

The role of chemistry in upper troposphere NO₂ under-predictions

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CMAQ compared with SCIAMACHY: worst in rural areas.

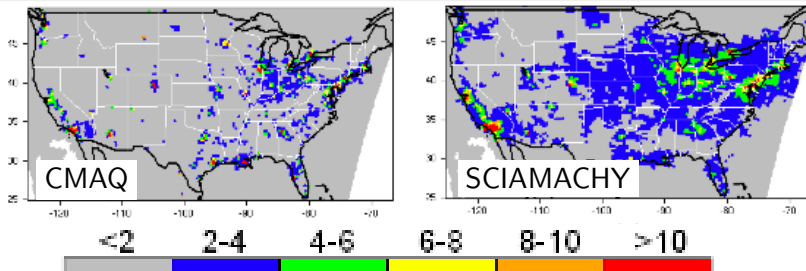


Figure 1: NO₂ columns (10¹⁵ molec/cm²) from Napelenok ACP 2008

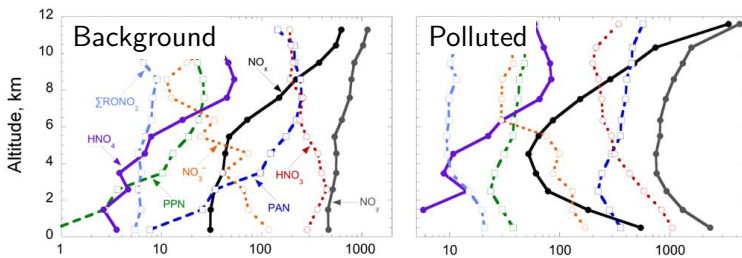


Figure 2: Vertical profiles of background and polluted conditions from Singh 2007.

Which model processes lead to under-prediction?

- Potential sources of error:
 - chemistry, photolysis, aerosols, advection, convection, diffusion, wet deposition, dry deposition, emissions, the stratosphere, the ocean, ...
- Modeled chemistry has been questioned (Olson 2006, Bertram 2007, Ren 2008)
 - **typically**: evaluate a model against a chamber study (i.e. a controlled timeseries of measurements)
 - **problem**: does anyone have a chamber at 236K and 0.298 atm?
- **What to do?**
 - 1 We need a timeseries of observations
 - 2 We need a timeseries of model results

Bertram results can derive air parcel ages

Deep convection sends a plug of surface air to upper troposphere

- wet scavenging removes HNO_3 and lightning adds NO_x
- Air parcels are mostly stable for up to 5 days
- Freshly convected: $\text{NO}_x:\text{HNO}_3 \gg 1$
- Aged air parcel: $\text{NO}_x:\text{HNO}_3 \ll 1$

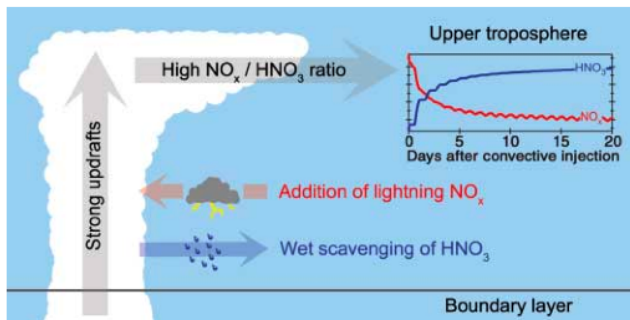


Figure 3: Deep convection from Bertram et al. Science 2007

Observation timeseries: classified by “derived age”

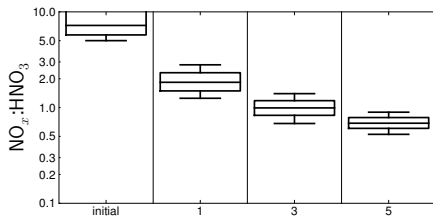


Figure 4: $\text{NO}_x:\text{HNO}_3$ is used to categorize days since convection. O_3 shows a monotonic increase with time. CO shows a monotonic decrease with time. NO_2 shows a gradual increase with time.

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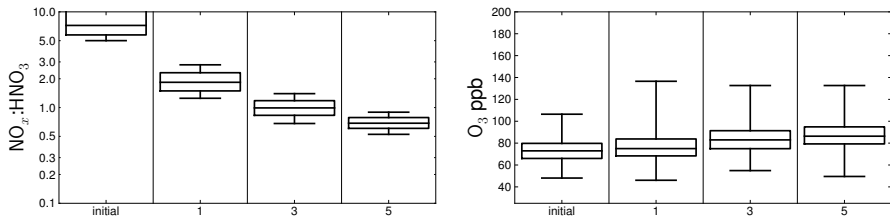


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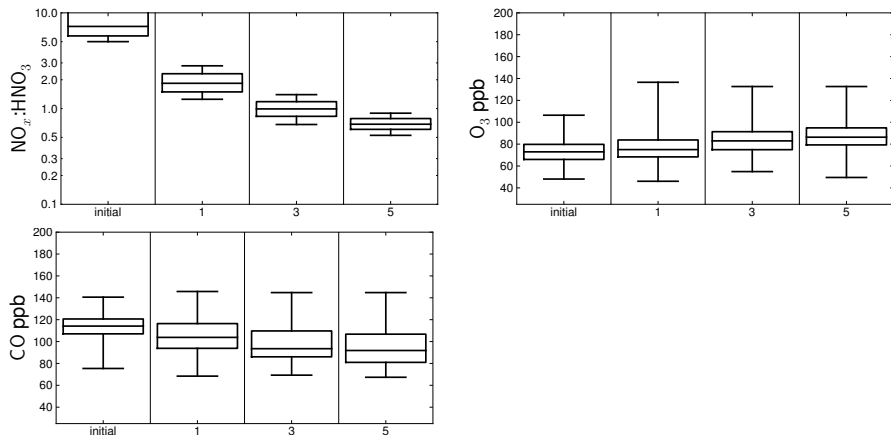


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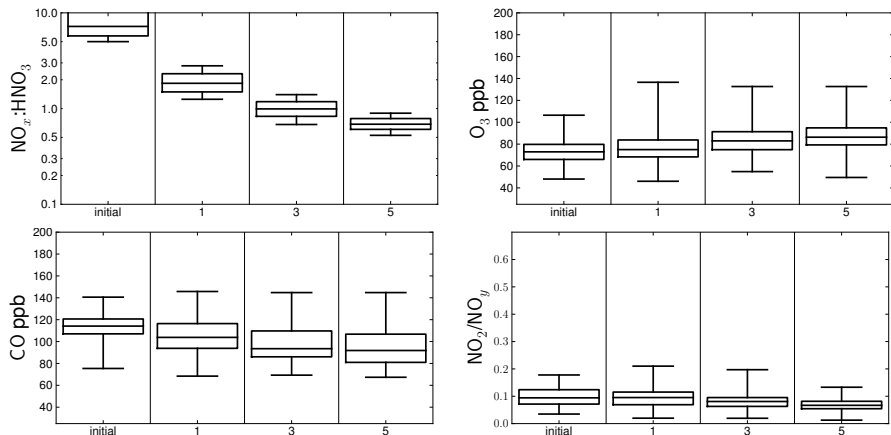


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Simulating aging of freshly convected air parcels

- Box modeling air parcels using LEEDS DSMACC box model
- Physical and initial conditions from “freshly convected” observations

Table 1: Overview of 7 chemical mechanisms in this study.

Model (abbreviation)	# Rxns	# Spcs
Carbon Bond '05 (CB05)	176	62
State Air Pollution Research Center '99 (SAPRC99)	222	77
SAPRC '07 (SAPRC07)	<700	153
Model for OZone And Related chemical Tracers “Standard” (MZ4)	290	88
GEOS-Chem “full” (GEOS)	290	88
Regional Atmospheric Chemistry Mech v.2 (RACM2)	341	117
Master Chemical Mechanism (MCM)	>4500	>1700

Chemical Model Evaluation

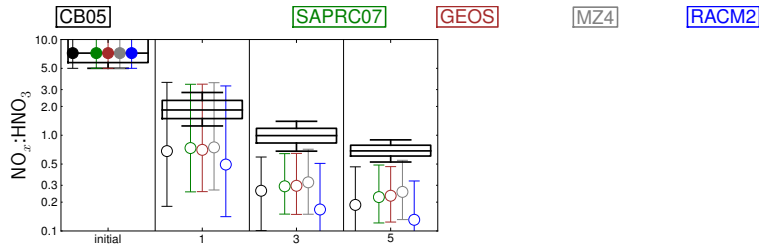


Figure 5: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).

Chemical Model Evaluation

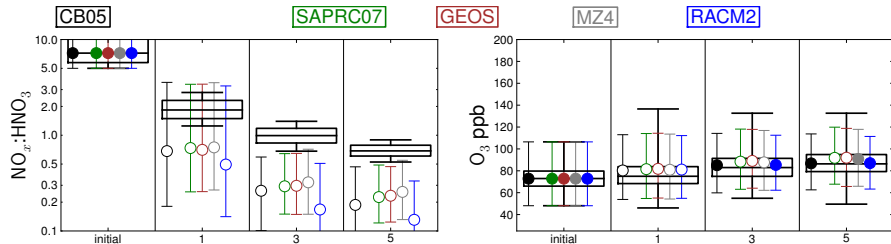


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Chemical Model Evaluation

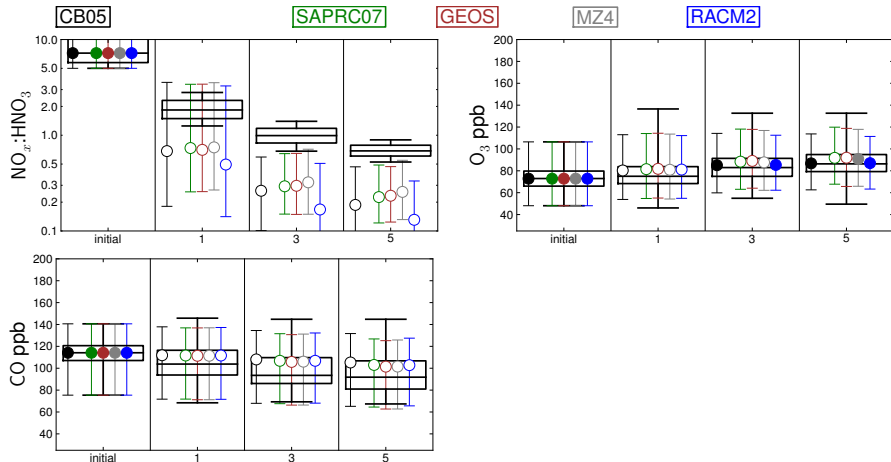


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Chemical Model Evaluation

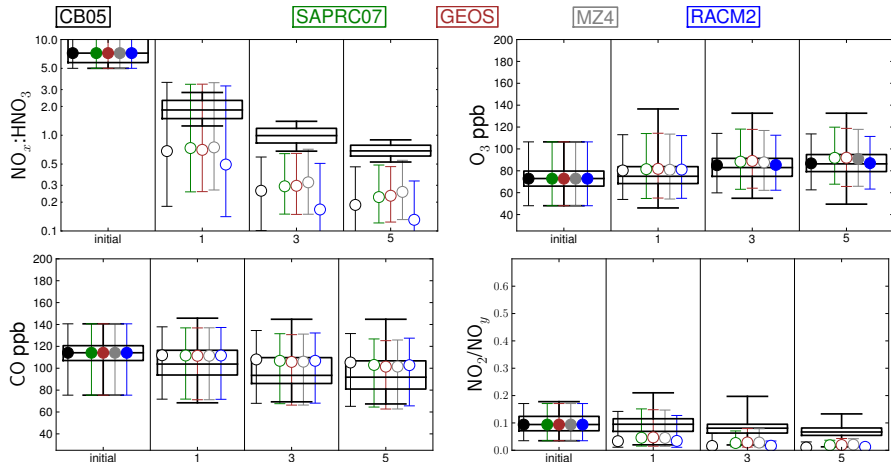


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Models over-predict NO_2/NO_x , PAN, and HNO_3

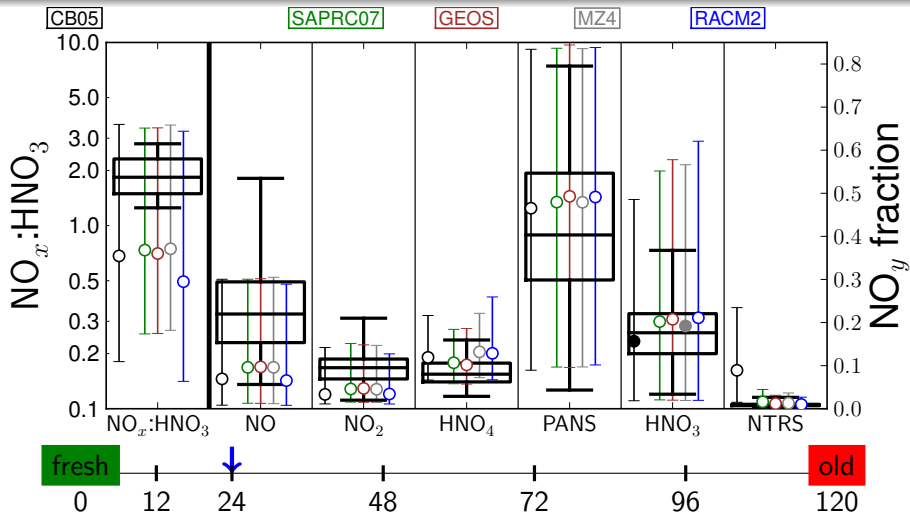


Figure 6: Nitrogen species 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations ($p < 0.0001$).

Conclusions: Model performance

- Semi-explicit, regional, and global models all
 - under-predict $\text{NO}_x:\text{HNO}_3$
 - under-prediction NO_x
 - over-predict NO_z , esp. $\text{CH}_3\text{C}(\text{O})\text{ONO}_2$ and HNO_3
 - over-prediction NO_2/NO_x
- All problems point to too many radical reactions

PAN Sensitivity Studies

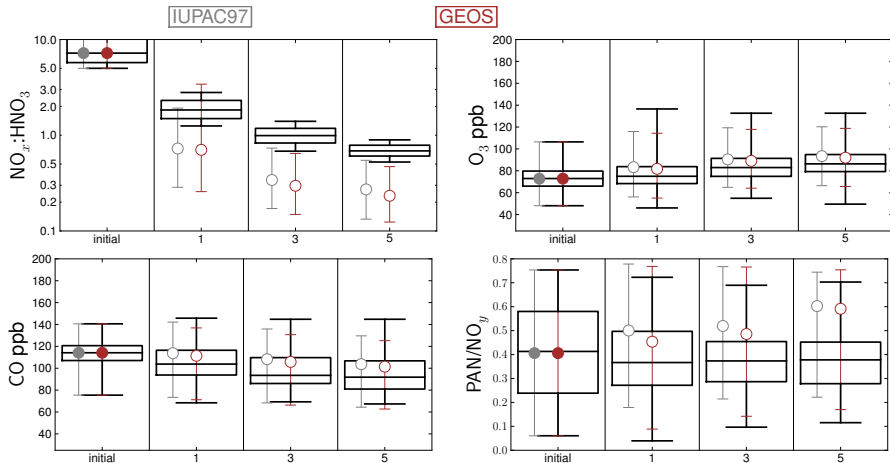


Figure 7: GEOS-Chem tested with old acetone quantum yield, with 2xCO, and with constrained acetaldehyde. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).

Models over-predict OH and HO₂

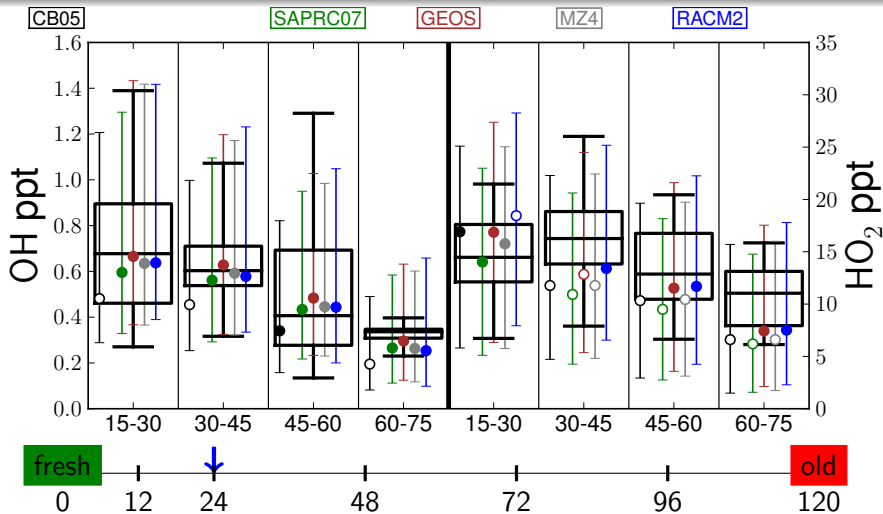


Figure 8: HO_x' by solar zenith angle 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations (p < 0.0001).

Potential issues

- Over-predicting radical source (i.e. photolysis)
- Over-predicting radical amplification
 - CH_2O
 - $\text{OH} + \text{CH}_2\text{O} \longrightarrow \text{CO} + \text{HO}_2^\cdot$
 - $\text{HO}_2^\cdot + \text{NO} \longrightarrow \text{NO}_2 + \text{HO}^\cdot$
 - CH_3CHO
 - $\text{OH} + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{C(O)OO}^\cdot$
 - $\text{CH}_3\text{C(O)OO}^\cdot + \text{NO} \longrightarrow \text{NO}_2 + \text{CH}_3\text{OO}^\cdot$
 - $\text{CH}_3\text{OO}^\cdot + \text{NO} \longrightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{HO}_2^\cdot$
 - $\text{HO}_2^\cdot + \text{NO} \longrightarrow \text{NO}_2 + \text{HO}^\cdot$
- Over-predicting radical cycling efficiency
 - ratio of radical propagating to radical terminating reactions
 - propagation (i.e. $\text{RO}_2 + \text{NO} \longrightarrow \text{NO}_2 + \text{RO}^\cdot$)
 - termination (i.e. $\text{OH} + \text{NO}_2 \longrightarrow \text{HNO}_3$)

Radicals sources in the first 4 hours

Table 2: Comparison of new radicals (ppt) by chemical mechanism.

Reaction	GEOS	CB05
$\text{CH}_2\text{O} \longrightarrow \text{CO} + 2 \cdot \text{HO}_2$	488	346
$\text{O}_3 \longrightarrow \text{O}^1\text{D}; \text{O}^1\text{D} + \text{H}_2\text{O} \longrightarrow 2 \cdot \text{HO}^\bullet$	215	246
$\text{HNO}_2 \longrightarrow \text{NO} + \text{HO}^\bullet$	226	186
$\text{H}_2\text{O}_2 \longrightarrow 2 \cdot \text{HO}^\bullet$	100	103
$\text{CH}_3\text{C}(\text{O})\text{OOH} \longrightarrow \text{CH}_3\text{OO}^\bullet + \text{HO}^\bullet$	38	59
$\text{CH}_3\text{CHO} \longrightarrow \text{CO} + \text{HO}_2^\bullet + \text{CH}_3\text{OO}^\bullet$	31	37
$\text{CH}_3\text{C}(\text{O})\text{CH}_3 \longrightarrow \text{CH}_3\text{C}(\text{O})\text{OO}^\bullet + \text{CH}_3\text{OO}^\bullet$	32	0
$\text{HNO}_4 \longrightarrow \text{HO}_2^\bullet + \text{NO}_2$	23	13
$\text{CH}_3\text{OOH} \longrightarrow \text{CH}_2\text{O} + \text{HO}_2^\bullet + \text{HO}^\bullet$	22	23
Total new Radicals	1199	1035
$\text{CH}_3\text{OOH} + \text{HO}^\bullet \longrightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{HO}^\bullet$	0	26
$\text{CH}_3\text{OOH} + \text{HO}^\bullet \longrightarrow \text{HO}_2 + \text{XO}_2 + \text{CH}_3\text{OO}^\bullet$		

Radicals sinks in the first 4 hours

Table 3: Comparison of radical removals (ppt) by chemical mechanism.

Reaction	GEOS	CB05
$\text{HO}\cdot + \text{HO}_2\cdot \longrightarrow \text{H}_2\text{O} + \text{O}_2$	363	266
$\text{HO}\cdot + \text{NO} \longrightarrow \text{HNO}_2$	234	192
$\text{NO}_2 + \text{HO}_2\cdot \longrightarrow \text{HNO}_4$	176	154
$\text{HO}\cdot + \text{NO}_2 \longrightarrow \text{HNO}_3$	131	104
$\text{HO}_2\cdot + \text{HO}_2\cdot \longrightarrow \text{H}_2\text{O}_2$	92	88
$\text{HO}\cdot + \text{HNO}_4 \longrightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$	83	71
$\text{CH}_3\text{OO}\cdot + \text{HO}_2\cdot \longrightarrow \text{CH}_3\text{OOH} + \text{O}_2$	43	29
$\text{HO}_2\cdot + \text{CH}_3\text{C}(\text{O})\text{OO}\cdot \longrightarrow \text{CH}_3\text{C}(\text{O})\text{OOH}$	16	9
Total Radical Sink	1219	1025

Conclusions

- Model performance
 - models under-predict NO_2 particularly after 1 day old
 - over-predict rate of “aging” in the first 24 hours (improves subsequently)
 - best O_3 came from worst HO_x^\bullet
 - HO_x^\bullet
 - Like other studies $\text{HO}_{\text{model}}^\bullet = 2 \times \text{HO}_{\text{obs}}^\bullet$
 - Unlike other studies $\text{HO}_{2\text{model}}^\bullet > \text{HO}_{2\text{obs}}^\bullet$
- Best practices
 - check model photolysis for pressure/temperature sensitivity
 - use detailed photolysis in the upper troposphere
 - use Blitz et al. 2004 $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ quantum yield
- Next steps
 - Investigate $\text{HO}_{2\text{model}}^\bullet$ improvement compared to other studies
 - Attribute radical production to initial species (not immediate precursor)
 - Assess uncertainty in major radical source species

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