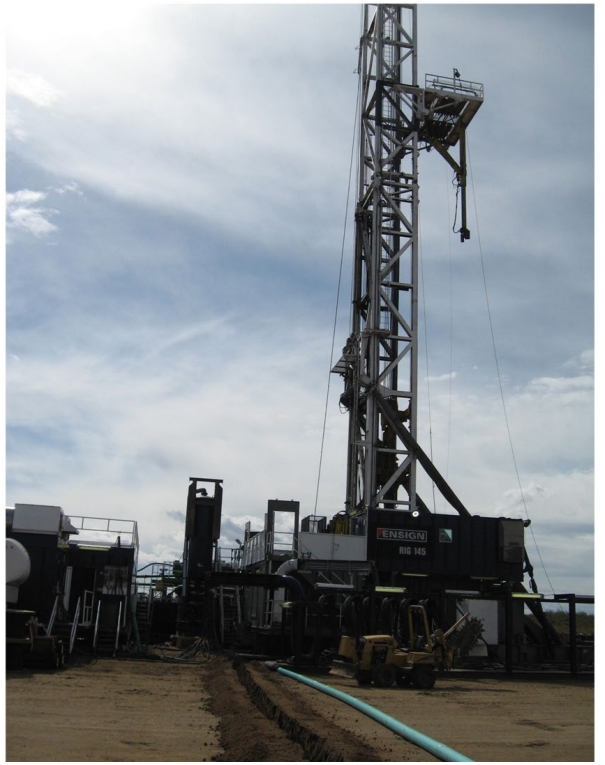


Figure 4 – Empire Abo NO_2 Ranked Q-Q Plot for the North Monitor



Model Performance Evaluation (MPE)

- On-site data from two well pads (Pad 1 & 2) in the Denver-Julesburg basin
- Pad 1 from Oct. 10-26, 2014
- Pad 2 from Nov. 3-16, 2014
- Data collected:
  - Continuous NO_x, NO, and NO_2 emissions from the three diesel engines that power the drilling rig
  - Continuous AQ levels of NO and NO_2 at 12 sites upwind, downwind, and crosswind to the drilling rig
  - Continuous levels of O_3 at one upwind and one downwind site
  - Meteorological data collected upwind and downwind of the site



Model Performance Evaluation (MPE)

- EPA published Technical Support Document (TSD) for GRSM in October 2023
- Some uncertainty in the quantification of downwash and in-stack ratios, especially at Pad 2

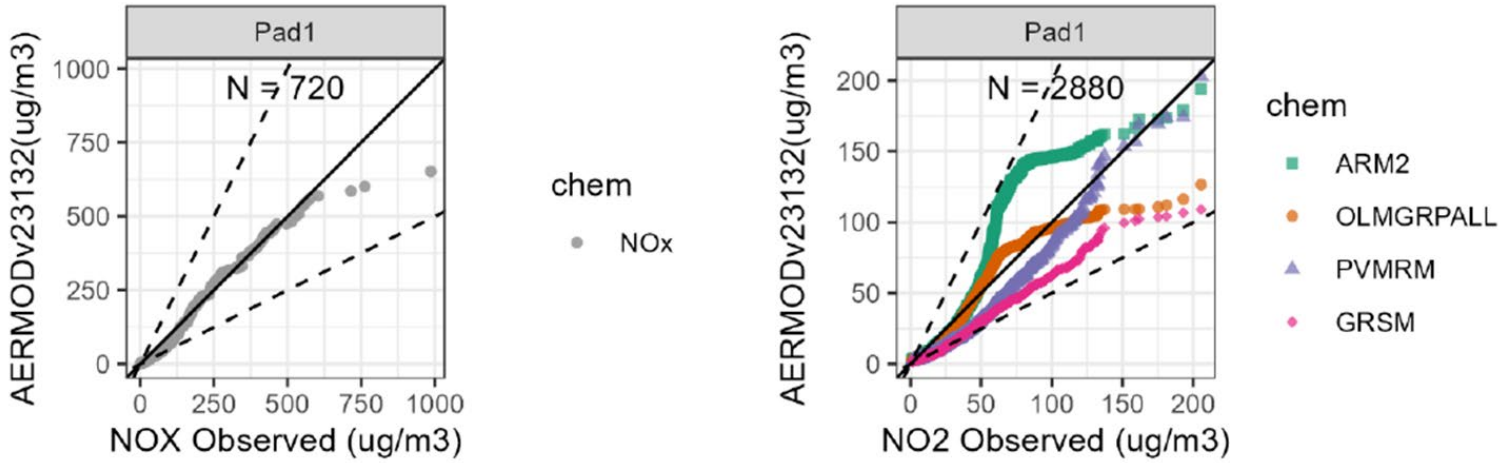


Figure 8 – Colorado NO_X and NO_2 Ranked Q-Q Plots for Pad 1

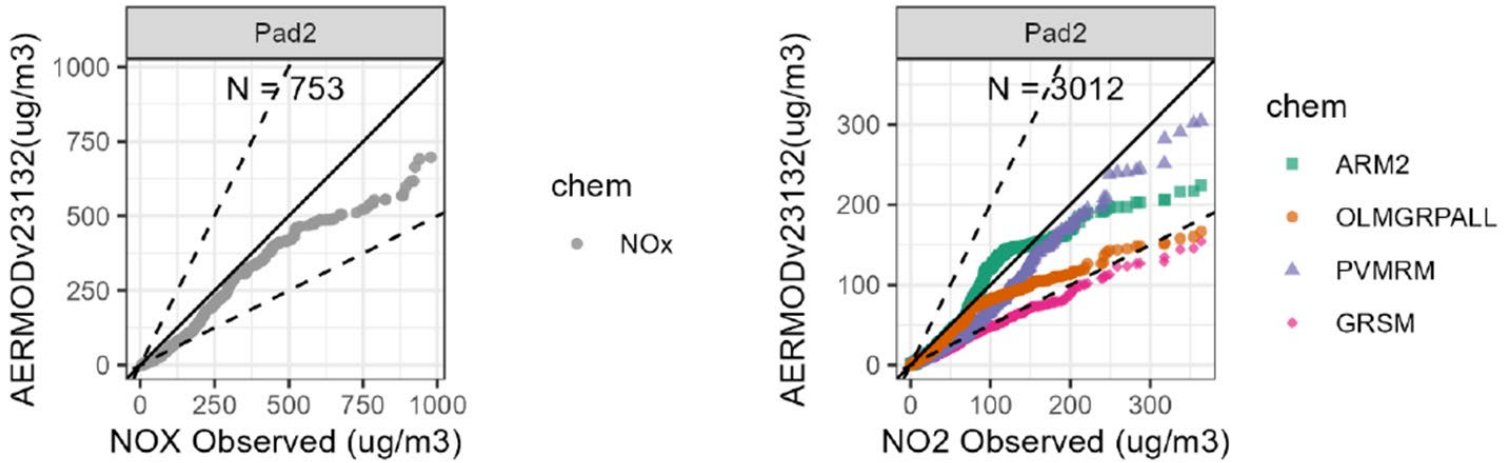
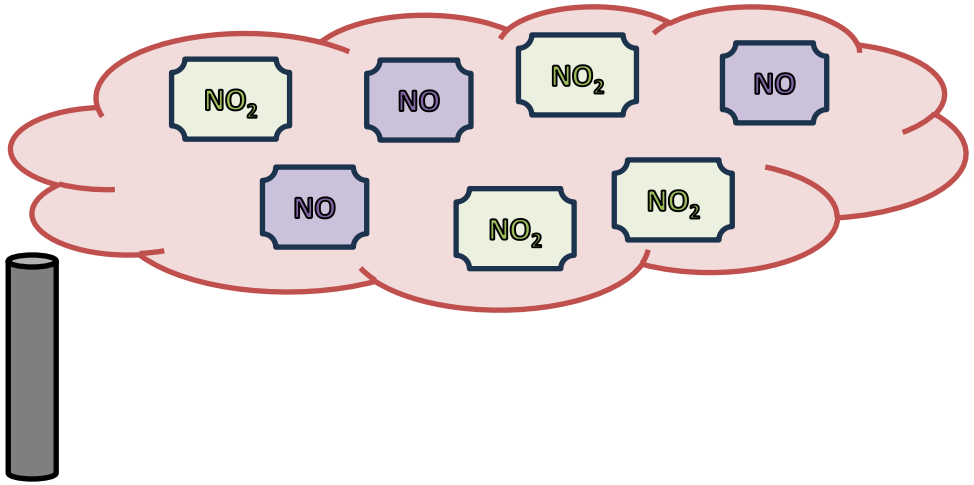
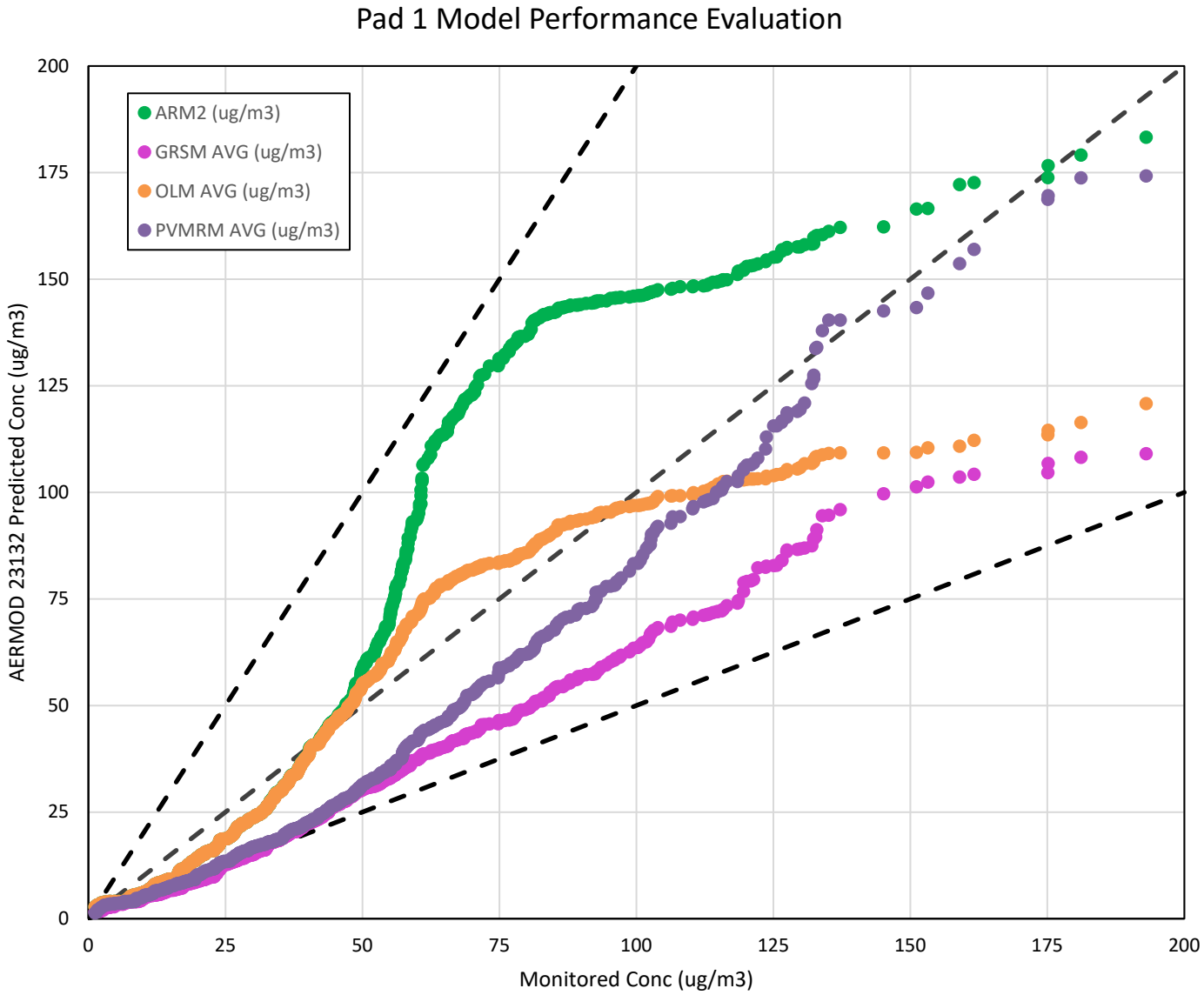


Figure 9 – Colorado NO_X and NO_2 Ranked Q-Q Plots for Pad 2

Model Performance Evaluation (MPE)

- Why is GRSM underpredicting?
- Downwash and in-stack ratios were cited as possible reasons for this underprediction
- In-stack ratios are input as a static (non-varying) value – but this value changes as the unit operations change



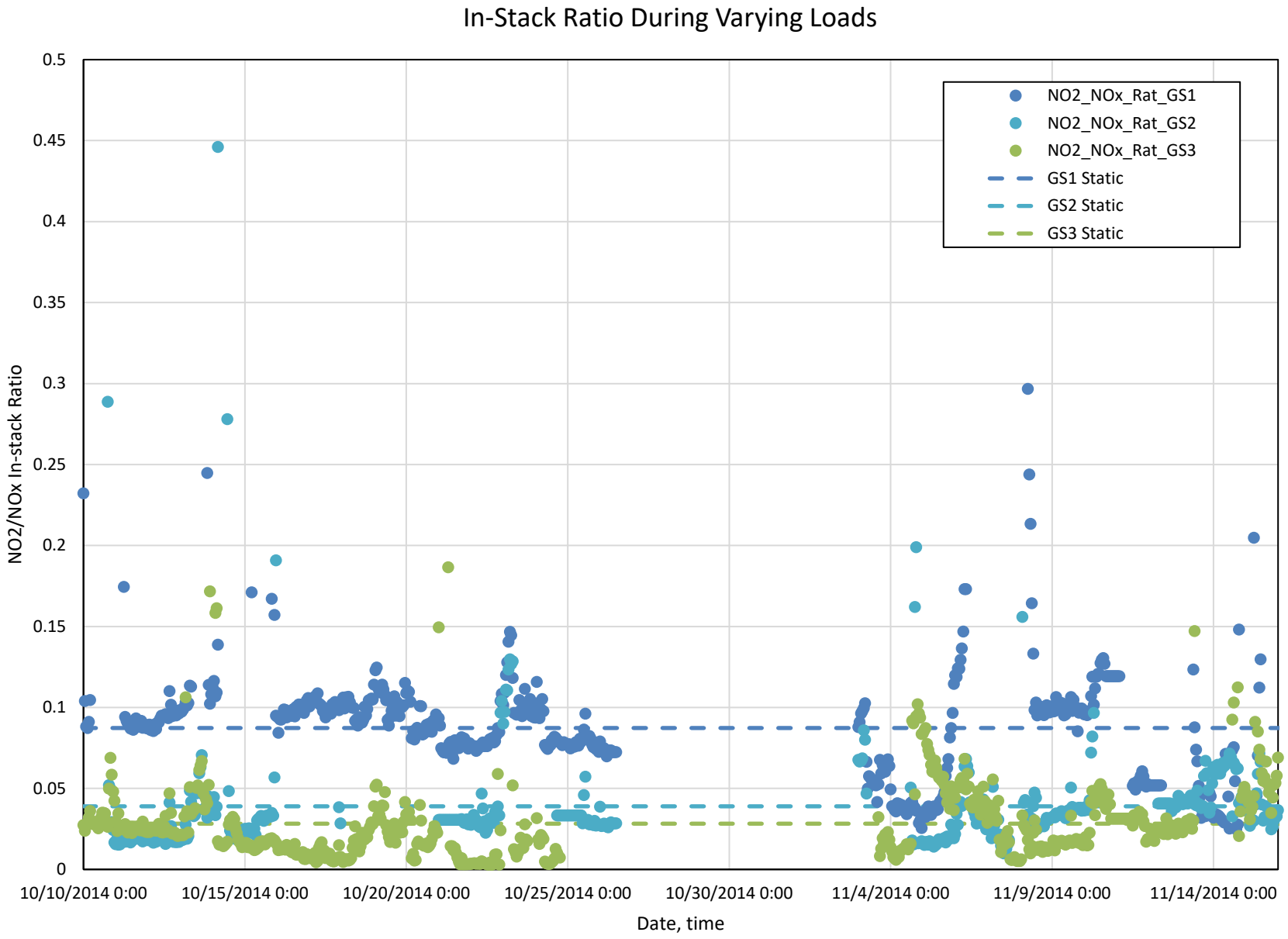


In-Stack Ratio

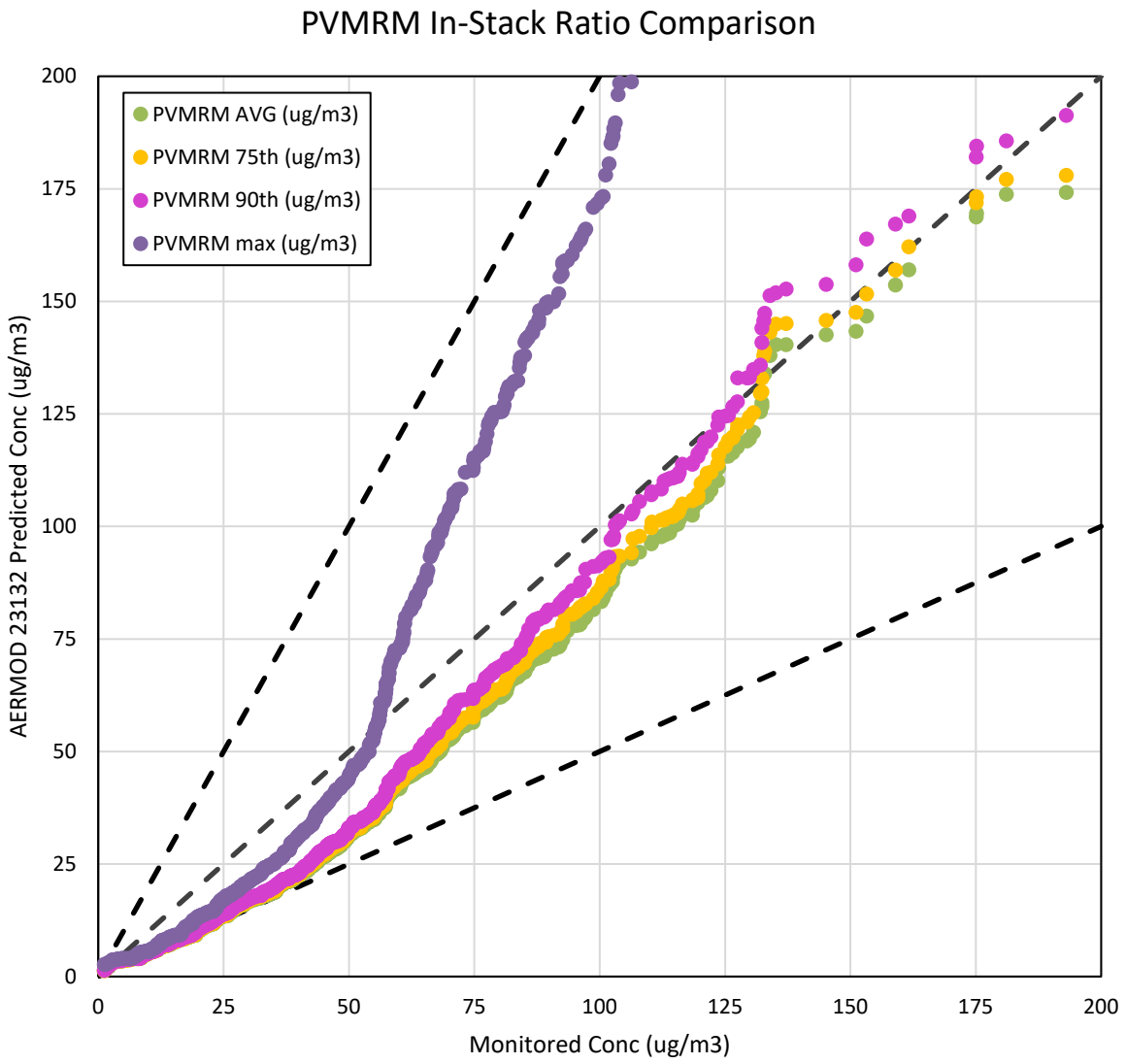
- ISR derived from 723 hours of NOx and NO_2 data collected for each source
- Minimum limits were set on the NOx and NO_2 ppm for an in-stack ratio to be calculated
- The ISR used in the modeling was the average of the data set

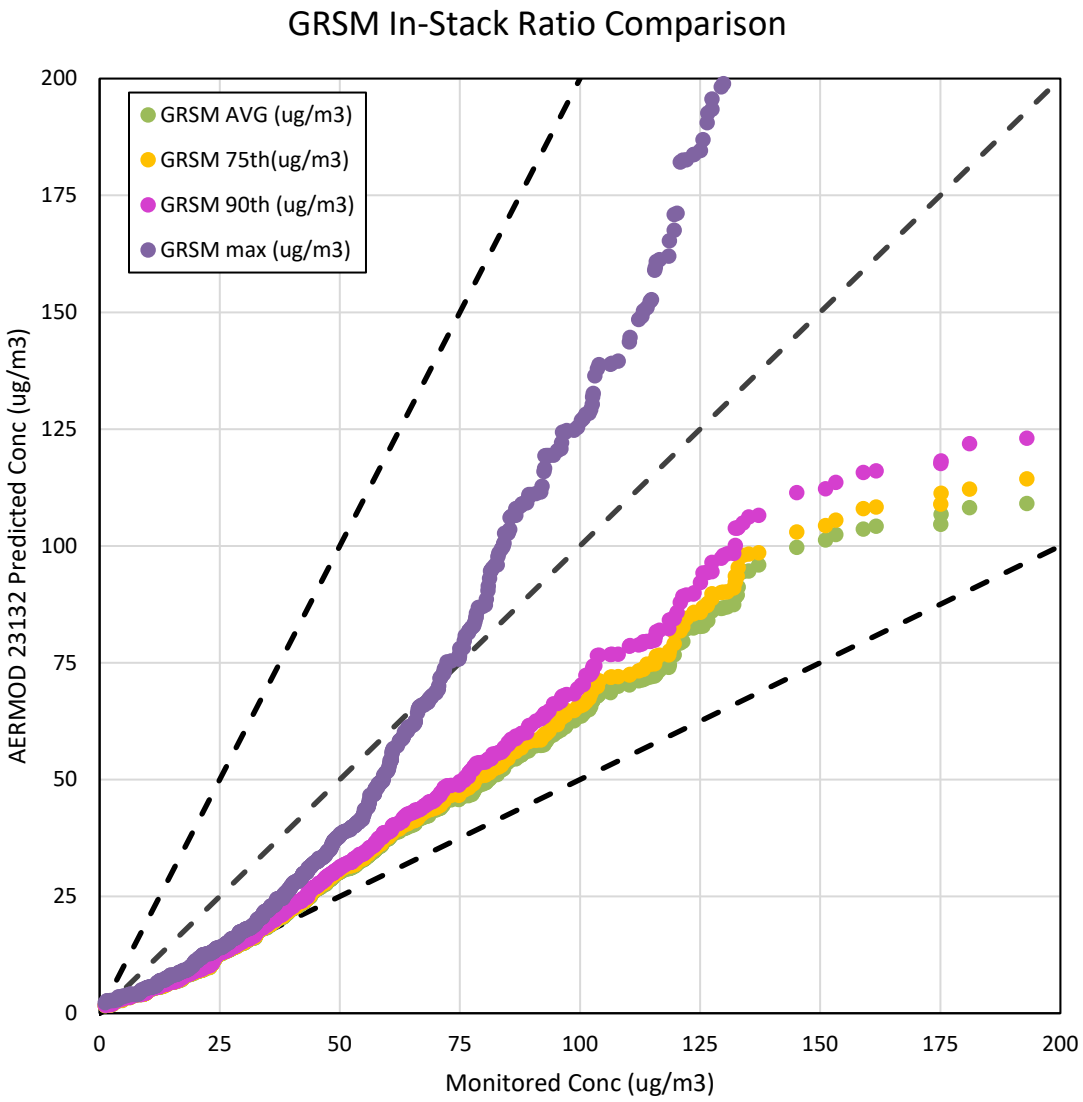
Unit	Min	Max	Average
GS01	0.0248	0.2967	0.0873
GS02	0.0099	0.4460	0.0390
GS03	0.0030	0.1865	0.0282

75th percentile	90th percentile
0.1012	0.1156
0.0407	0.0630
0.0346	0.0526



Pad 1


PVMRM In-Stack Ratio Comparison
PVMRM AVG (ug/m3)
PVMRM 75th (ug/m3)
PVMRM 90th (ug/m3)
PVMRM max (ug/m3)
AERMOD 23132 Predicted Conc (ug/m3)
Monitored Conc (ug/m3)
0
25
50
75
100
125
150
175
200


GRSM In-Stack Ratio Comparison
GRSM AVG (ug/m3)
GRSM 75th(ug/m3)
GRSM 90th (ug/m3)
GRSM max (ug/m3)
AERMOD 23132 Predicted Conc (ug/m3)
Monitored Conc (ug/m3)
0
25
50
75
100
125
150
175
200

Implications and Next Steps

- Applicant Considerations:
  - OLM is effectively a screening option
  - PVMRM similar to GRSM, but noted issues at high concentrations
  - GRSM is better science; availability of NOx/NO_2/O_3 data? ease of approval process?
- Agency Considerations:
  - NO_2 monitors concentrated in urban areas
  - NO_2 background no longer static value, now used in the chemistry
  - Importance of other inputs such as radiation for photolysis
  - General EPA guidance was that PVMRM was for "isolated sources", since GRSM is based on similar concepts – does that hold?

Another layer of paint?!

Thank you

Emily Tupper
etupper@ramboll.com
Jason Reed
jreed@ramboll.com

RAMBOLL

Bright ideas.
Sustainable change.