

# Process Analysis for Photochemical Reaction Mechanisms

2006 International Conference on Atmospheric Chemical Mechanisms

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## Session F: Use of other scientific tools to aid the development of chemical mechanisms

- ▶ 8:00–9:50 am
- ▶ 5 presentations
- ▶ Process Analysis
- ▶ Adjoint Sensitivity Analysis Procedure
- ▶ Quantum Chemistry and Chemical Mechanism Development

- ▶ Chemical Transport Models are a complex interrelated system of chemical and physical processes
  - ▶ Emissions
  - ▶ Chemistry
  - ▶ Meteorology
- ▶ Chemical mechanisms should be evaluated separate from 3-D models.
- ▶ The number one killer **Compensating Errors**

## How do you choose the “right” model or chemical mechanism?

- ▶ What is “right”?
- ▶ CAM<sub>x</sub>, CMAQ, WRFChem, SAPRC99, CBIV, CB05, RACM1, RACM2
- ▶ Deborah Luecken/Sharon Phillips 3 mechanism comparison
- ▶ Houston, Texas
  - ▶ Multiple emission Inventories
  - ▶ Multiple meteorological inputs
  - ▶ Multiple chemical mechanisms
  - ▶ Maedah Faraji increase of 45 ppb.

## How do you choose the “right” model or chemical mechanism?

- ▶ Use of alternative formulations alternative models is important
- ▶ An examination of model predictions alone is not a sufficient method to understand the reasons for differences
- ▶ What is needed is a process based evaluation

# Integrated Process Rates

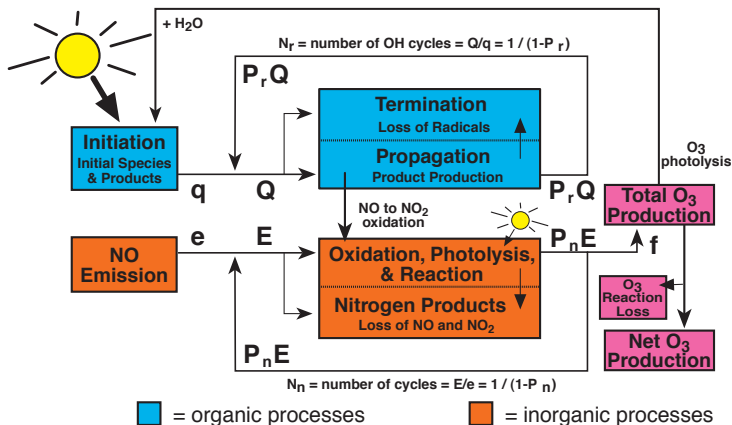
## Previous Work

- ▶ Jeffries and Tonnesen *et. al* 1994<sup>2</sup> modified the OZIPR model to calculate an integrated rate, or mass throughput, for every chemical reaction and physical process.
- ▶ Integrated rate data was then used to calculate key chemical parameters that included: the OH and NO cycle; OH budget; O<sub>3</sub> yields and production.
- ▶ These parameters were used to compare in Chicago two photochemical reaction mechanisms, CBIV and SAPRC90.
- ▶ Differences in terms of the radical budget
- ▶ CAMx and CMAQ now output this data as Integrated Process Rate (IPR) and Integrated Reaction Rate (IRR) files.

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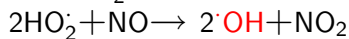
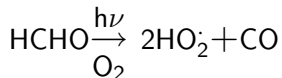
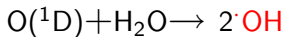
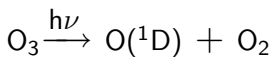
<sup>2</sup>Jeffries H.E., Tonnesen S., "A Comparison of two photochemical reaction mechanisms using mass balance and process analysis," *Atmospheric Environment*, Vol 28., pp. 2991-3003, 1994.

## Radical and NOx Cycles

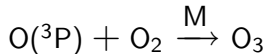
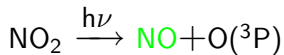
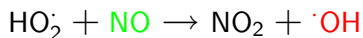
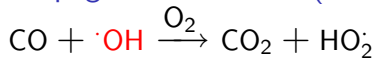


# $\cdot\text{OH}$ Initiation, Propagation, and Termination Chemistry

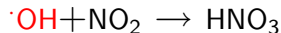
## Initiation Reactions ("New" $\cdot\text{OH}$ )



## Propagation Reactions ("Recreated" $\cdot\text{OH}$ )



## Termination Reaction

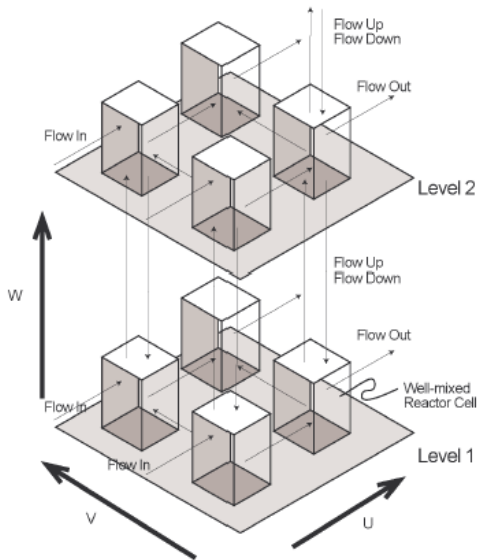






## Process Analysis Chemical Parameters

- ▶ new  $\cdot\text{OH}$
- ▶  $\cdot\text{OH}$  chain length
- ▶ total  $\cdot\text{OH}$  reacted
- ▶  $\cdot\text{OH} + \text{VOC}$
- ▶  $\cdot\text{OH} + \text{NO}_2$
- ▶  $\text{NO} + (\text{HO}_2, \text{RO}_2)$
- ▶ NO chain length
- ▶  $\text{NO}_2 \xrightarrow{h\nu}$
- ▶  $\text{O}_3$  produced
- ▶  $\text{O}_3$  fate



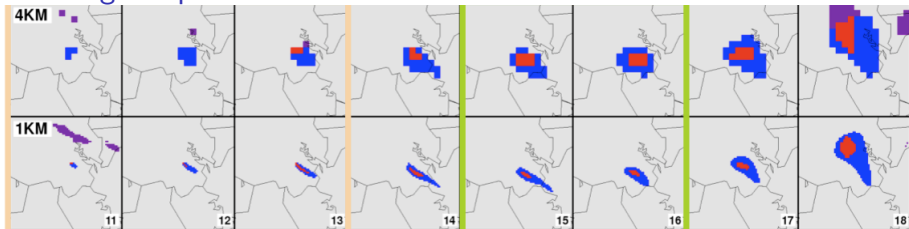
# “Langrangian” Plume Tracking Process Analysis

## “Industrial Releases of Highly Reactive VOCs”

Henderson B., *et al.*

AGU Poster Tuesday December 12

### Tracking the plume



- ▶ Hypothetical industrial releases simulated in a 1-km grid model produced a peak ozone concentration 65 ppb higher than the same release in a 4-km grid model
- ▶ 1.5 ppb increase in organically derived  $\cdot\text{OH}$  led to a 11 ppb increase in net chemical ozone production

# Process Analysis Application in Houston Texas

Finding: 2000 HGA Basecase is "radical limited"

Modeling System: CAMx4.2 with TCEQ base1b.psito2n2

- ▶ Simulations predictions are often biased high for NO<sub>2</sub> and HRVOC yet under predict observed peak O<sub>3</sub>.
- ▶ This is not the 'latest' version of the inventories, but new changes are unlikely to have remedied these problems.

Process Analysis shows that model system produces too few new radicals

- ▶ Not a problem with mechanism "internal radical" production.
- ▶ Inputs to model system fail to produce an environment where sufficient sources of radicals can be made from direct photolysis of carbonyls.

Can be caused by:

- ▶ Insufficient primary carbonyls in inventory
- ▶ Not accounting for production of carbonyls in control devices such as flares
- ▶ Not accounting for creation of carbonyls in "event emissions" releases
- ▶ Use of incorrect speciation profiles in industrial and mobile sources
- ▶ HONO sources?

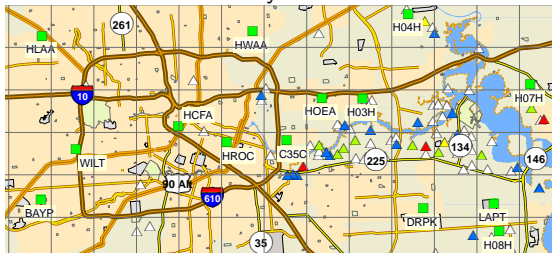
# UNC Modeling Sensitivity Study

## Explore effects of VOC input changes on radical budget

- ▶ No changes to NO<sub>x</sub> emissions.
- ▶ Made a single change to four areas within the VOC emissions files.
  1. Carbon Monoxide
  2. Aromatics
  3. Ethylene
  4. Formaldehyde
- ▶ These changes impact radical *initiation* and *propagation* rates in different ways.
- ▶ A detailed process analysis was used to quantify these changes in the radical budget.

# The VOC and NO<sub>x</sub> Conditions for Seven Scenarios

## Process Analysis Focus Area



### Emissions Changes In

Parameter (ppb)	Base base1b	Carbon Monoxide		Aromatics	Ethylene	Formaldehyde	
		25% base	400% base	200% base	2% area CO	1% flare VOC	4% area CO
10 VOC available	205.8	205.3	205.8	210.2	214.9	214.3	223.1
11 NO <sub>x</sub> available	75.8	75.9	75.8	75.8	75.8	75.6	75.6
12 avg VOC/NO <sub>x</sub>	4.2	4.2	4.3	4.5	4.5	4.6	4.8
13 avg VOCC/NO <sub>x</sub>	5.4	5.3	5.4	6.1	5.7	5.8	5.9

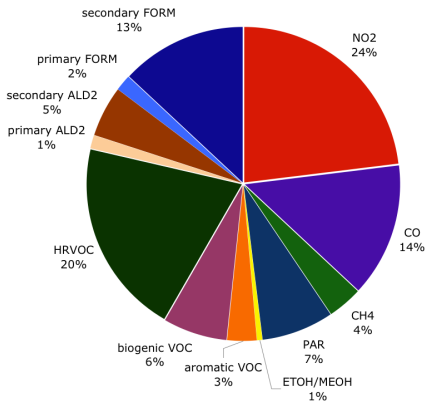
## Total ·OH Reacted in Each Scenario

- ▶ Organic new ·OH mainly from  $\text{HCHO}+h\nu$
- ▶ Total ·OH reacted is controlled by **organic** new ·OH

Parameter (ppb)	Base base1b	Emissions Changes In					
		Carbon Monoxide		Aromatics	Ethylene	Formaldehyde	
		25% base	400% base	200% base	2% area CO	1% flare VOC	4% area CO
1 HCHO+h $\nu$	5.6	5.6	5.5	5.7	6.1	6.9	7.6
2 organic new ·OH	14.4	14.4	14.4	16.0	15.4	16.8	18.4
3 O <sub>3</sub> new ·OH	19.3	18.7	20.3	20.3	19.9	21.4	21.2
4 total new ·OH	33.7	33.1	34.7	36.3	35.4	38.2	39.6
5 ·OH chain len	3.2	3.1	3.6	3.3	3.3	3.2	3.3
6 ·OH reacted	107.8	101.7	125.6	118.1	115.7	123.4	129.4

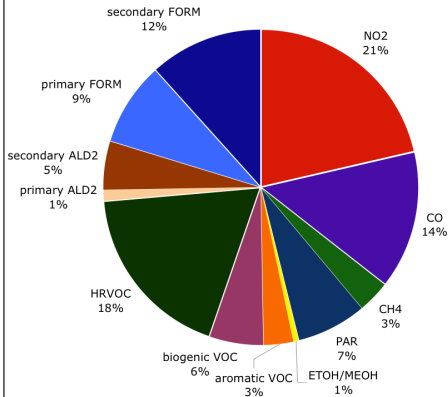
# How "Total ·OH" reacted

## 8/25 Base Case



Total ·OH Reacted: 108 ppb  
Available VOC reacted: 32%

## 8/25 CO\_FORM Case



Total ·OH Reacted: 129 ppb  
Available VOC reacted: 36%

## O<sub>3</sub> Production

- ▶ a 2.0 ppb difference in HCHO + hν resulted in a 24.1 ppb difference in O<sub>3</sub> over the entire 78 4-km grids
- ▶ adding HRVOC is **not as** effective, because these compounds need to react with ·OH before they can produce new ·OH from their products

Parameter (ppb)	Emissions Changes In						
	Base base1b	Carbon Monoxide		Aromatics	Ethylene	Formaldehyde	
		25% base	400% base	200% base	2% area CO	1% flare VOC	4% area CO
1 HCHO+hν	5.6	5.6	5.5	5.7	6.1	6.9	7.6
4 total new ·OH	33.7	33.1	34.7	36.3	35.4	38.2	39.6
15 O <sub>3</sub> produced	104.9	99.8	119.8	118.9	115.4	122.5	129.0
16 O <sub>3</sub> peak	87.1	84.6	93.3	94.1	91.7	99.0	98.9
17 O <sub>3</sub> Horz. export	73.2	69.5	84.2	83.2	81.1	83.3	90.1

## Conclusions

- ▶ Explaining changes in model predictions is difficult with only output concentrations
- ▶ Investigation of chemical and physical process rates significantly increases the ability to explain air quality model predictions.
- ▶ A detailed process based evaluation is critical for evaluations and intercomparisons of chemical mechanisms within air quality models.
- ▶ Provide guidance for the types of observations needed to challenge model predictions.

## Future Work

- ▶ Multi-model and Multi-Mechanism process analysis based comparisons (CMAQ, WRFChem, SAPRC99, RACM, etc.)
- ▶ Kinetic Process Analysis Source Apportionment (KPASA)
- ▶ Process analysis methods for PM formation

# This Work Supported By

## HARC Project H60

- ▶ "Regional Transport Modeling For East Texas", Jay Olaguer, Project Officer

## TCEQ

- ▶ Thanks to Jim Smith for supplying CAMx ready files for SIP modeling

## Alpine Geophysics

- ▶ Thanks to Dennis McNally and Tom Tesche for sharing simulation results.

## Eight Hour Ozone Coalition Group

## UNC Modeling Air Quality Lab

- ▶ Thanks to Barron Henderson, Leiran Biton, Kat Galloway.