

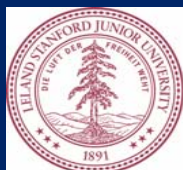
Testing the Speed of a 13,500- Reaction Chemical Mechanism with **SMVGEAR II** and the Accuracy of the Mechanism Against Smog Chamber Data

International Conference on Atmospheric
Chemical Mechanisms

Diana Ginnebaugh

Mark Jacobson, Jinyou Liang

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Outline

- Motivation
- Master Chemical Mechanism v3.1
- SMVGEAR II
- Model comparison
- Smog Chamber comparison



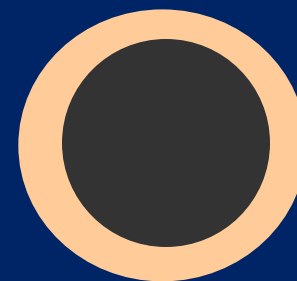
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Motivation

- Model organic chemistry explicitly
- Condensation and aerosol formation of organic species
 - Climate implications
- Local and global 3D simulations
 - Need fast and accurate model





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Master Chemical Mechanism

- “...a near-explicit chemical mechanism describing the degradation of 135 volatile organic compounds (VOCs) in the troposphere” for the purpose of investigating ozone production
- University of LEEDS in the UK



Master Chemical Mechanism

- Based on available laboratory data
 - Not fully tested versus field/photochemical reactor data
- Latest update – version 3.1 (2002)
- 13,500 reactions and 4,600 chemical species



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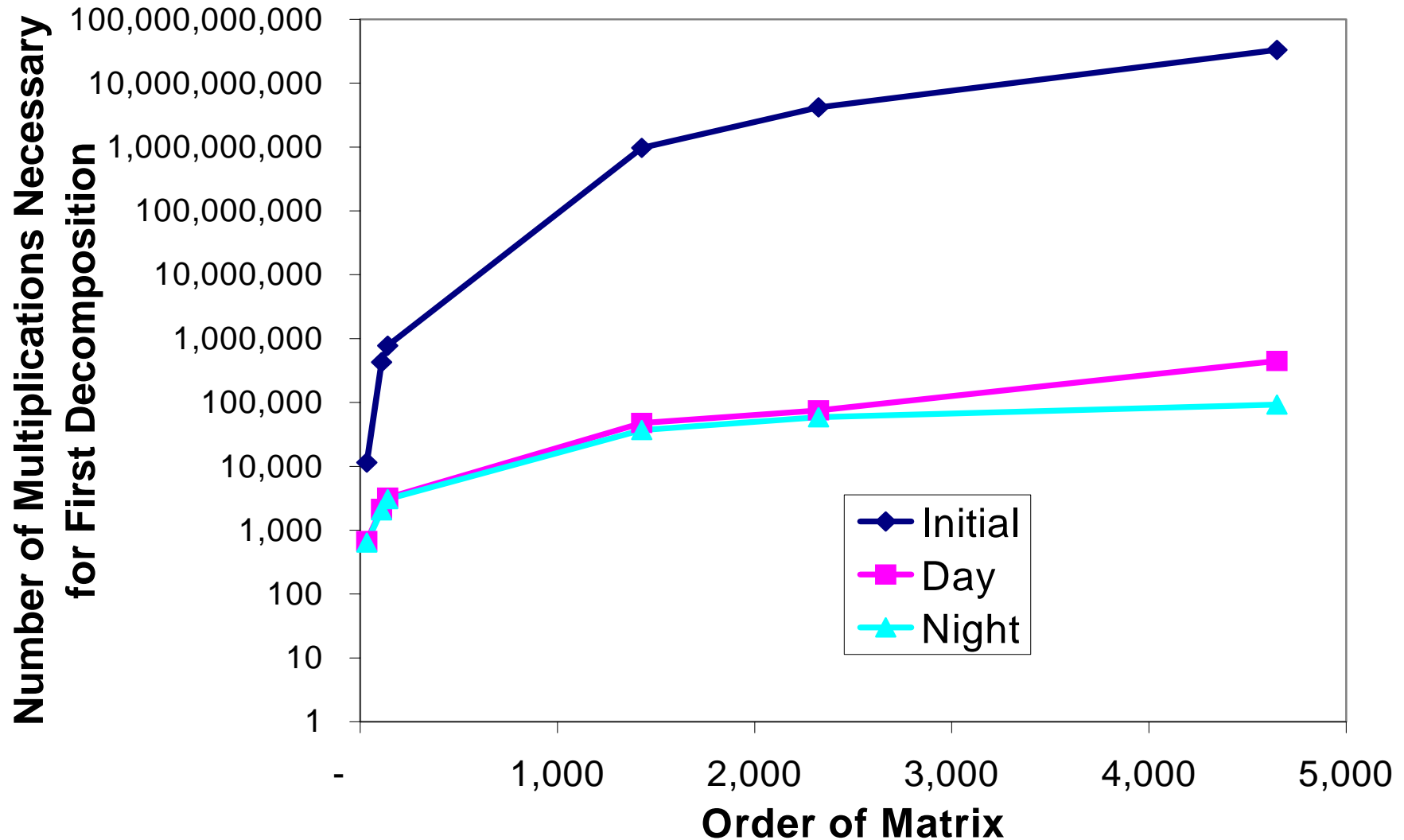


SMVGEAR II

- Sparse-matrix ODE solver
 - Gear solution mechanism – accurate
 - Sparse-matrix - fast

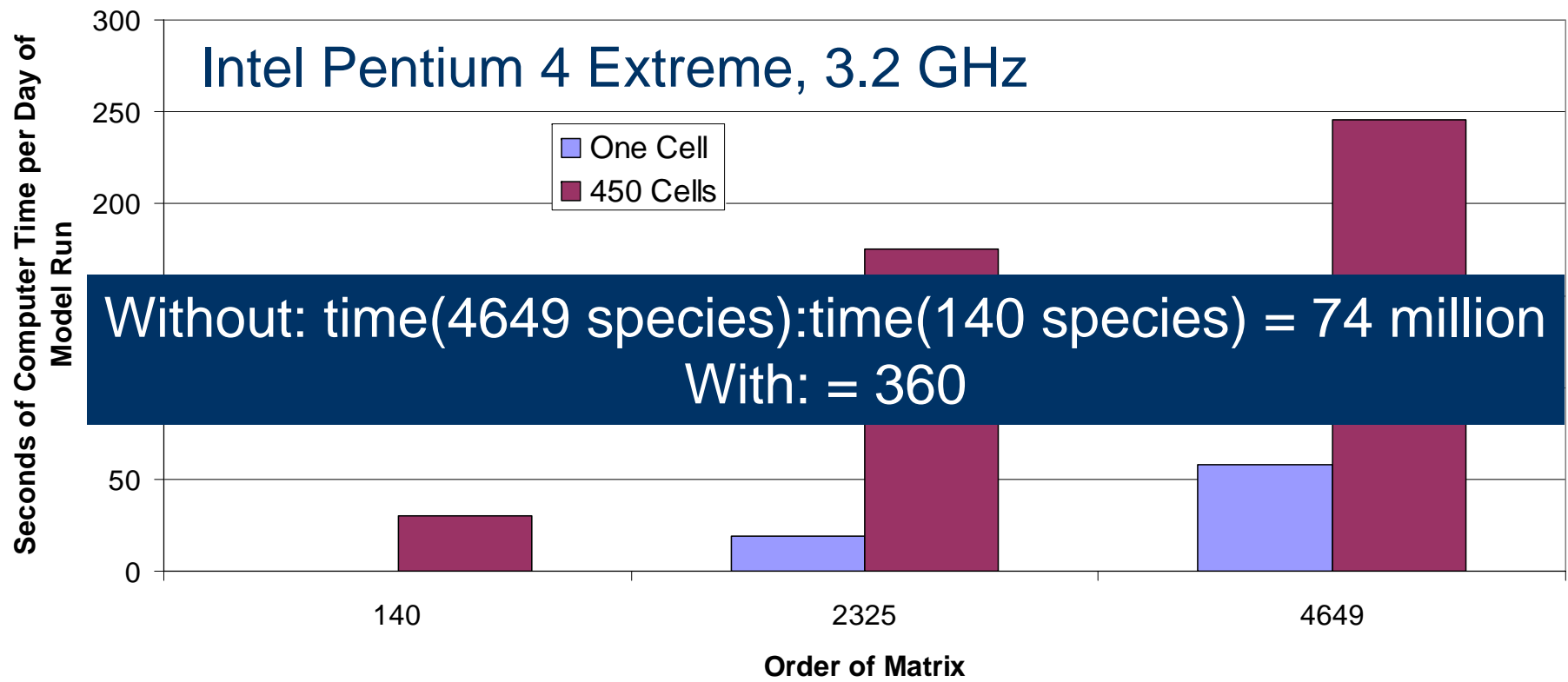
Number of Operations - MCM v. 3.1					
	Initial	After sparse matrix reductions			
		Day	% Reduction	Night	% Reduction
Order of matrix	4,649	4,649	0	4,649	0
Decomp. 1	33,374,524,734	446,030	99.9987	92,948	99.9997
Decomp. 2	10,781,046	25,412	99.76	21,231	99.80
Backsub. 1	10,781,046	25,412	99.76	21,231	99.80
Backsub. 2	10,781,046	19,013	99.82	17,455	99.84

Sparse-Matrix Reductions





Computer Timings

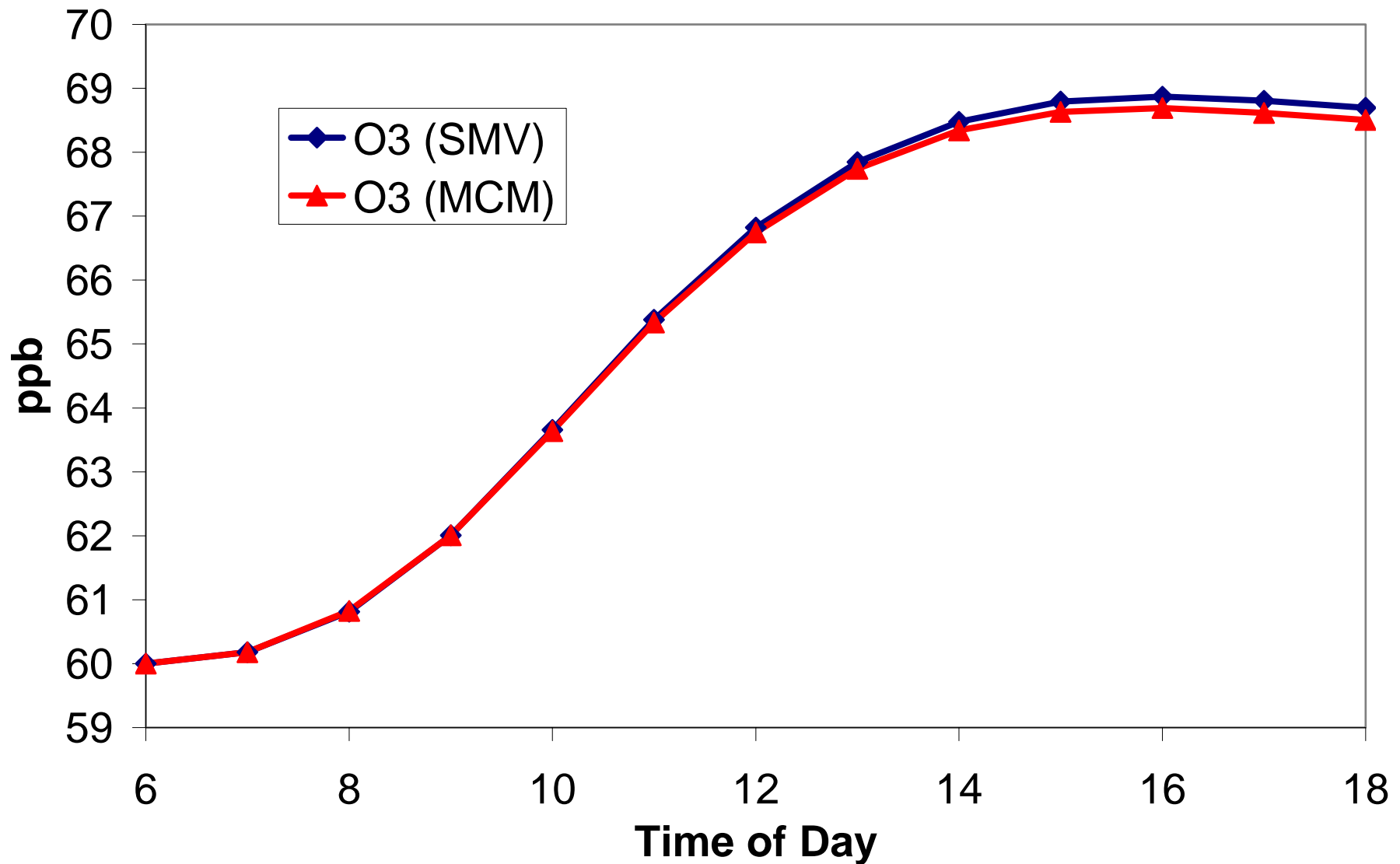




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ACBM vs MCM





Outline

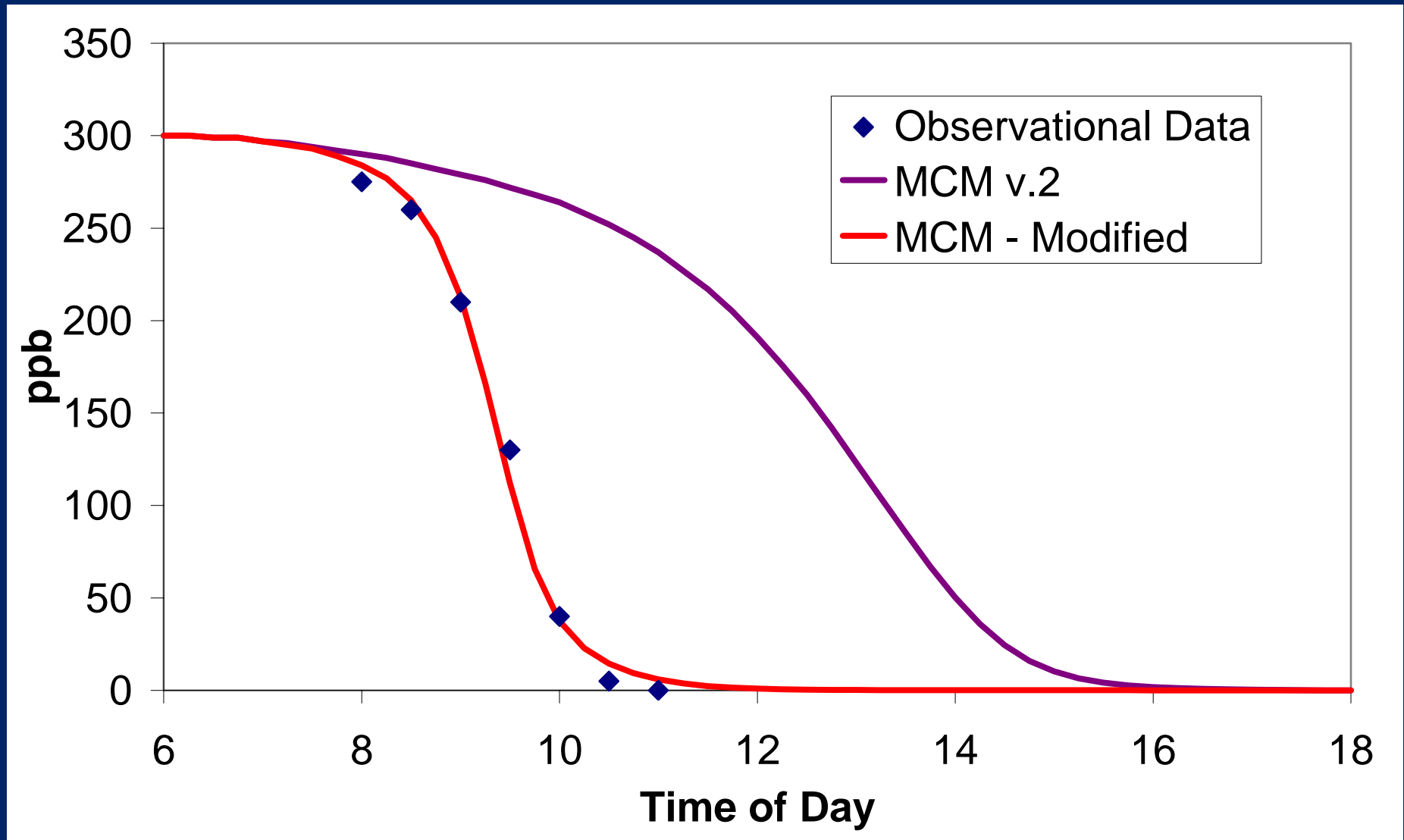
- Motivation
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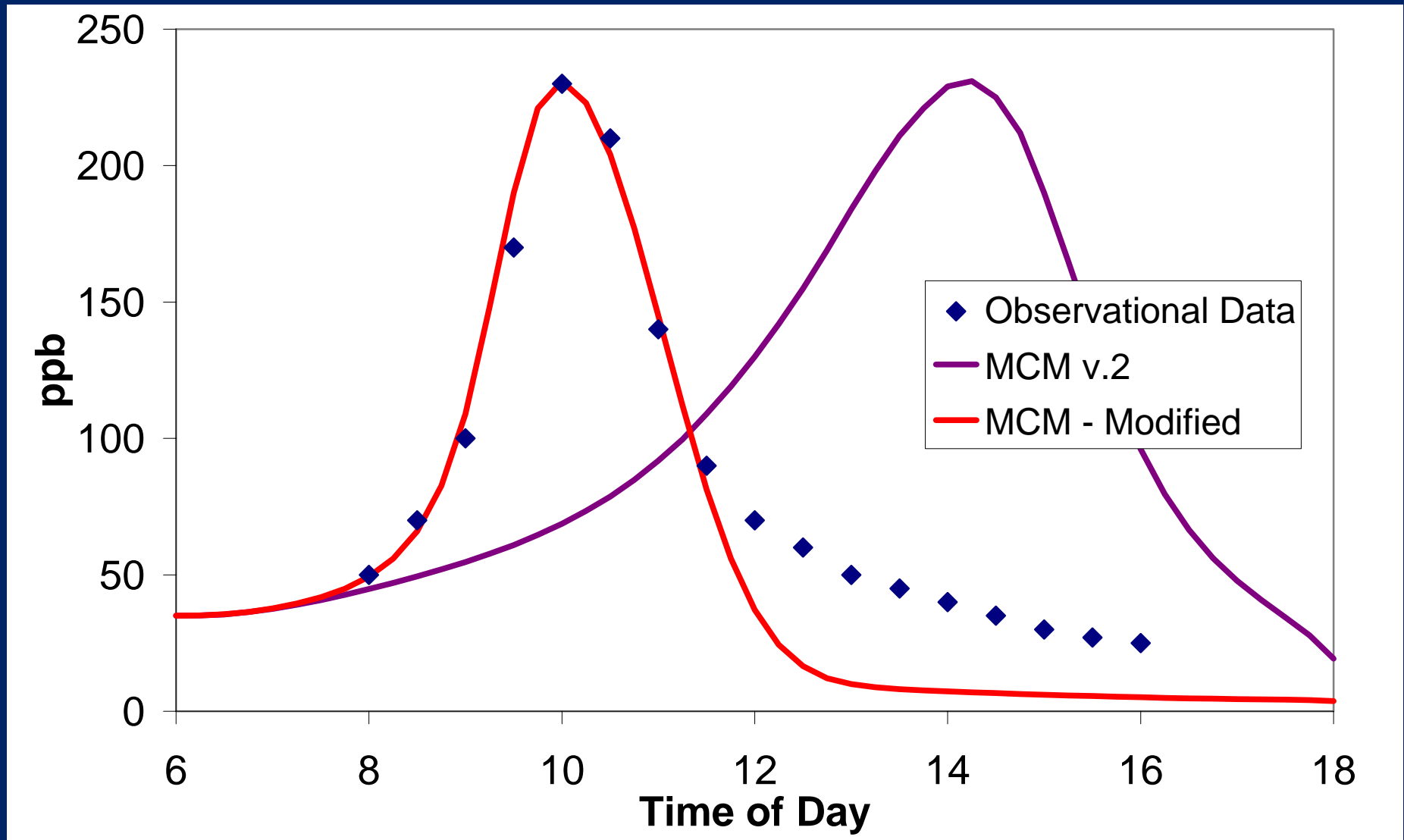
MCM v. 2

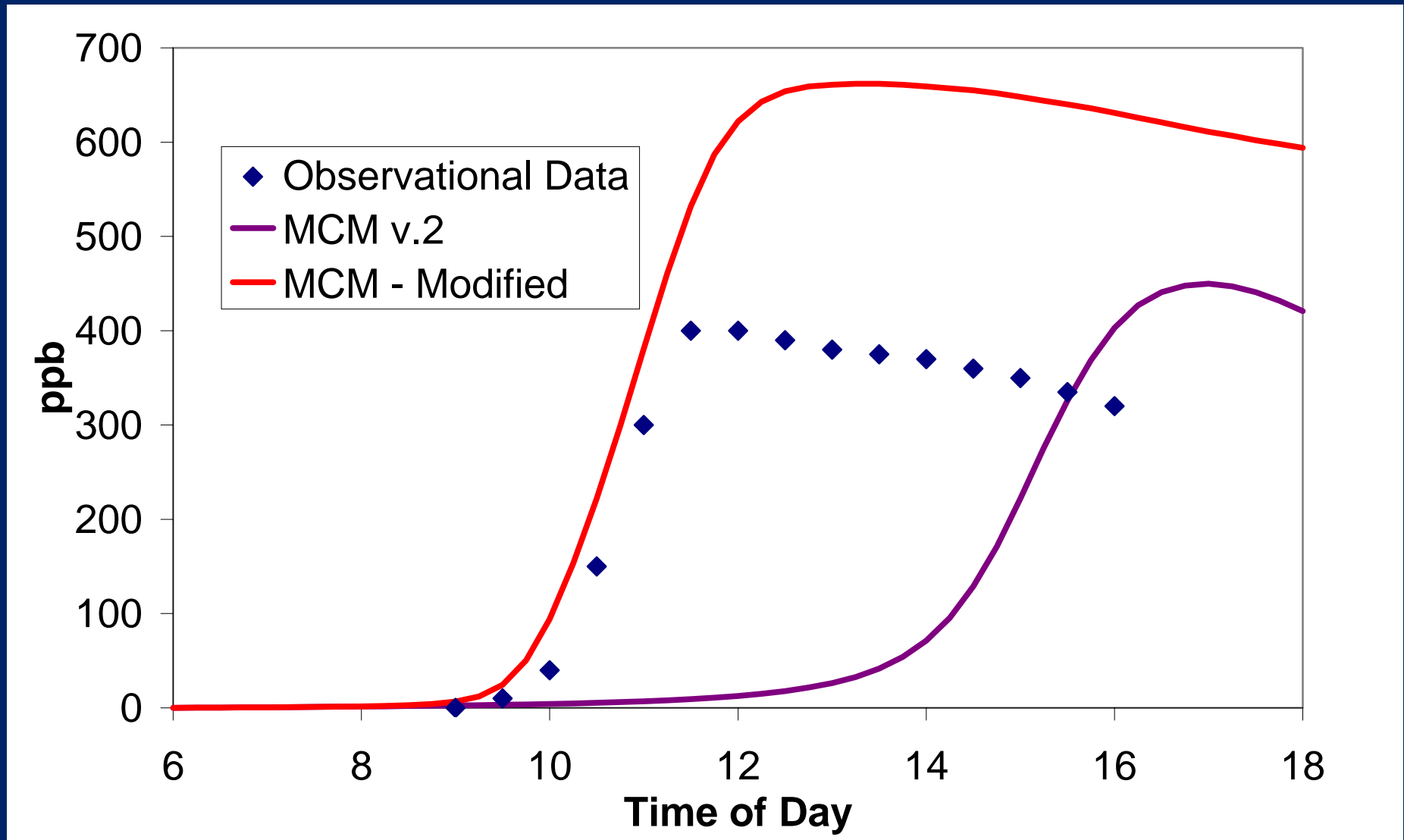
- Previous work by Jinyou Liang, 2002
- Comparing MCM v. 2 with smog-chamber data
 - 7000 Reactions
 - Modified four reaction rates for toluene and m-xylene intermediates to more closely match CBIV rates

NO

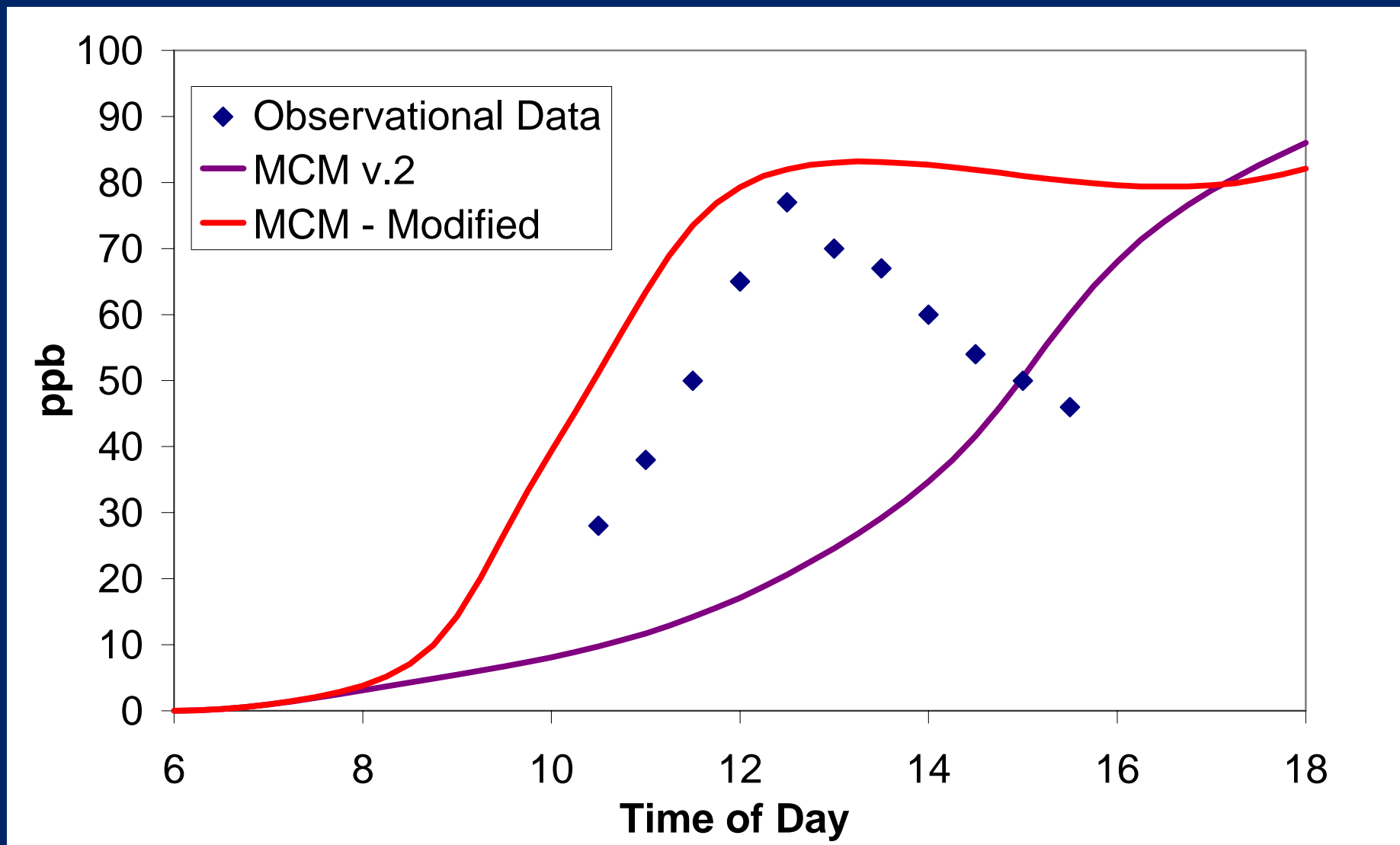


NO₂





HCHO





MCM v.3.1 – What's Next

- Verify with smog-chamber data
 - Improved aromatics reactions
- Compare with field data
- Add vapor pressures and model condensation

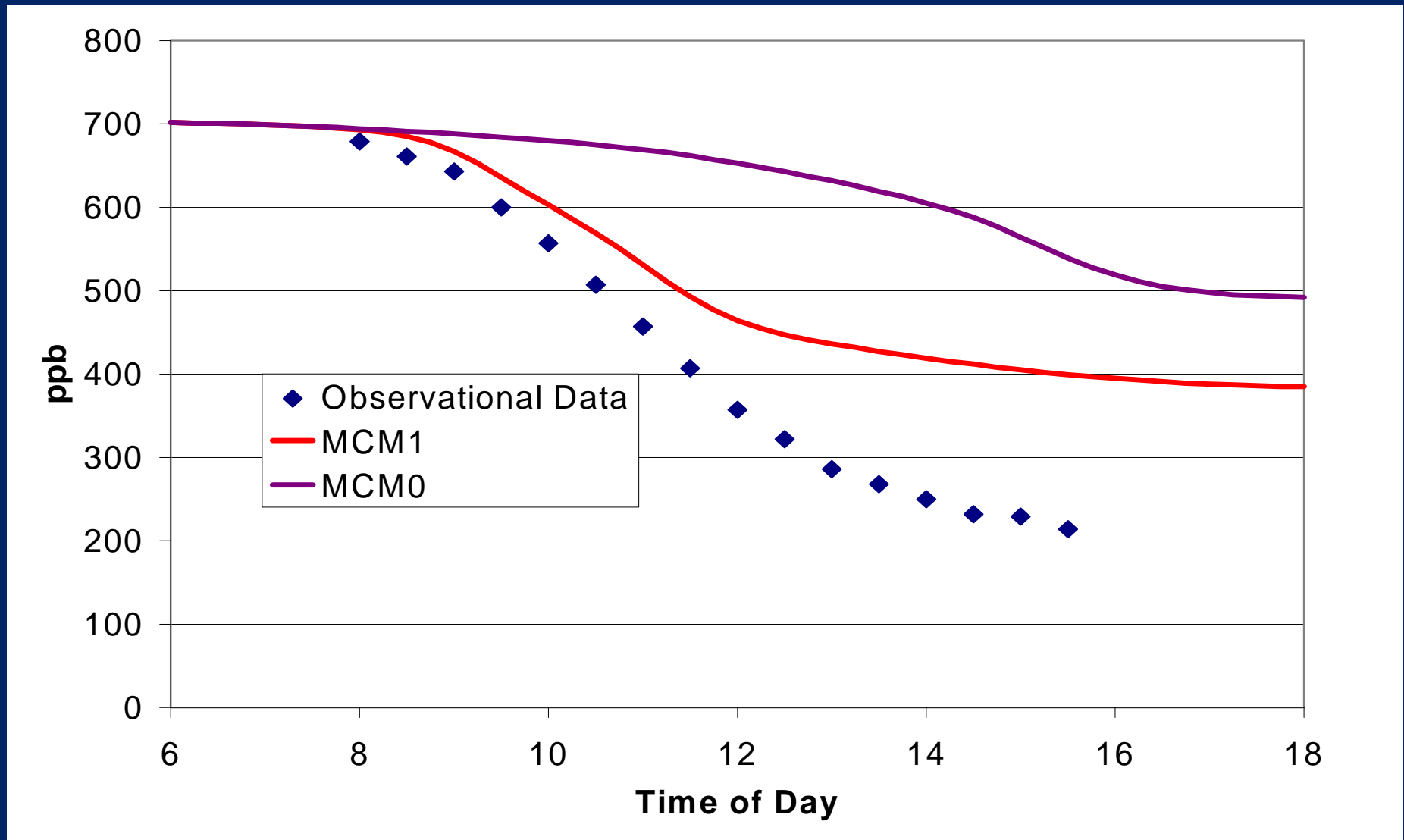


Acknowledgements

- NASA
- Jinyou Liang, CARB
- Mark Jacobson, Stanford University

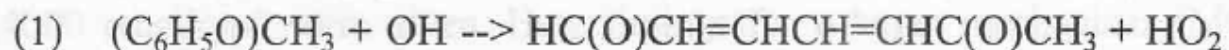


Toluene



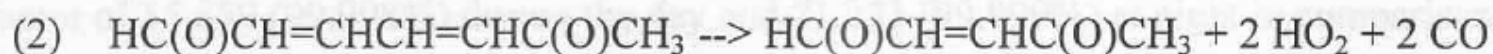


MCM v. 2 Modifications



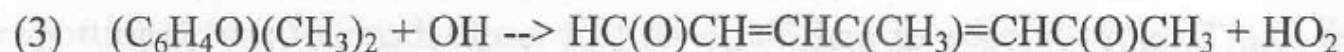
Original $k = 1 \times 10^{-10}$

Modified $k = 3 \times 10^{-10}$



Original $J = 8.46 \times 10^{-6}$

Modified $J = 1 \times 10^{-3}$



Original $k = 1 \times 10^{-10}$

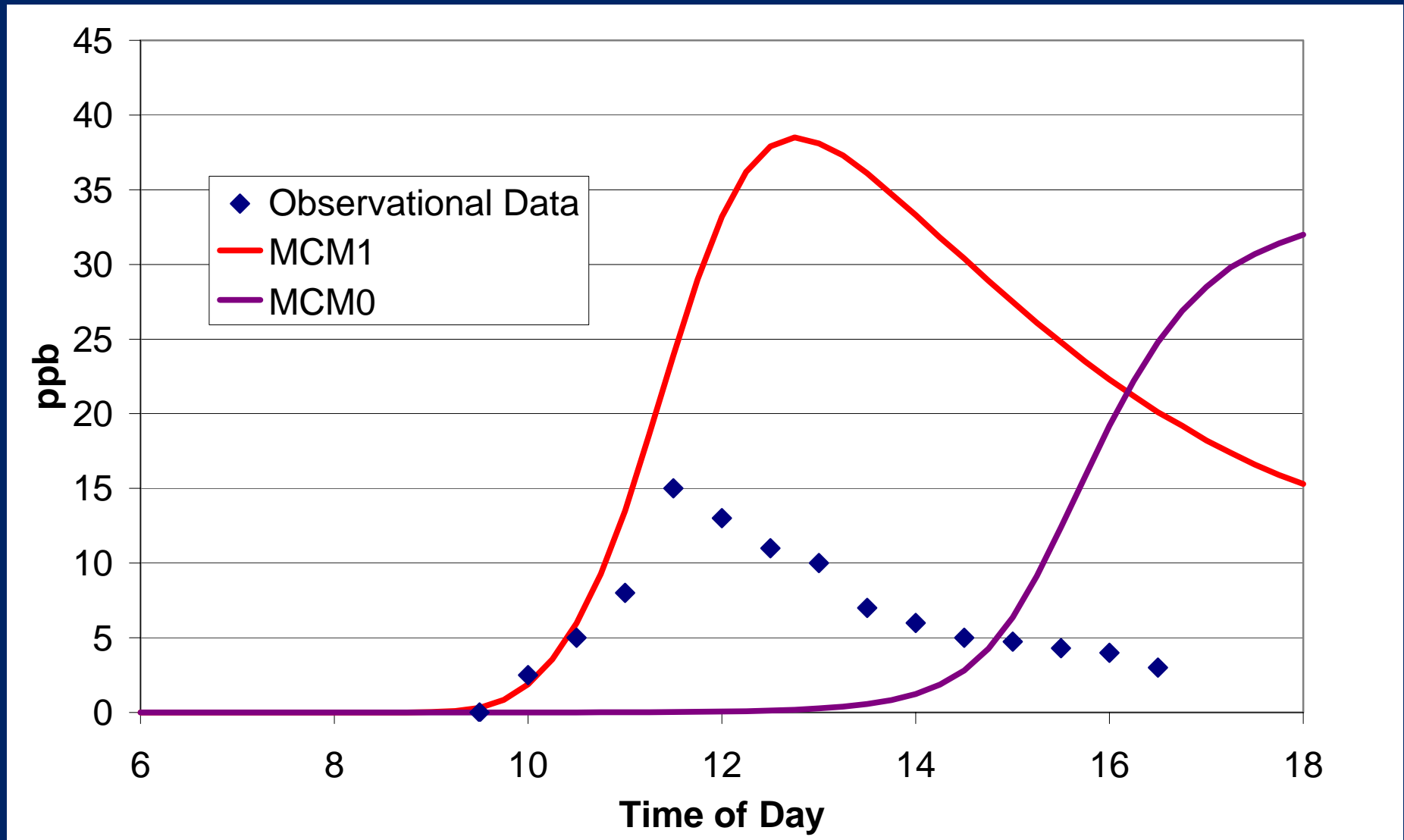
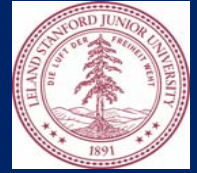
Modified $k = 3 \times 10^{-10}$



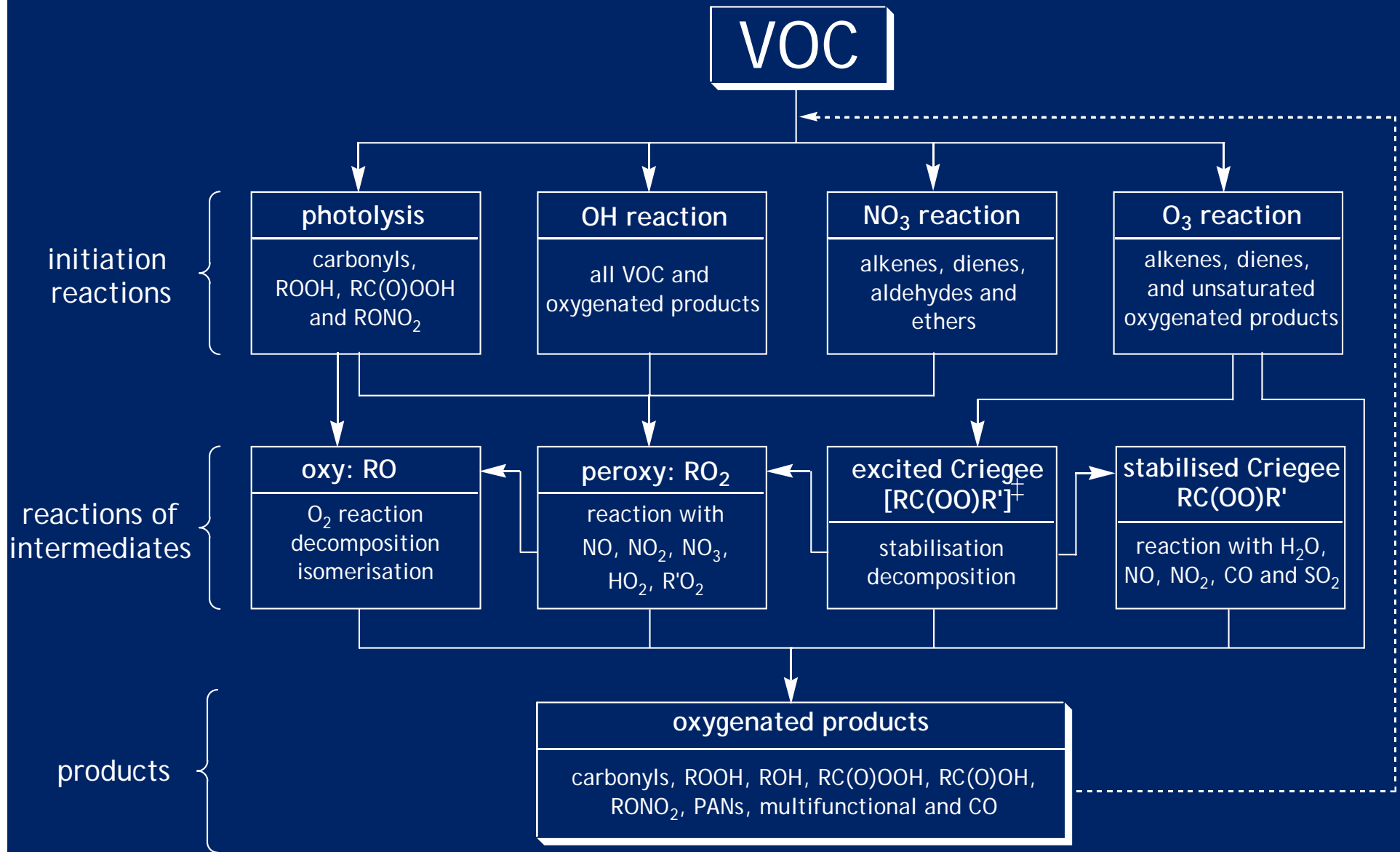
Original $J = 8.46 \times 10^{-6}$

Modified $J = 1 \times 10^{-3}$

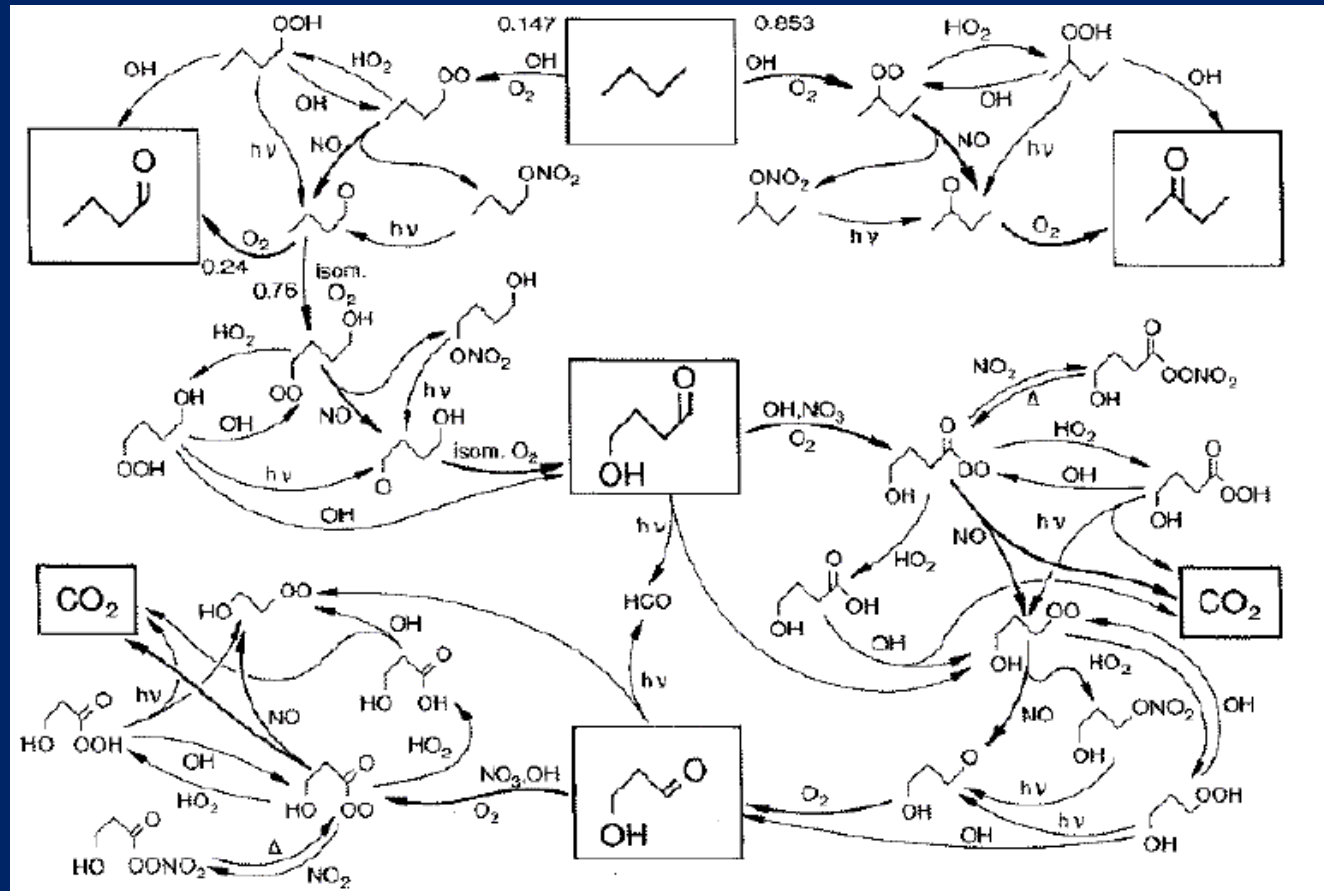
PAN



MCM Chemistry Summary



Degradation of Butane



- Broken down into CO_2 , CO , or organic chemicals
- 510 reactions, 186 Species, 20 primary emitted VOC

What do you do with it?

1. Validate MCM with data and by comparing to other mechanisms
2. Use in air pollution modeling
 - Ozone



What's been done (recently)?

Evaluation of isoprene degradation in the detailed tropospheric chemical mechanism, MCM v3, using environmental chamber data

- P.G. Pinhoa, C.A. Pioa, M.E. Jenkinb,
- Both isoprene and butane generally performed well
- a number of parameter modifications were identified which resulted in an improved performance
 - Relate to the magnitude of sources of free radicals from organic chemical process and the yields of radicals from the reactions of O₃ with unsaturated oxygenates
 - It was necessary to include a representation of the reactions of O(3P) with isoprene, MACR and MVK (which were not previously treated in MCM v3)
- MCM v3 was also compared with that of the SAPRC-99 mechanism

What's been done (recently)?

Modelling of the photooxidation of toluene: conceptual ideas for validating detailed mechanisms (2002)

- V. Wagner¹, M. E. Jenkin², S.M. Saunders^{1*}, J. Stanton¹, K. Wirtz³, and M. J. Pilling¹
- Model simulations for toluene-NO_x experiment
- Two major shortcomings
 - OH production is too low by 80%
 - Ozone concentration at the end of the experiment is overpredicted by 55%

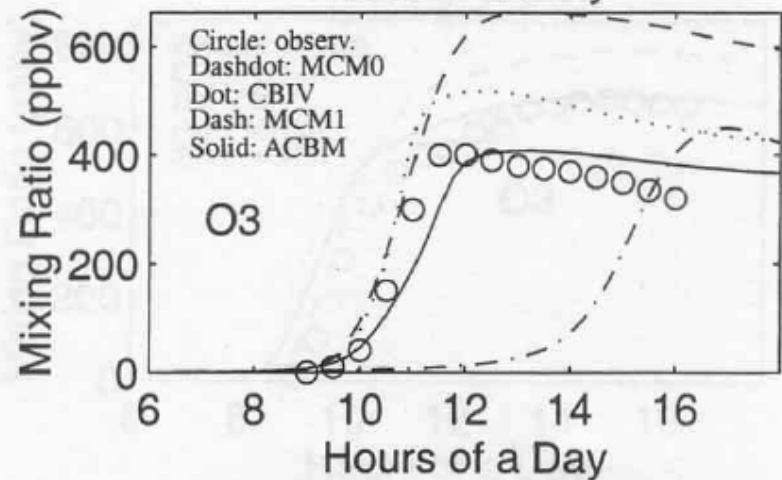
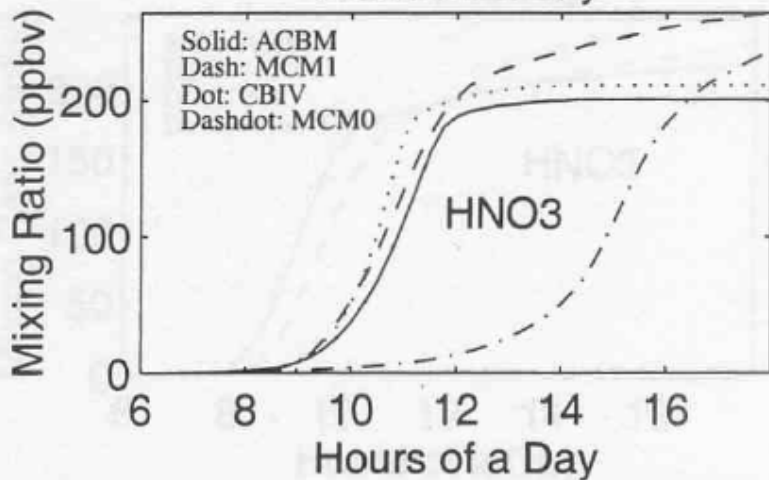
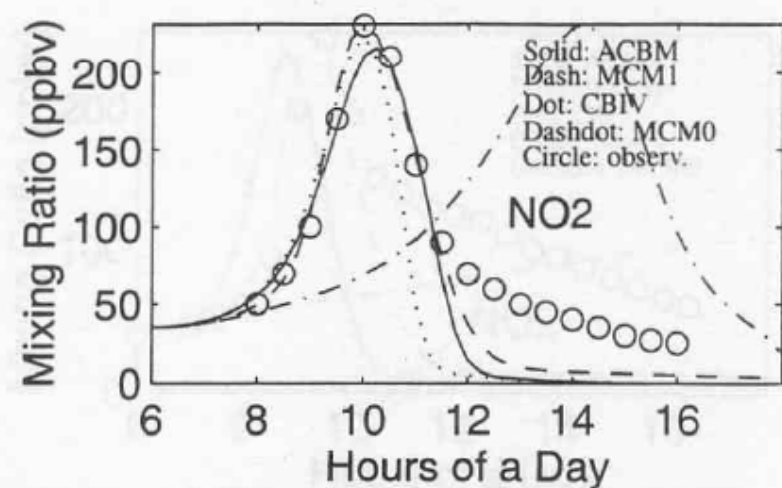
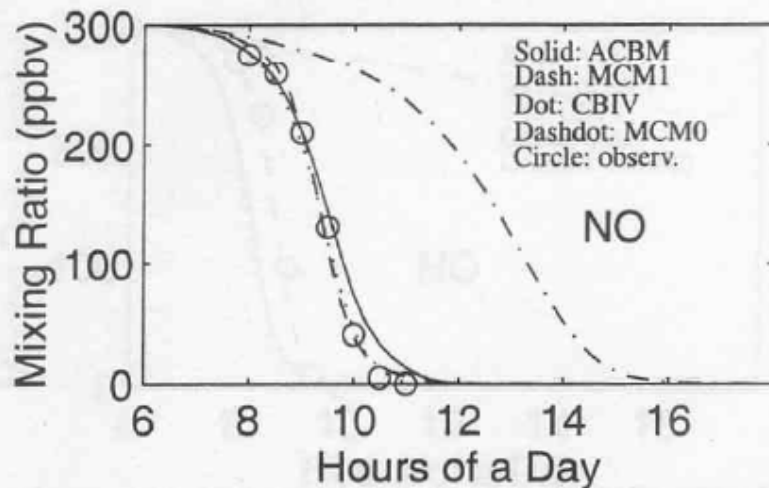
What's been done (here)?

- Jinyou Liang and Mark Jacobson -
1999 Paper, MCM v1
 - Compared with 2 other mechanisms
 - Utilized SMVGEAR II – reduced calculations by a factor of 15,000
 - Compared to smog-chamber data and L.A. field data
- Similar study done in 2002 with MCM v2
 - Version 3 came out

Improvement in Computer Time using SVMGEAR II

	Initial	After Sparse Matrix Reductions			
		Day	% Reduction	Night	% Reduction
Order of matrix	2325	2325	0	2325	0
No. init. matrix spots filled	5,405,625	23,116	99.57	20,566	99.62
No. fin. matrix spots filled	5,405,625	27,763	99.49	24,012	99.56
No. operations decomp. 1	4,186,656,950	74,950	99.998	58,759	99.999
No. operations decomp. 2	2,701,650	15,223	99.44	12,042	99.55
No. operations backsub. 1	2,701,650	15,223	99.44	12,042	99.55
No. operations backsub. 2	2,701,650	10,215	99.62	9,645	99.64

Results for Toluene



What am I going to do?

- Similar to Jinyou Liang, with MCM v3.1
 1. Update SVMGEARII code with latest mechanism
 2. Compare data to smog chamber data, field measurements and other mechanisms
 3. (Maybe) determine condensable species with vapor pressure data