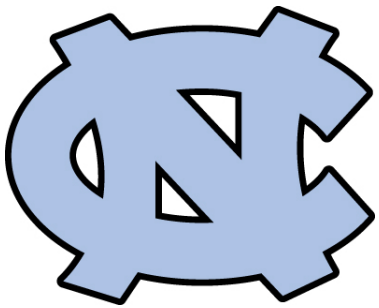
The role of chemistry in upper troposphere NO_2 under-predictions

Barron Henderson[1,2], Robert Pinder[2], Wendy Goliff[3], William Stockwell[4], Askar Fahr[4], Golam Sarwar[2], Bill Hutzell[2], Rohit Mathur[2], William Vizuete[1], Ron Cohen[5]

[1]Dept. of Environmental Science and Engineering UNC Chapel Hill
[2]Atmospheric Modeling and Analysis Division, U.S. EPA
[3]Division of Atmospheric Sciences, Desert Research Institute
[4]Dept. of Chemistry, Howard University
[5]Depts. of Chemistry and Earth and Planetary Sciences, University of California Berkeley



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CMAQ compared with SCIAMACHY: worst in rural areas.

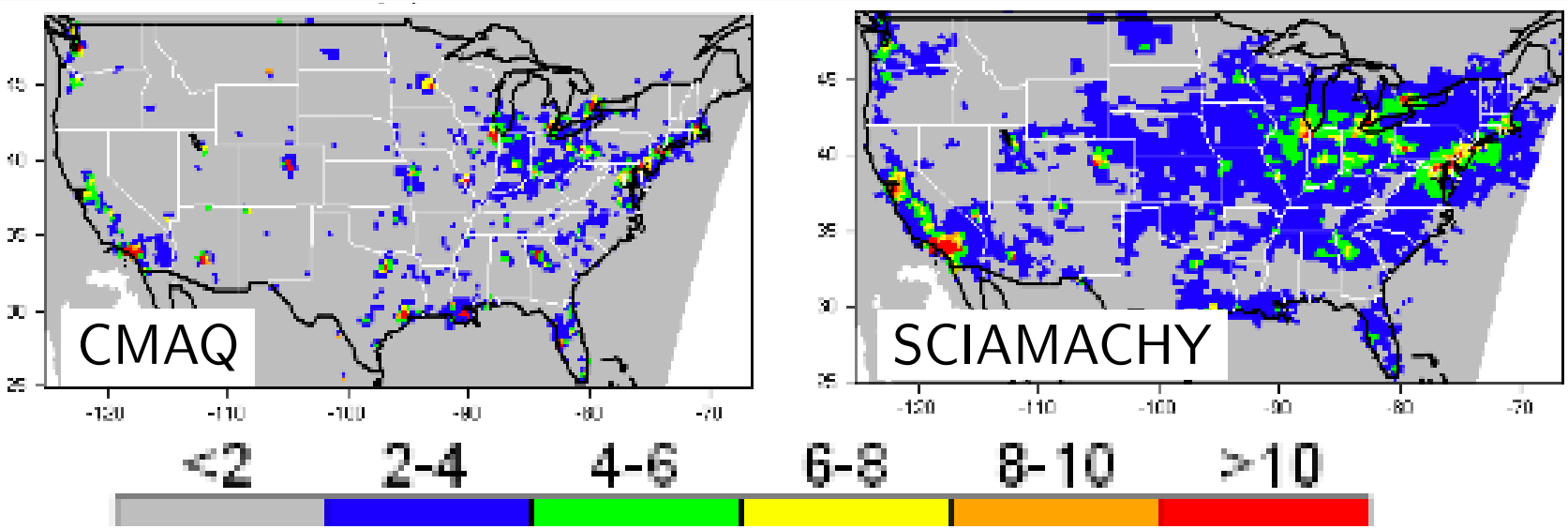

Figure 1: NO_2 columns (10^{15} $molec/cm^2$) from Napelenok ACP 2008

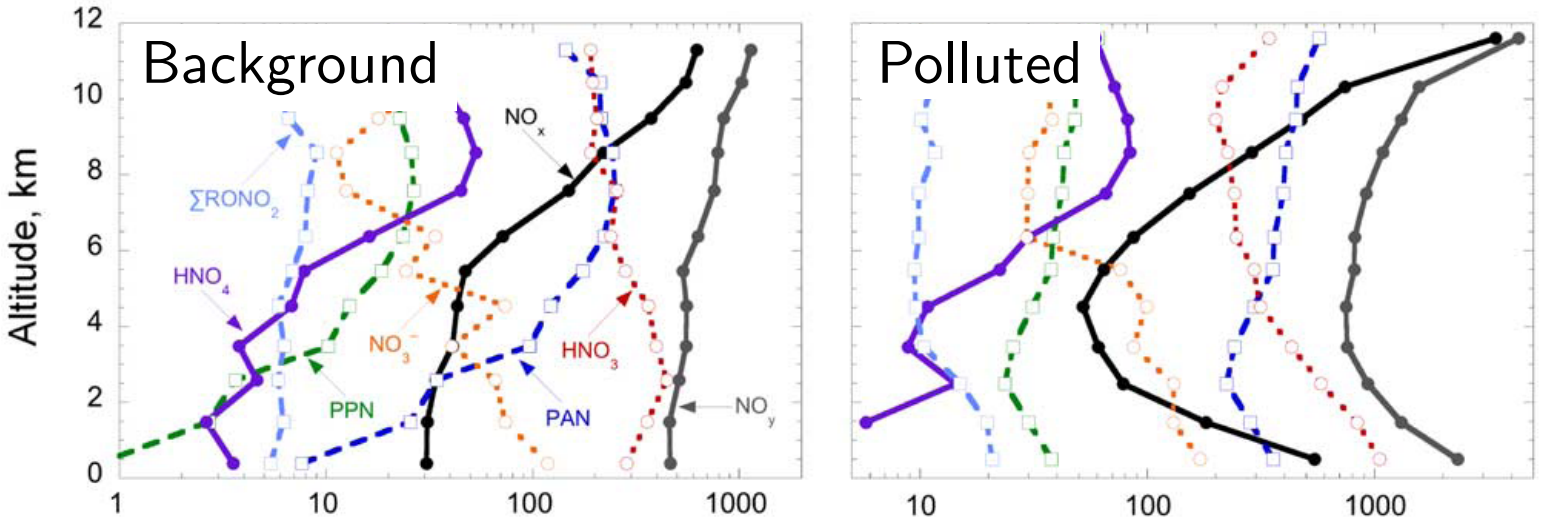

Figure 2: Vertical profiles of background and polluted conditions from Singh 2007.

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: NO_x:HNO_3 $>>$ 1
- Aged air parcel: NO_x:HNO_3 $<<$ 1

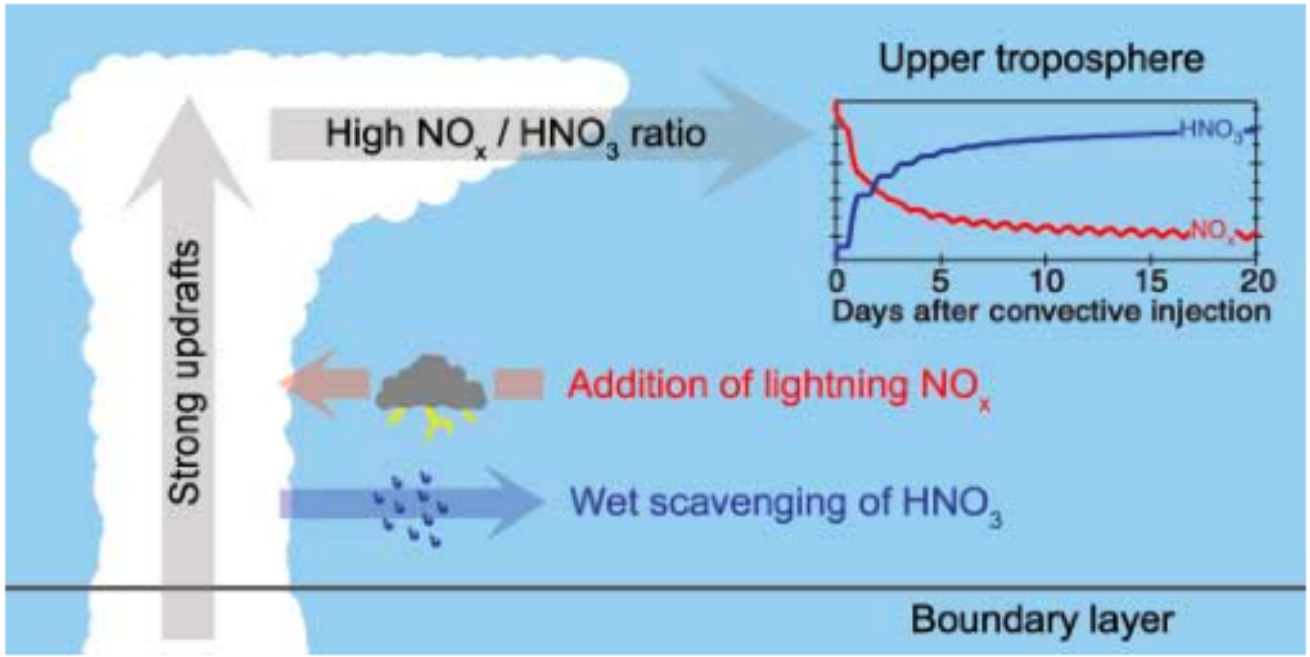

Figure 3: Deep convection from Bertram et al. Science 2007

Observation timeseries: classified by "derived age"

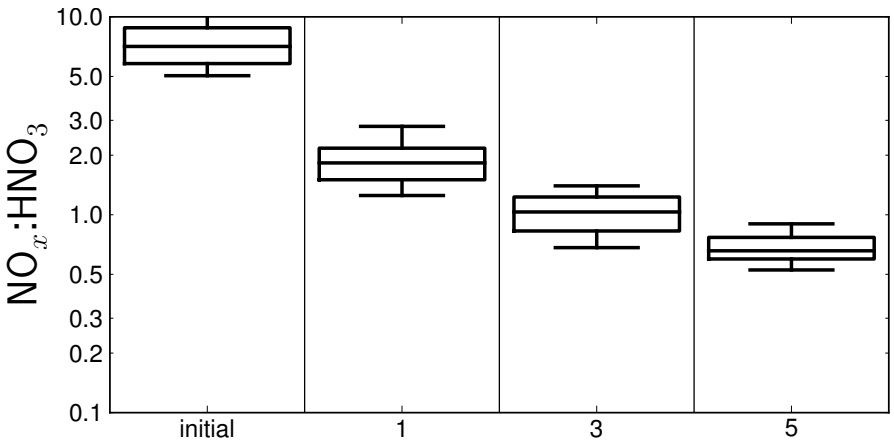

Figure 4: NO_x:HNO_3 is used to categorize days since convection. O_3 shows a monotonic increase with time. CO shows a monotonic decrease with time. NO_2 shows a gradual increase with time.

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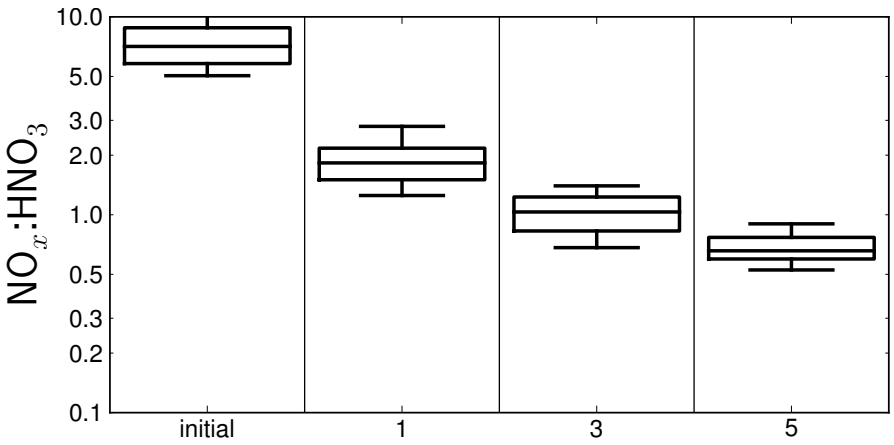

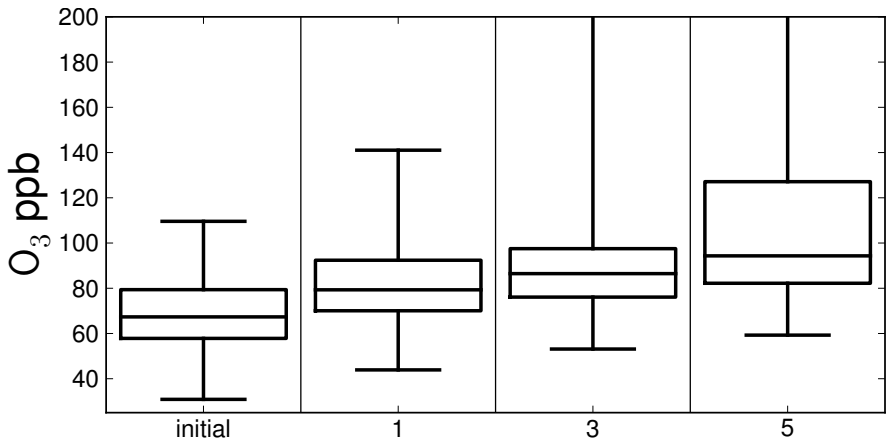

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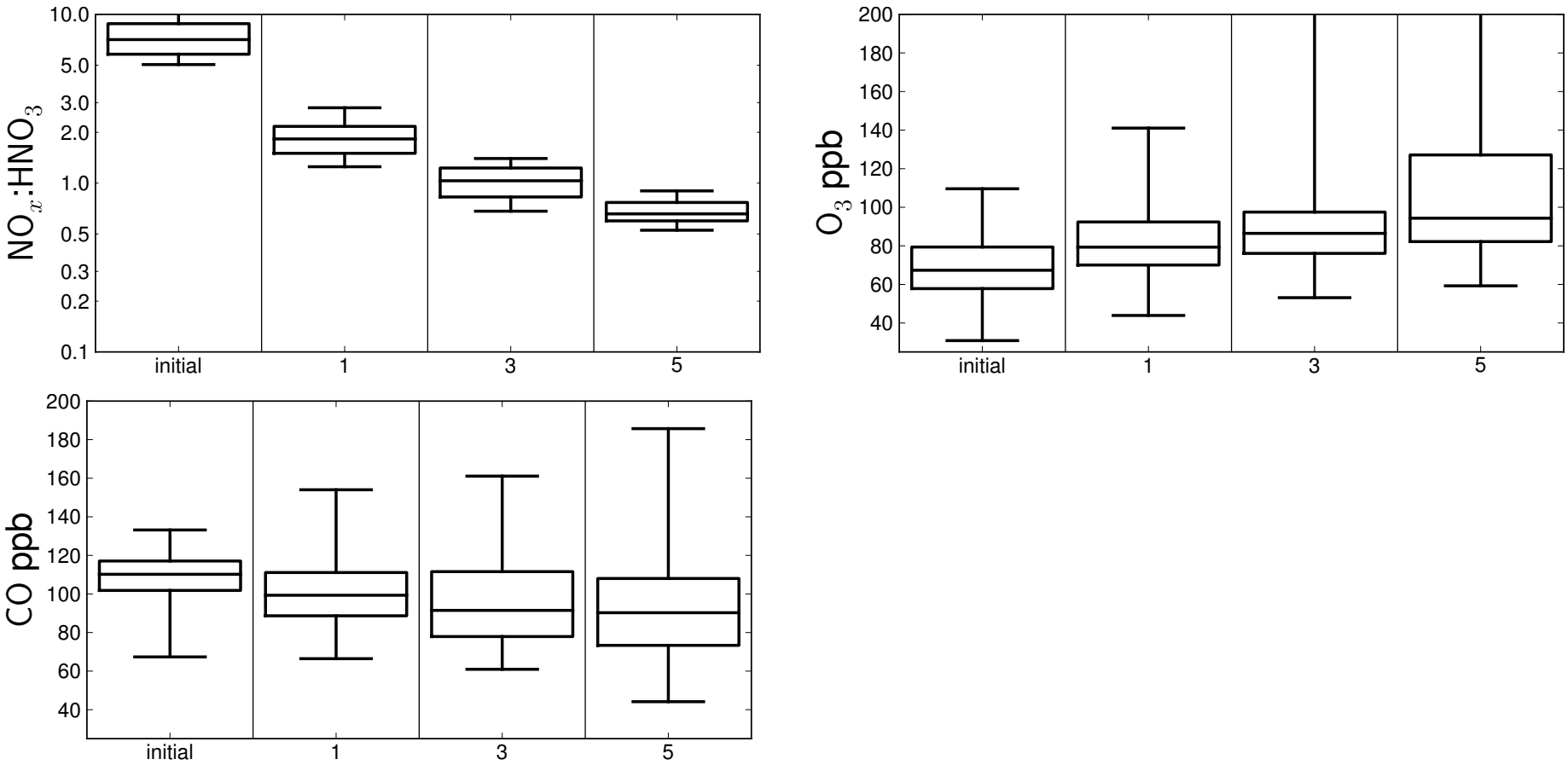

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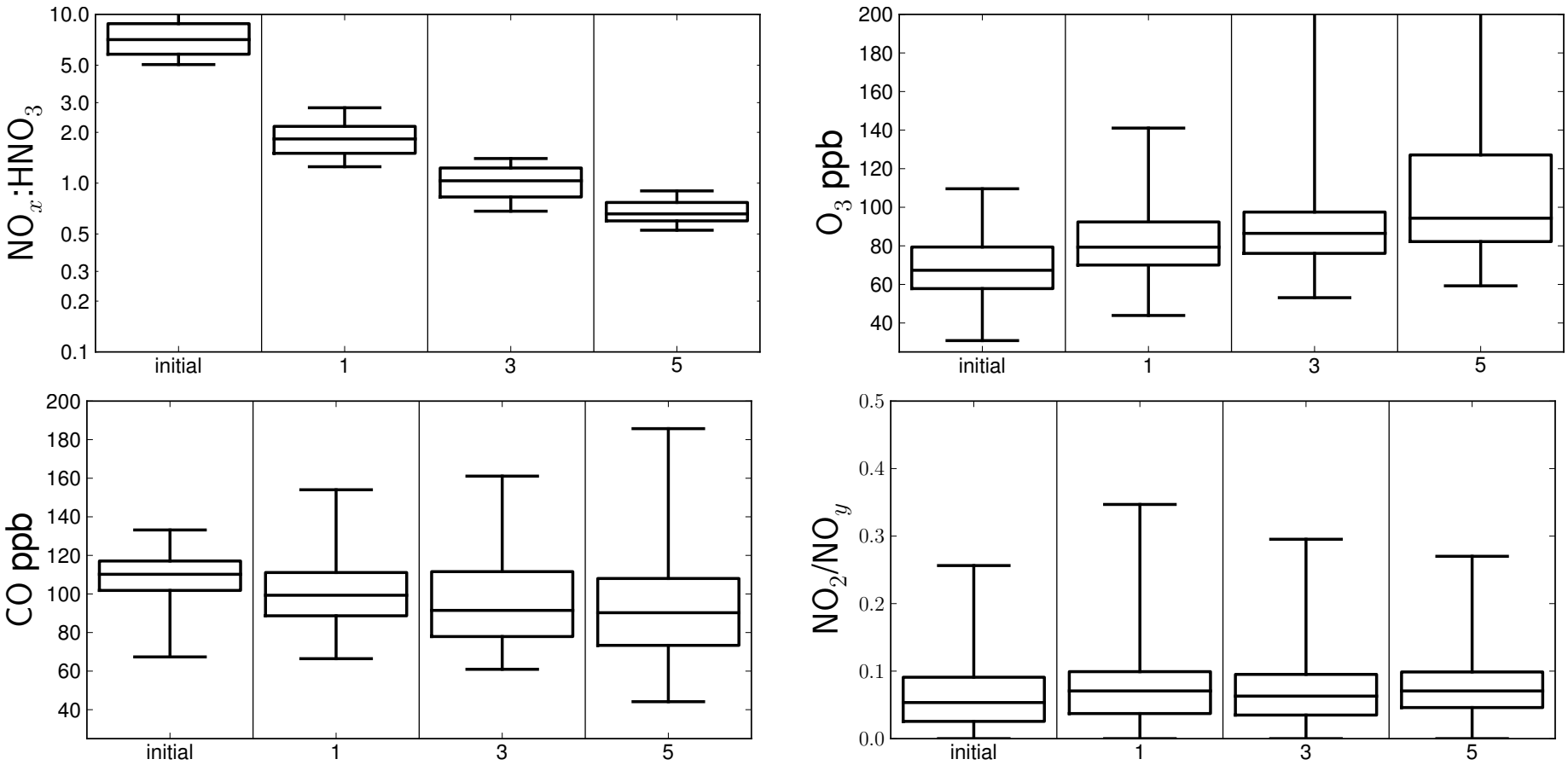

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Simulating aging of freshly convected air parcels

- 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

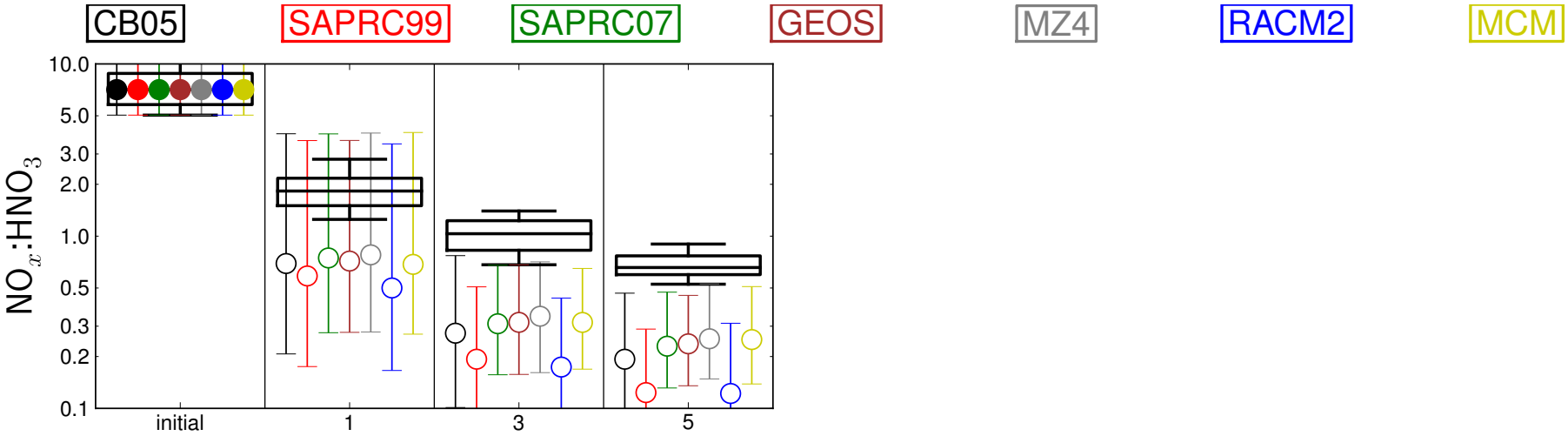
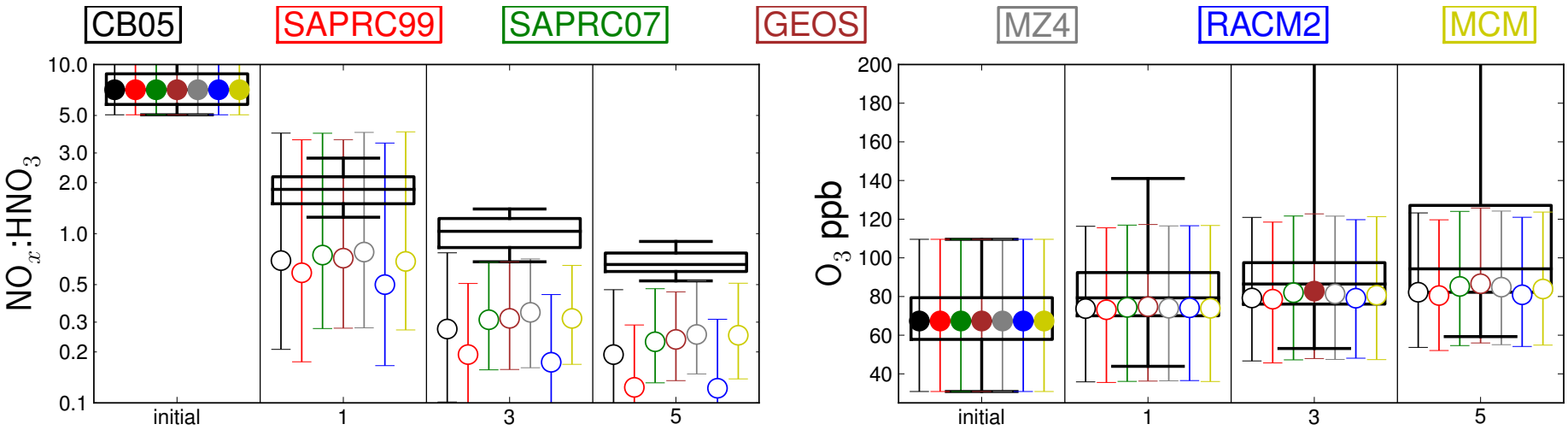


Figure 5: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).

Chemical Model Evaluation



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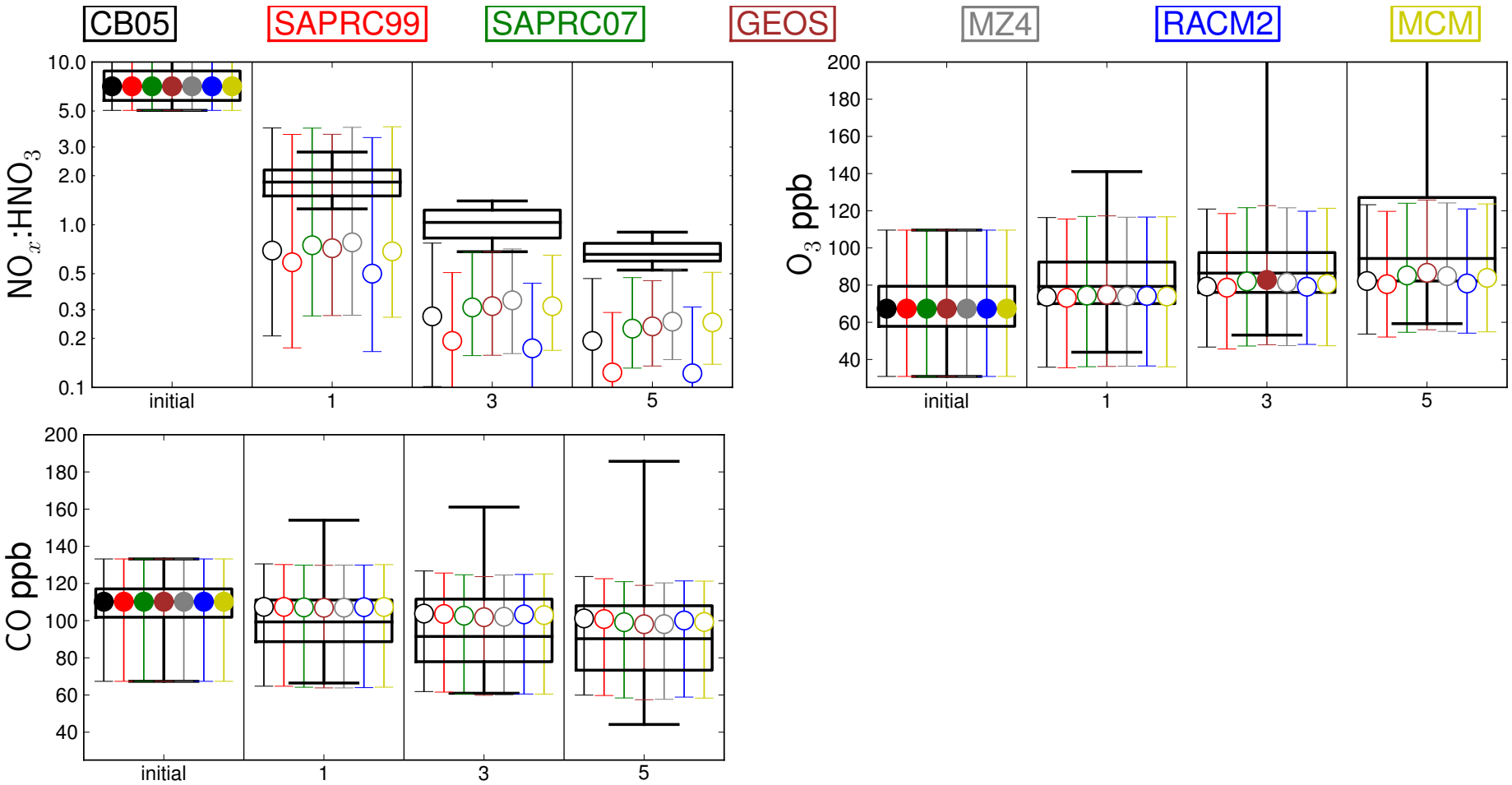

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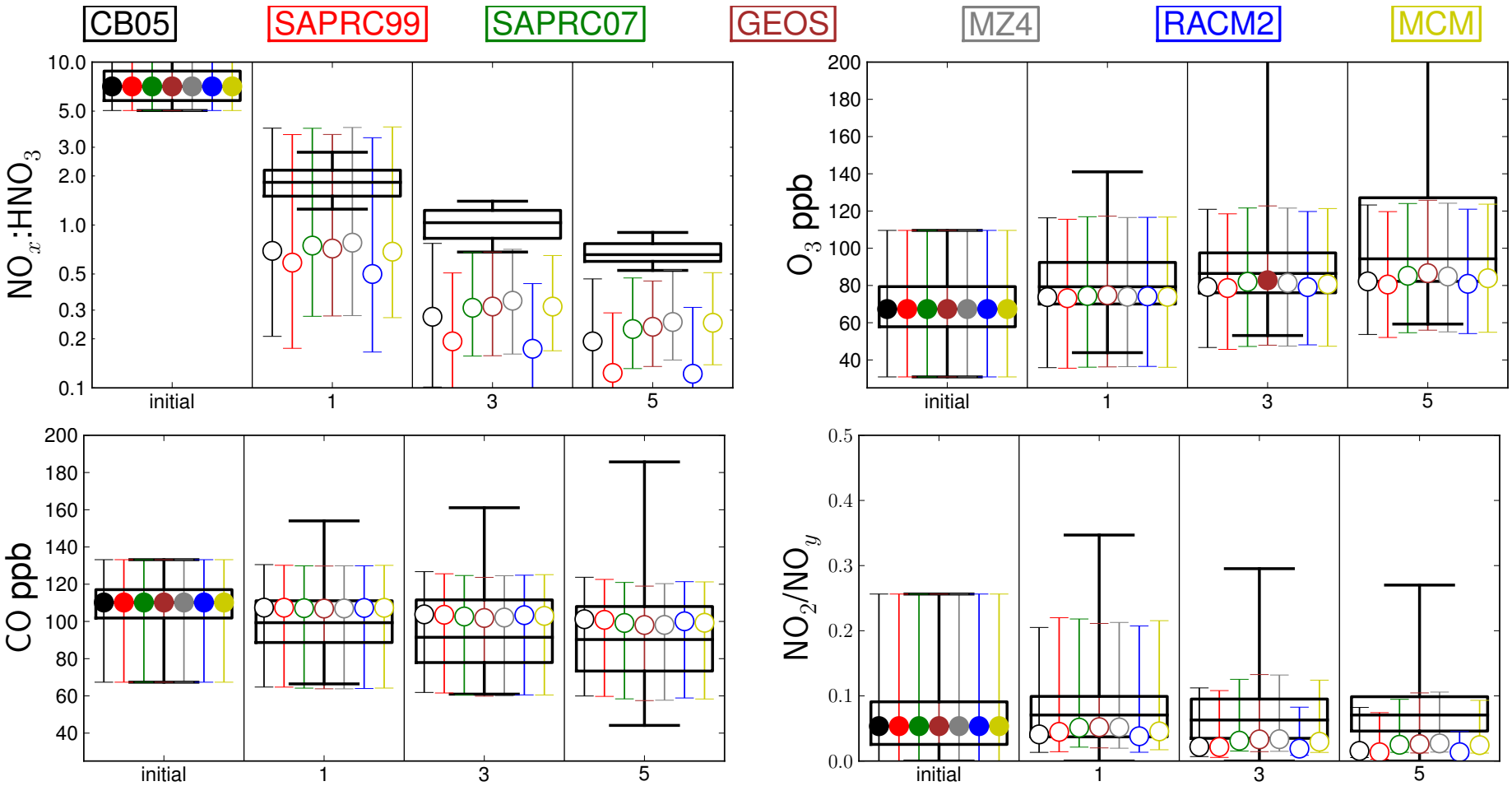

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Models over-predict NO_2/NO_x, PAN, and HNO_3

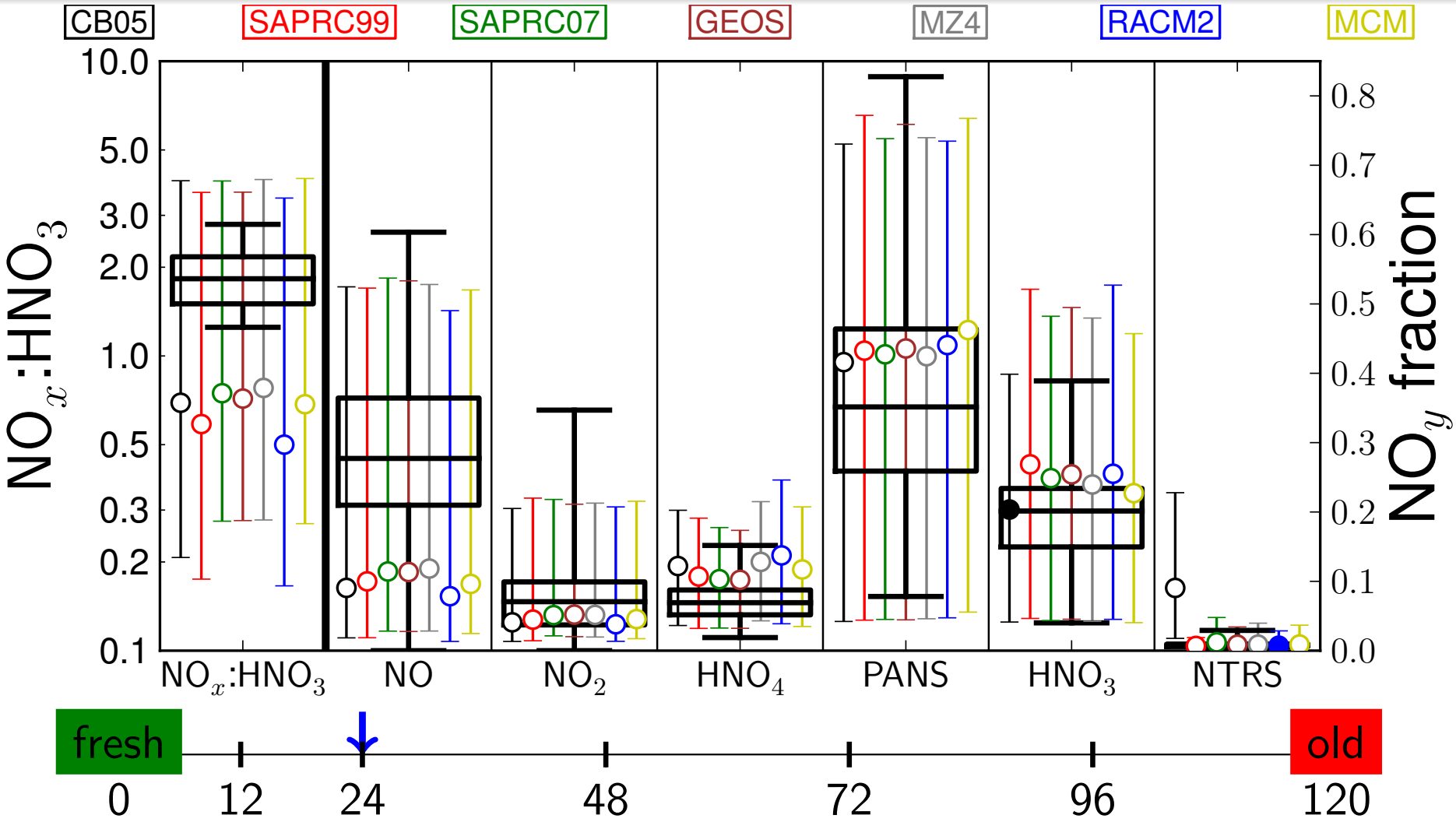

Figure 6: Nitrogen species 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations ($p < 0.0001$).

Conclusions: Model performance

- Semi-explicit, regional, and global models all
  - under-predict NO_x:HNO_3
  - under-prediction NO_x
  - over-predict NO_z, esp. $CH_3C(O)ONO_2$ and HNO_3
  - over-prediction NO_2/NO_x
- All problems point to too many radical reactions

PAN Sensitivity Studies

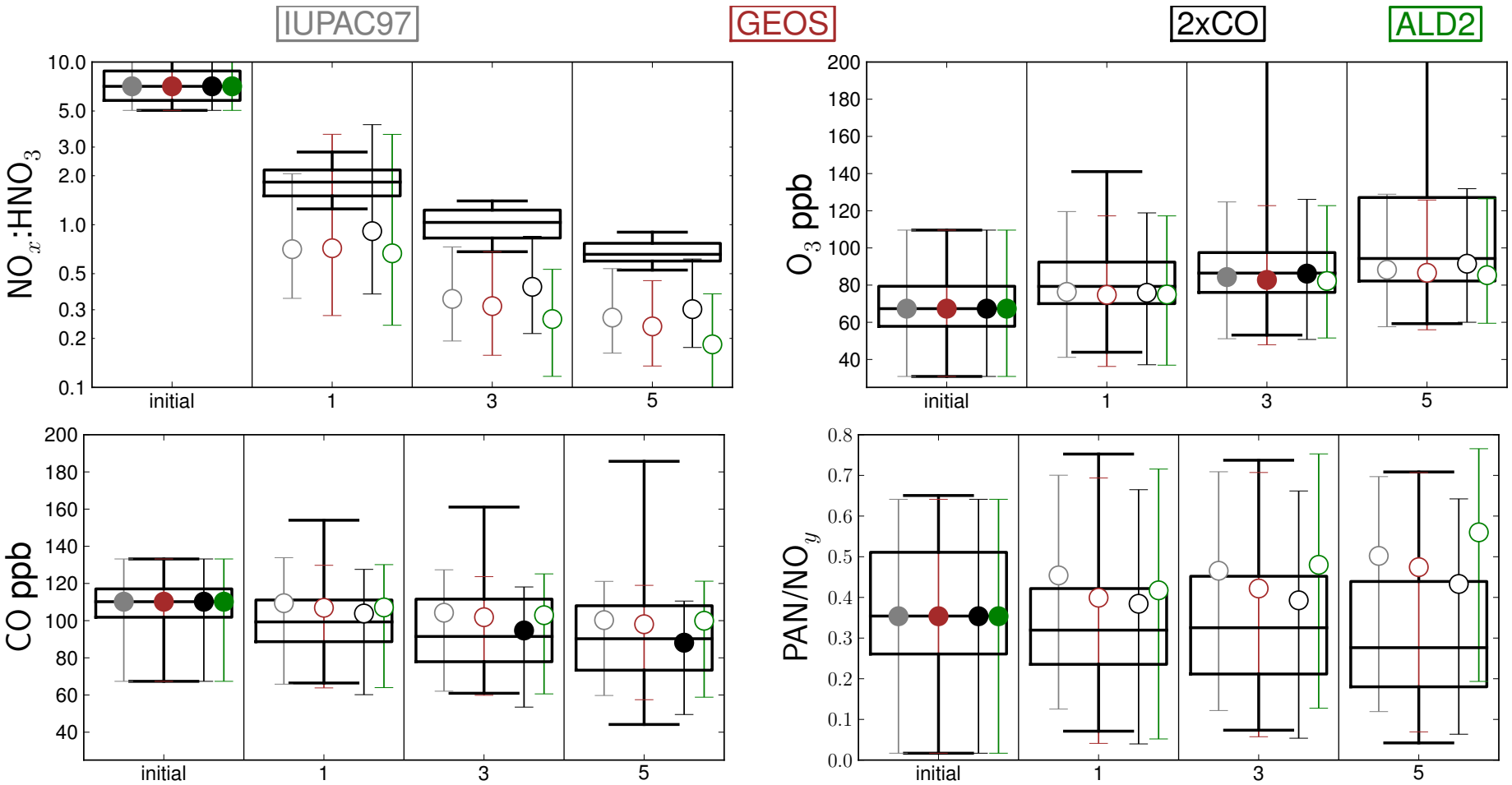

Figure 7: GEOS-Chem tested with old acetone quantum yield, with 2xCO, and with constrained acetaldehyde. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).

Models over-predict OH and HO_2

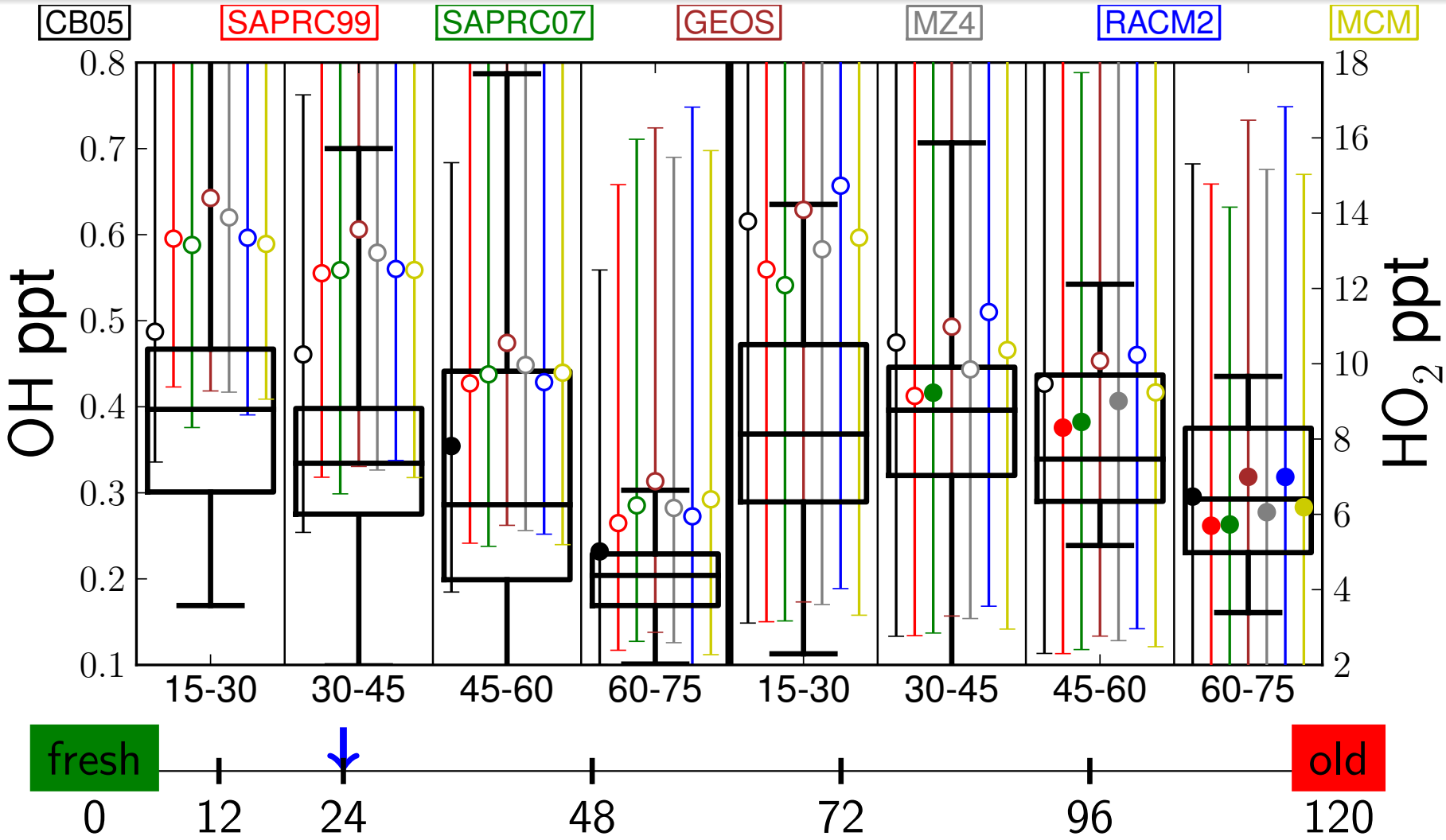

Figure 8: HOx˙ by solar zenith angle 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations ($p < 0.0001$).

Potential issues

- Over-predicting radical source (i.e. photolysis)
- Over-predicting radical amplification
  - CH_2O
    - $OH + CH_2O \longrightarrow CO + HO_2^{\cdot}$
    - $HO_2^{\cdot} + NO \longrightarrow NO_2 + HO^{\cdot}$
  - CH_3CHO
    - $OH + CH_3CHO \longrightarrow CH_3C(O)OO^{\cdot}$
    - $CH_3C(O)OO^{\cdot} + NO \longrightarrow NO_2 + CH_3OO^{\cdot}$
    - $CH_3OO^{\cdot} + NO \longrightarrow NO_2 + CH_2O + HO_2^{\cdot}$
    - $HO_2^{\cdot} + NO \longrightarrow NO_2 + HO^{\cdot}$
- Over-predicting radical cycling efficiency
  - ratio of radical propagating to radical terminating reactions
  - propagation (i.e. $RO_2 + NO \longrightarrow NO_2 + RO^{\cdot}$)
  - termination (i.e. $OH + NO_2 \longrightarrow HNO_3$)

Radicals sources in the first 4 hours

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

Reaction	**GEOS**	**CB05**
$CH_2O \longrightarrow CO + 2 \cdot HO_2^{\cdot}$	488	346
$O_3 \longrightarrow O^1D;\ O^1D + H_2O \longrightarrow 2 \cdot HO^{\cdot}$	215	246
$HNO_2 \longrightarrow NO + HO^{\cdot}$	226	186
$H_2O_2 \longrightarrow 2 \cdot HO^{\cdot}$	100	103
$CH_3C(O)OOH \longrightarrow CH_3OO^{\cdot} + HO^{\cdot}$	38	59
$CH_3CHO \longrightarrow CO + HO_2^{\cdot} + CH_3OO^{\cdot}$	31	37
$CH_3C(O)CH_3 \longrightarrow CH_3C(O)OO^{\cdot} + CH_3OO^{\cdot}$	32	0
$HNO_4 \longrightarrow HO_2^{\cdot} + NO_2$	23	13
$CH_3OOH \longrightarrow CH_2O + HO_2^{\cdot} + HO^{\cdot}$	22	23
Total new Radicals	**1199**	**1035**
$CH_3OOH + HO^{\cdot} \longrightarrow CH_2O + H_2O + HO^{\cdot}$ $CH_3OOH + HO^{\cdot} \longrightarrow HO_2 + XO_2 + CH_3OO^{\cdot}$	0	26

Radicals sinks in the first 4 hours

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

Reaction	**GEOS**	**CB05**
$HO^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O + O_2$	363	266
$HO^{\cdot} + NO \longrightarrow HNO_2$	234	192
$NO_2 + HO_2^{\cdot} \longrightarrow HNO_4$	176	154
$HO^{\cdot} + NO_2 \longrightarrow HNO_3$	131	104
$HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2$	92	88
$HO^{\cdot} + HNO_4 \longrightarrow H_2O + NO_2 + O_2$	83	71
$CH_3OO^{\cdot} + HO_2^{\cdot} \longrightarrow CH_3OOH + O_2$	43	29
$HO_2^{\cdot} + CH_3C(O)OO^{\cdot} \longrightarrow CH_3C(O)OOH$	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 $HO_x^{\cdot}$
  - HOx$^{\cdot}$
    - Like other studies $HO^{\cdot}_{model} = 2 \times HO^{\cdot}_{obs}$
    - Unlike other studies $HO^{\cdot}_{2model} > HO^{\cdot}_{2obs}$
- Best practices
  - check model photolysis for pressure/temperature sensitivity
  - use detailed photolysis in the upper troposphere
  - use Blitz et al. 2004 $CH_3C(O)CH_3$ quantum yield
- Next steps
  - Investigate $HO^{\cdot}_{2model}$ 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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