The role of chemistry in upper troposphere NO_2 under-predictions

Barron Henderson[1,2], Robert Pinder[2], Ron Cohen[3], Wendy Goliff[4], William Stockwell[5], Askar Fahr[5], Golam Sarwar[2], Bill Hutzell[2], Rohit Mathur[2], Ann Marie Carlton[2], Paul Wennberg[6], William Vizuete[1]

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Models Under-predict NO_x above 8km

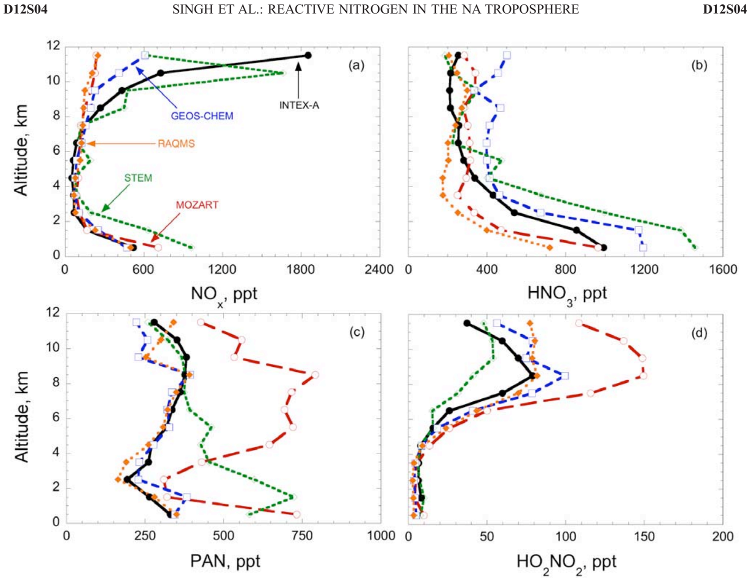

Figure 1: Simulated NO_y compared to INTEX-NA observations (Singh 2007)

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
- Evaluation of a chemical mechanism
  - **typically**: evaluate a model against a chamber study (i.e. a controlled time series of measurements)
  - **problem**: does anyone have a chamber at 236 K and 0.298 atm?
- This study statistically compares model predictions to observations using a chemical indicator of age.

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:$HNO_3 >> 1$

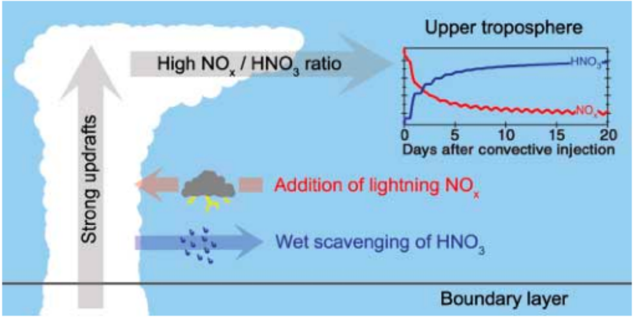

Figure 2: Deep convection from Bertram et al. Science 2007

Observation time series: classified by "derived age"

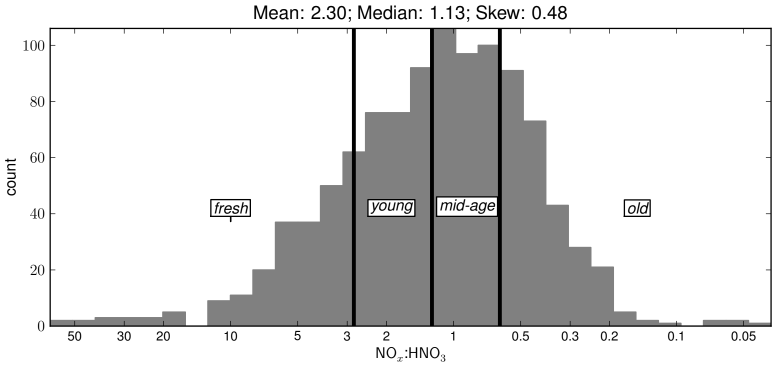

Figure 3: INTEX-NA aircraft observations of NO_x:HNO_3. NO_x:HNO_3 can be used to split the observations into four groups of decreasing (left to right) photochemical age.

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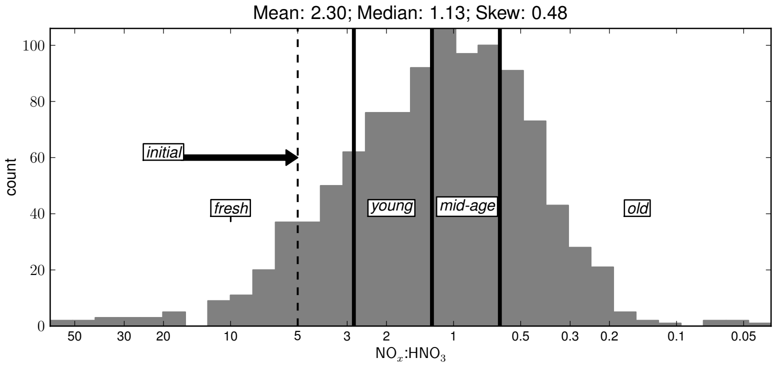

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Observations initialize our box model

Table 1: Median values from the 95 *initial* observations.

Altitude	**Pressure**	**Temperature**	**CO**	**O_3**	**H_2O_2**
9 051m	28 739 Pa	236.6K	106.4ppb	67.6ppb	384.0ppt

CH_2O	**$CH_3C(O)H$**	**$CH_3C(O)CH_3$**	**CH_4**	**C_2H_6**	**C_3H_8**
92.0ppt	64.0ppt	1 420.7ppt	1 794 ppb	639.0ppt	217.0ppt

C_2H_4	**$CH_3C(O)OOH$**	**$CH_3C(O)C_2H_5$**	**CH_3ONO_2**	**$^{\cdot}OH$**	**$HO_2^{\cdot}$**
99.0ppt	237.1 ppt	98.8 ppt	2.3 ppt	0.59 ppt	13.7 ppt

Univ. LEEDS DSMACC Box Model

- 95 initial parcels
- chemistry only
- 120 hour integration time
- TUV photolysis model

- used process analysis to quantify
  - gross production by reaction
  - gross loss by reaction

Testing a range of chemical mechanisms

Table 2: 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)	333	105
Model for OZone And Related chemical Tracers "Standard" (MZ4)	200	90
GEOS-Chem "full" (GEOS)	290	88
Regional Atmospheric Chemistry Mech v.2 (RACM2)	349	117
Master Chemical Mechanism (MCM)	$>$12600	$>$4500

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Why so many mechanisms?

- Only CB05: critics say condensation is too simplified
- Only MCM: critics say semi-explicit assumes more knowledge than we have

Chemical Mechanism Evaluation: Results

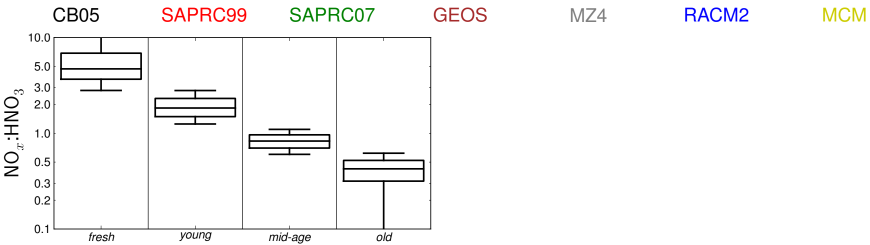

Figure 4: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p > 0.0001$).

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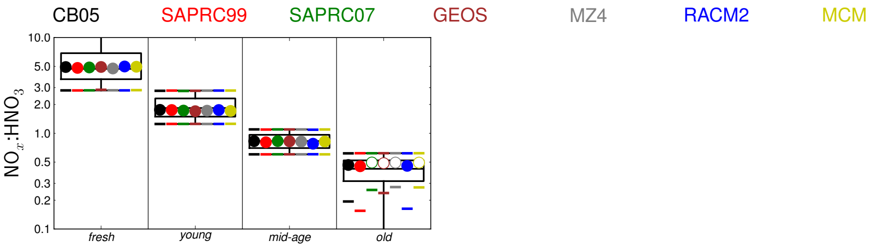

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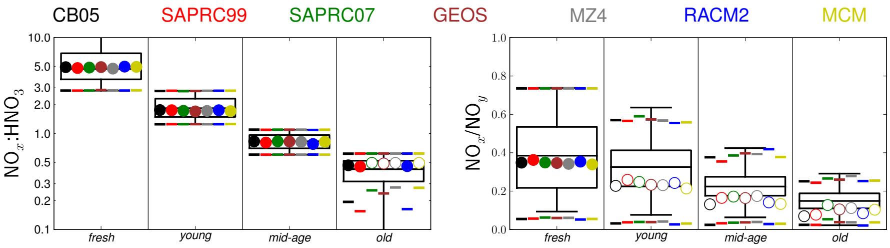

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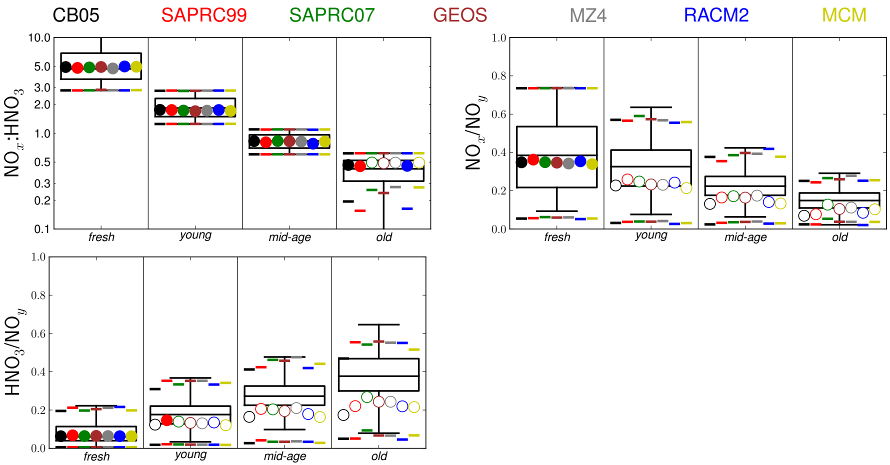

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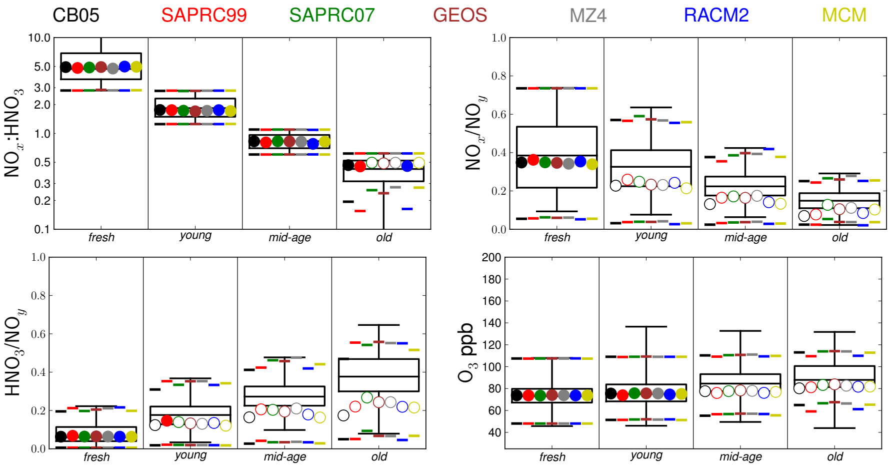

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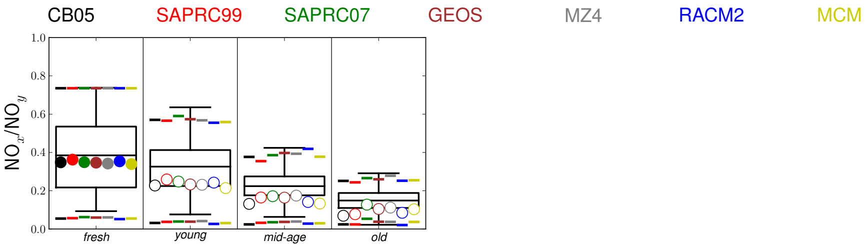
Completing the nitrogen budget



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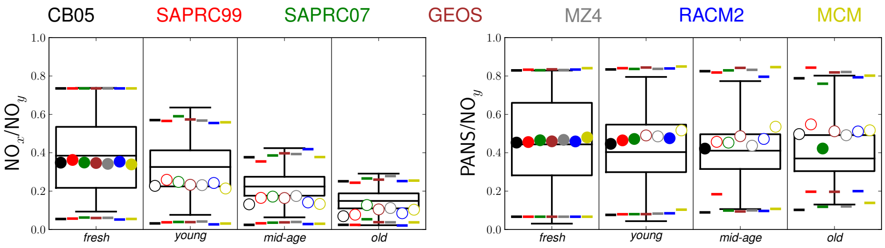

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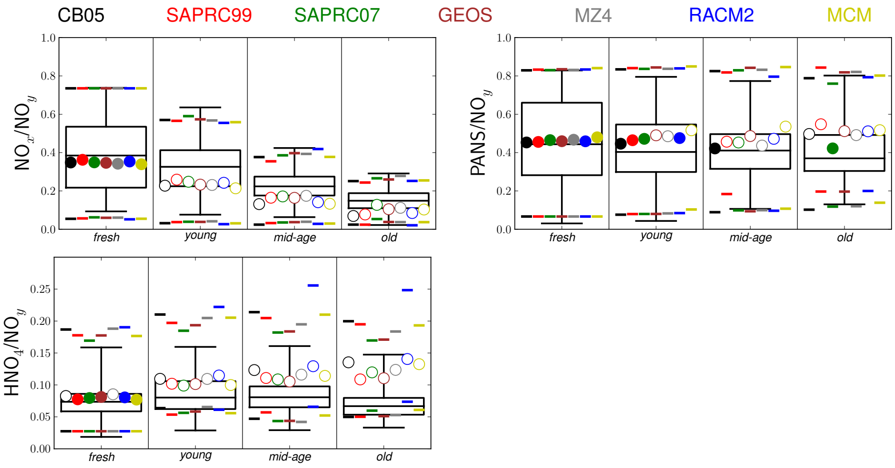

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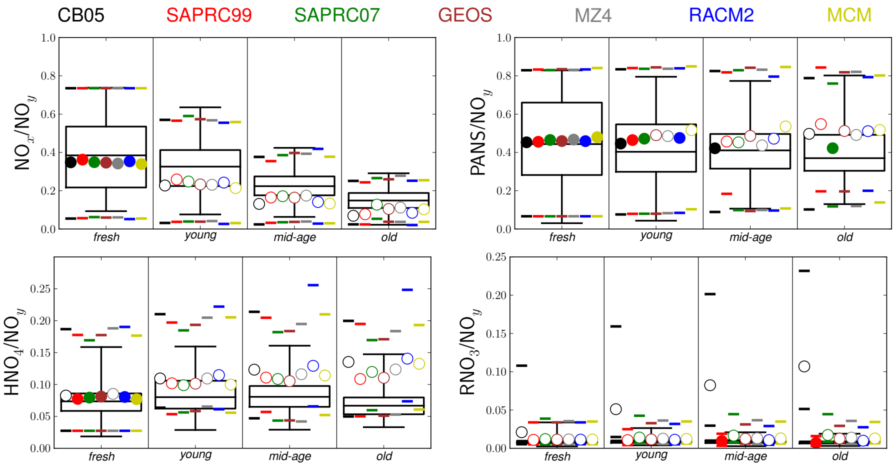

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CB05: Alkyl nitrate source uncertainty

Acetone yields of alkyl nitrate producing radicals

CB05	SAPRC99	SAPRC07	GEOS	MZ4	RACM2	MCM
13%	< 3%					

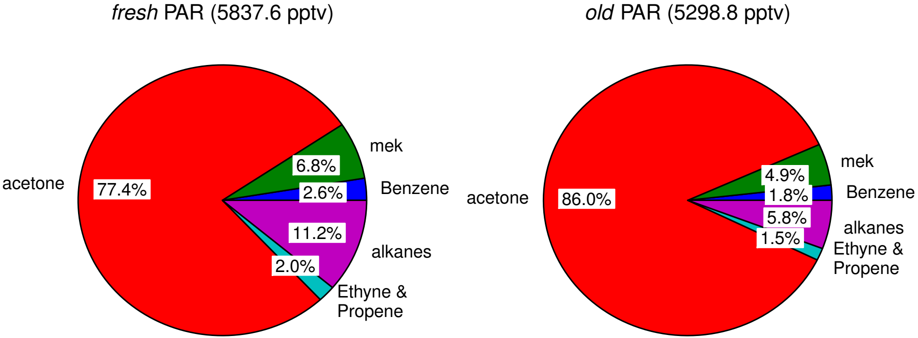

Figure 6: Composition of CB05 PAR chemical mechanism species for *fresh* and *old* air parcels.

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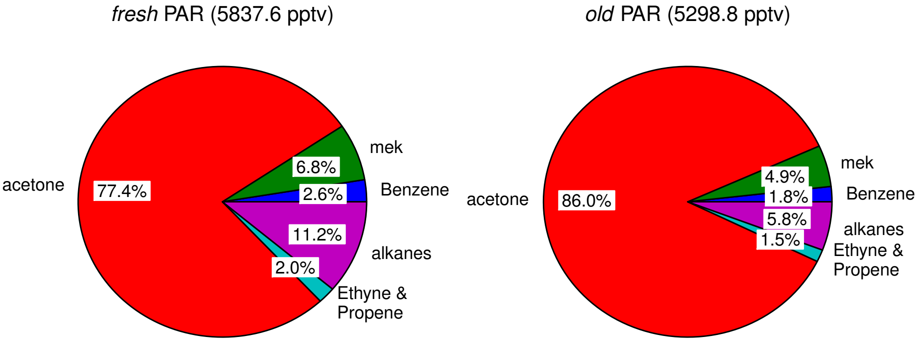


Figure 6: Composition of CB05 PAR chemical mechanism species for *fresh* and *old* air parcels.

Recommendation: Explicit acetone or dynamic XO_2N yield

HNO_4 sources, sinks, and uncertainty

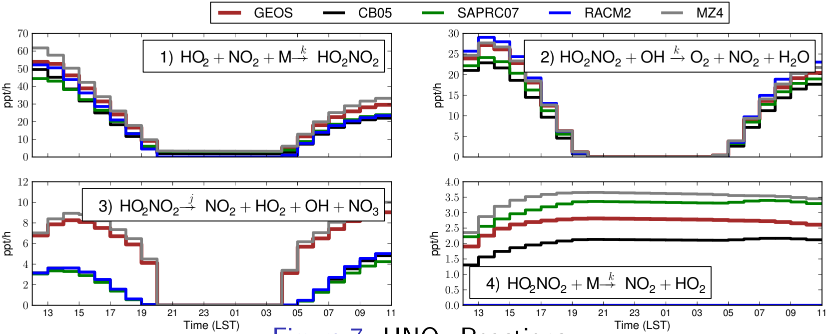
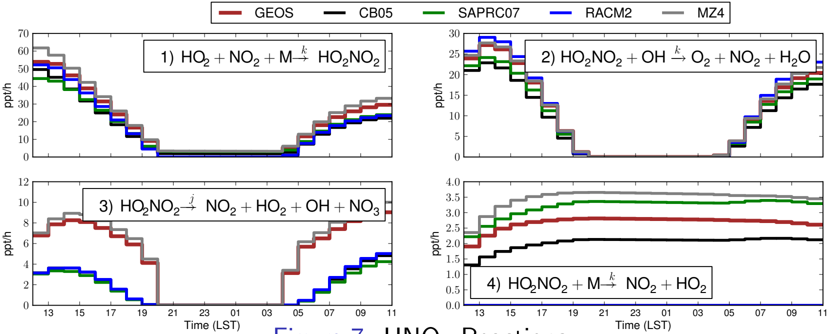


Figure 7: HNO_4 Reactions

Source Uncertainty

1. $HO_2 + NO_2 \xrightarrow{k} HO_2NO_2$: $\approx 10\%$

HNO_4 sources, sinks, and uncertainty



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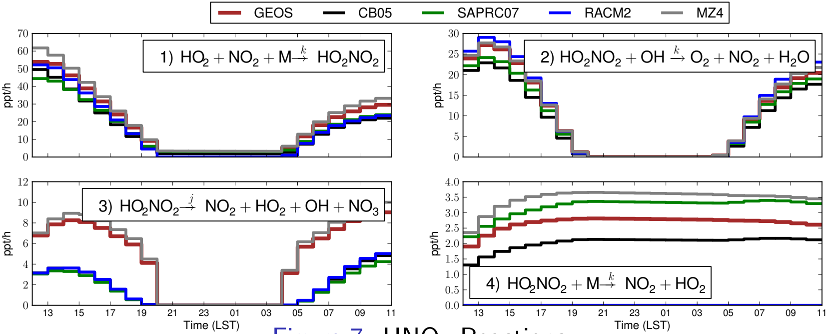
Sink Uncertainties

2. $HO_2NO_2 + OH \xrightarrow{k} H_2O + NO_2 + O_2$: $\approx 30\%$

HNO_4 sources, sinks, and uncertainty



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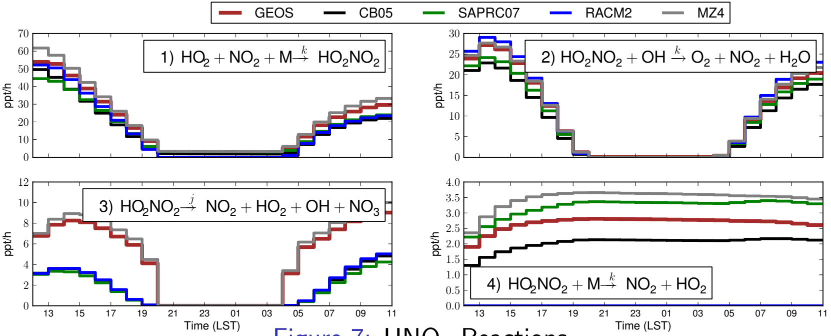
HNO_4 sources, sinks, and uncertainty



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4. $HO_2NO_2 + M \longrightarrow HO_2 + NO_2$: $\approx$ 2x at 260 K

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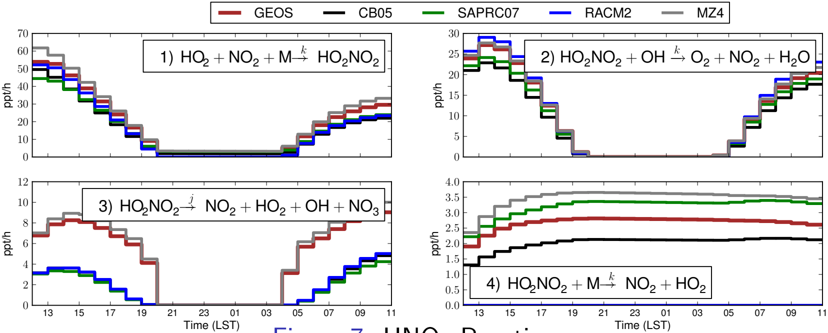

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Recommendation: Further study $HO_2NO_2 + OH$ at low temperatures

PAN sources and uncertainty

$CH_3C(O)OO^{\cdot} + NO_2 \longrightarrow PAN$

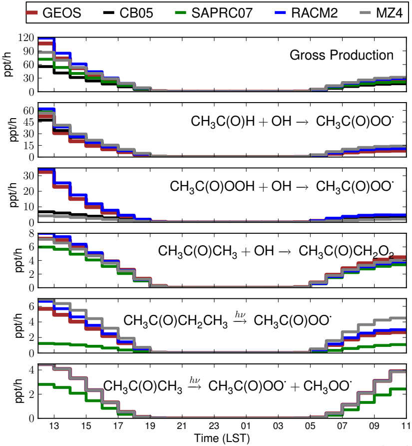
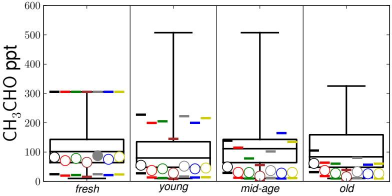


Figure 8: Source reactions of $CH_3C(O)OO^{\cdot}$

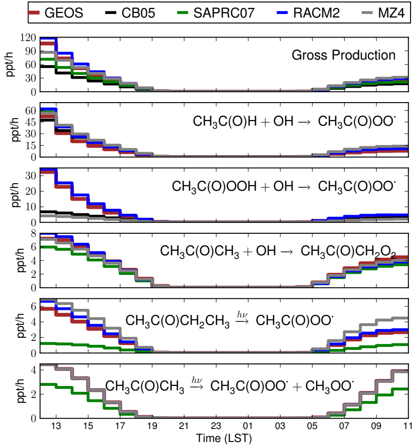
Uncertainty in Sources

- $CH_3C(O)H$ under-predicted
  - observation uncertainty?
  - missing source?
  - over-predicted OH sink?



- $CH_3C(O)OOH + OH$ has no kinetic value in the literature
- Ketone photolysis rates recently updated

$CH_3C(O)OO^{\cdot} + NO_2 \longrightarrow PAN$



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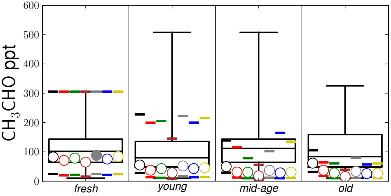

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Recommendation: use acetic acid k for $CH_3C(O)OOH$; use Blitz for ketones; $CH_3C(O)H$ need further study

Conclusions

Chemical Mechanism Performance

- all mechanisms have similar errors*
- under-predict NO_x, HNO_3, and O_3
- over-predict PAN and HNO_4
- *CB05 alkyl nitrate over-prediction due to acetone representation

Uncertainty Review

- PAN source uncertainties are sufficient to correct over-prediction
- HNO_4 loss uncertainties sufficient to correct over-prediction

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- Jingqiu Mao, Ph.D., Harvard
- Gao Chen, Ph.D., NASA
- Kinetic Pre-Processor (Damien et al. 2002)
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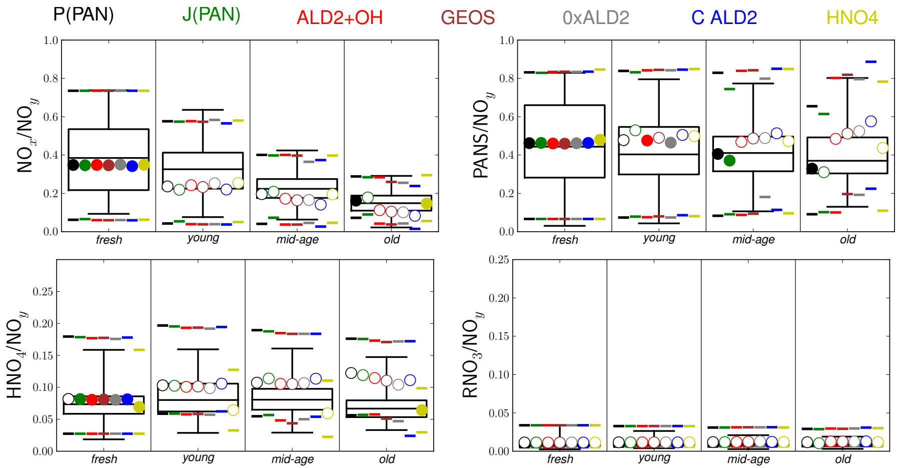
GEOS-Chem Sensitivity Analysis Results



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