PM and ozone formation from toluene and the importance of "NOx-sinks" under NOx-limited conditions

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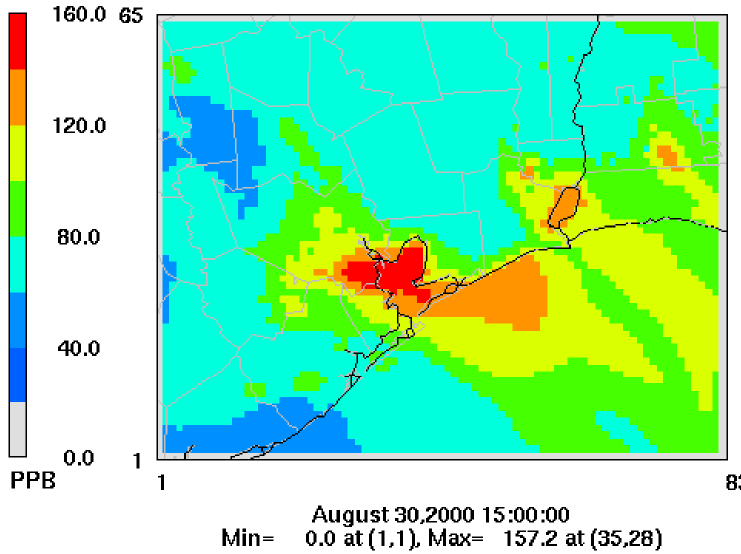
Outline

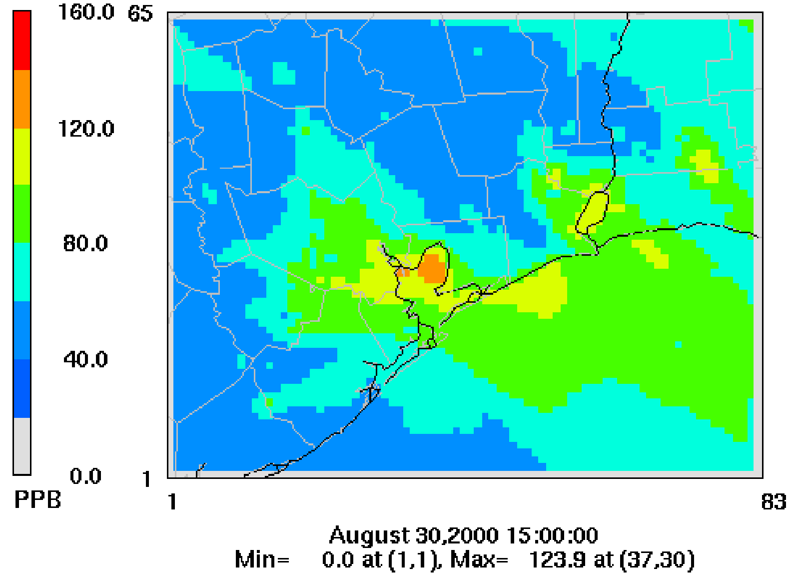
- Toluene and other aromatics are important PM and ozone precursors
- Toluene chemistry has unique aspects
  - Tendency to sequester NOx: called "NOx-sink"
  - Major source of differences between CB and SAPRC mechanisms
- Recent work by ENVIRON and UT has improved the CB toluene mechanism by using current knowledge
  - Available research tends to focus on radical production
- New chamber experiments are needed that focus specifically on NOx-sink
  - UNC has appropriate chamber facilities nd experience

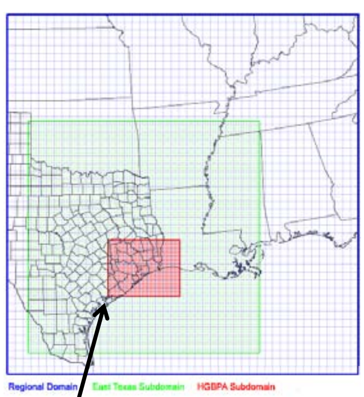
Houston Ozone Differences

SAPRC99

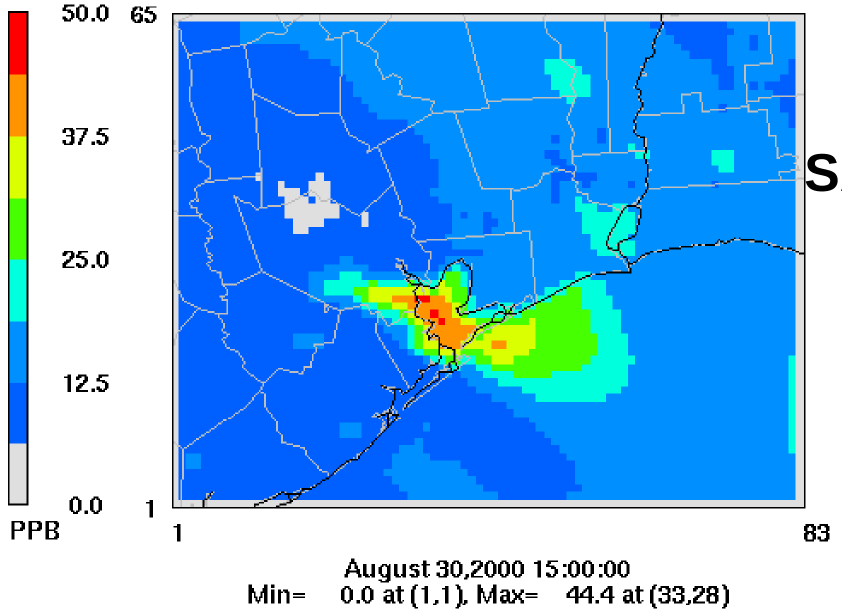


CB4





Modeling Domain



SAPRC minus CB4

Differences up to 45 ppb

Aug. 30, 2000

Policy Implications

Required vs. predicted relative reductions in ozone with 75% NOx cut

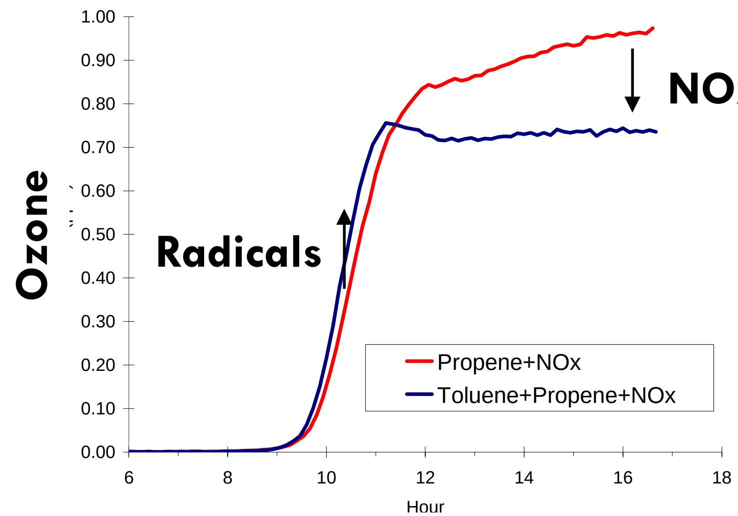
Monitor	Design Value (2003-2005)	Required for Attainment	Predicted with SAPRC99	Predicted with CB4
BaylandPk	102 ppb	16.0 %	16.2 %	13.6 %
Deer Park	101 ppb	15.0 %	15.6 %	8.9 %

Sensitivity results from earlier modeling with year 2000 episode

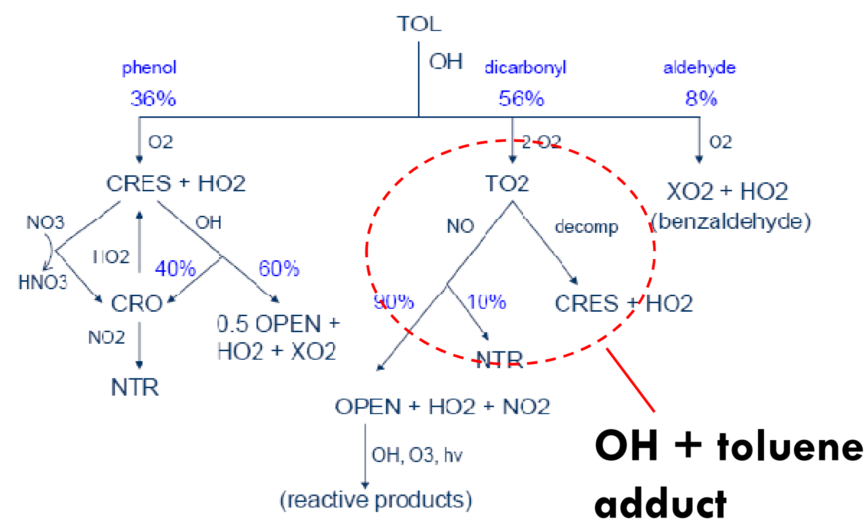
Toluene Chemistry is Different

- Toluene has strong radical sources <u>and</u> strong NOx-sinks
  - Majority of experimental work on radical sources
  - 1979 experiment at UNC demonstrates strong NOx-sink can curtail ozone formation
- Phenolic products known to be important NOx sinks
  - Cresols, catechols, nitrocresols
- Fate of OH-toluene adduct (TO2 in CB05) important
  - Depends on NO concentration
  - Controls PM formation
  - Strongly influences O3 formation
  - <u>NOx-sinks need to be characterized</u>

Toluene impact on propene/NOx expt.



CB05 Toluene Mechanism



Mechanism Performance

- Toluene mechanisms diverge more other VOCs
- More reactions is not the solution
  - E.g., MCM performance poor
  - However, MCM contributed valuable product characterization and mechanistic insight
- Need to better understand chemistry of toluene degradation products
  - Some work by MCM and UNC

Published performance of highly detailed "Master Chemical Mechanism"

- Includes thousands of reactions
- Problems related to NOx removal

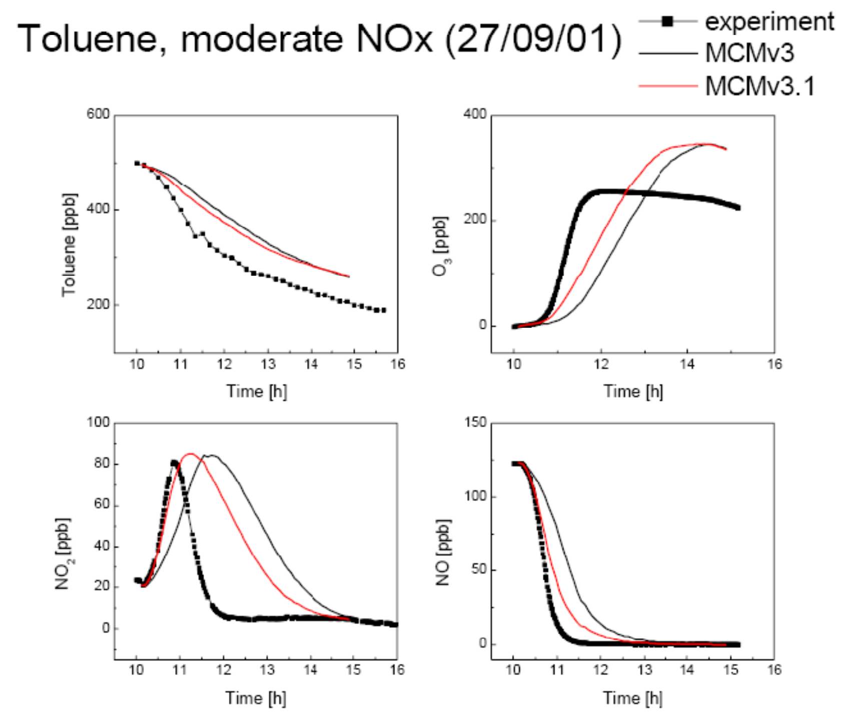


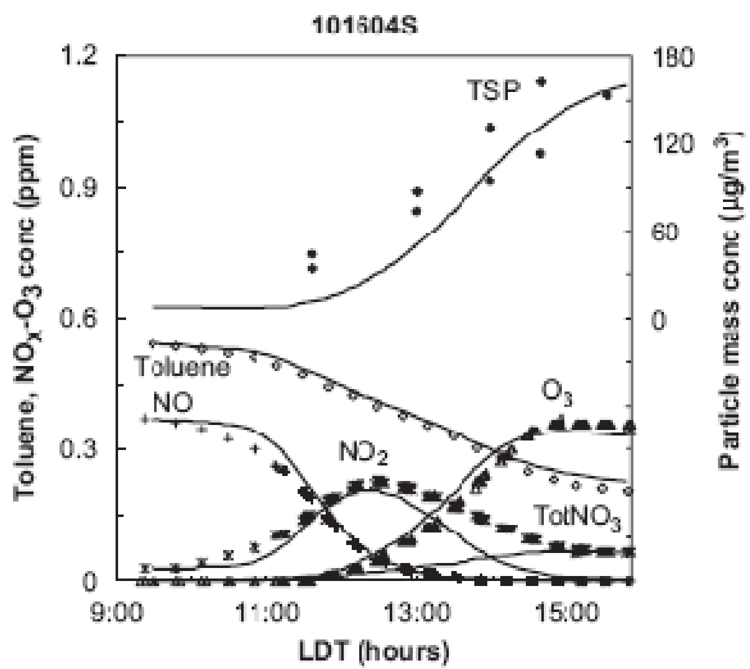
Fig. 5. Model-measurement comparison for toluene, O_3, NO_2 and NO in toluene photosmog experiment of 27 September 2001.

Recent Work by ENVIRON, UT and UNC

- UT/ENVIRON/UCR investigated differences between CB05 and SAPRC99
  - Alkanes, alkenes, aldehydes similar
  - Toluene different
- ENVIRON/UT improving CB05 toluene mechanism
  - Condensed version of UNC's toluene mechanism called "UNClite"
    - Lowered cresol yield
    - Different "NOx-switch" for TO2
    - NOx-sinks in addition to cresol

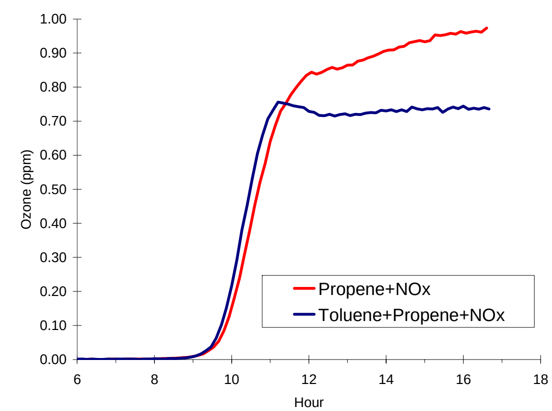
Published performance of detailed UNC toluene mechanism

- Has ~250 reactions
- Good performance for O3, PM and NOx
- Still need additional NOx-sinks



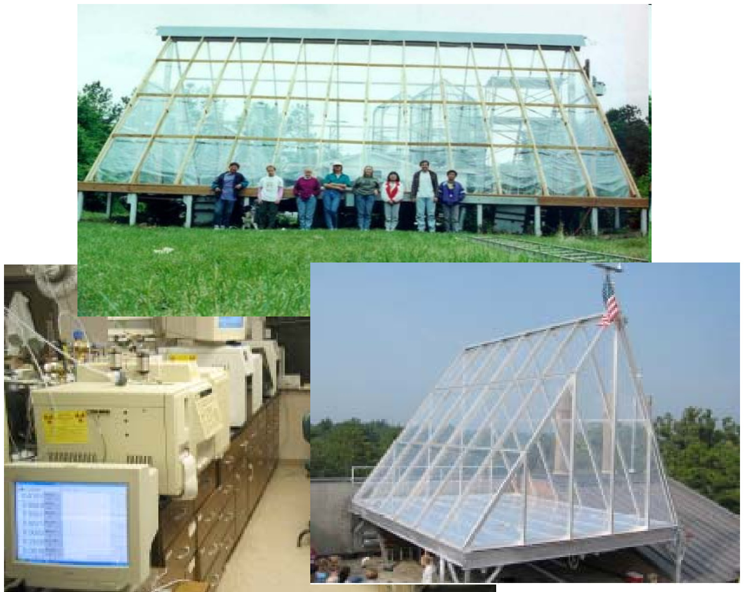
Proposed Research

- New experiments adding compounds to propene/NOx mixtures that will become NOx-limited
  - Use dual-sided outdoor chamber with natural sunlight
  - Differential impact on ozone and PM formation
  - Composition of PM nitrogen compounds
  - NO, NO2, PAN
  - Organics



- Experiments with toluene and key degradation products
  - Ring-retaining products: cresols, catechols
  - Ring-opening products: butenedial, methylbutenedial

Research Team



Parameter	Sample Device	Sample Media	Analysis Method	Instrument
PM Mass	Filter Holder/ Denuder	Filter*/ XAD-4	Gravimetric	Mettler Balance
PM Mass/size	Continuous	Air	Electrical Differential Mobility	Scanning Mobility Particle Sizer
PM Mass/size	Continuous	Air	Optical aerodynamic diameter, time-of-flight	Aerodynamic Particle Size Spectrometer
Ozone	Continuous	Air	UV Photometry	Thermo Electron Corp 49C
Nitrogen Oxides	Continuous	Air	Chemiluminescence	Monitor Labs 9841
Sulfur Dioxide	Continuous	Air	Pulse Fluorescence	Thermo Electron Corp 43C
Carbon Monoxide	Continuous	Air	Infrared Absorption	Thermo Electron Corp 48
Gaseous VOC C_1-C_{10}	Loop and Cryo	Air	Non-derivatized	GC/FID and GCMS
Semivolatile PM Organics	Filter Holder/ Denuder	Filter*/ XAD-4	Non-derivatized	GCMS
Gaseous Carbonyls, C_1-C_8	Filter Holder/ Denuder	Filter*/ XAD-4	Derivatized and Non-derivatized	GCMS/HPLC
Semivolatile PM Carbonyls	Filter Holder/ Denuder	Filter*/ XAD-4	Derivatized and Non-derivatized	GCMS/HPLC
Gaseous Organic Nitrates C_1-C_5	Gas Loop	Air	Non-derivatized	GC-ECD

- UNC (Vizuete, Sexton) to perform new chamber experiments
- ENVIRON (Yarwood, Whitten) to design experiments and develop new condensed mechanisms
- UT (Allen) to test new mechanisms against existing and new chamber experiments

Benefits

- Characterize NOx-sinks in toluene degradation
  - How strong?
  - Which compounds?
  - What products?
- Improve chemical mechanisms for toluene and aromatics
  - Near term benefit for Houston modeling
- Develop new ways of characterizing how organic compounds influence atmospheric reactivity
  - Increasingly important as NOx emissions are reduced and the atmosphere becomes more NOx-limited

End

Appendix: PM Chamber Measurement Methods

1 Collection Methods for Smog Chamber Instruments

Methods for Aerosol/PM mass concentration

Particulate mass samples to determine particle mass concentrations will be collected on 47-mm filters (Teflon Impregnated Glass fiber or Teflon), frequently at flows of 20 L/min. AALBORG mass flow controllers will be used. Calibration will be checked with a large spirometer. Mass will be measured with a Mettler Toledo MX5 microbalance. Although it has internal weights for calibration, it is checked with standard weights. Its repeatability is 0.9 micrograms.

Methods for gaseous and semivolatile organic compounds:

A Varian 3400 capillary gas chromatograph with flame ionization detector (GC-FID) with a cryogenic cooled sample loop, which allows for direct real-time sampling and analysis of gaseous and semivolatile organic compounds, is used with a Varian Saturn 2000 ion trap mass spectrometer to analyze air samples taken before, at the beginning, and during each exposure to help analyze for both known and unknown products created during the photochemical reactions.

Methods for gaseous and semivolatile carbonyls and semivolatile organics on particles

The organic composition of both the gas phase and particle phase will be analyzed from solvent extracted filter and mister or denuder samples. These analyses will require a combination of gas chromatography and mass spectrometry methods. Semivolatile organics on particles will be analyzed directly from extracted samples from filter samples. Multifunctional oxygenated products (variations of aldehydes and ketones for example) from oxidation of hydrocarbon precursor products will be analyzed using several derivatization methods for polar functionalities and analyzed using gas chromatograph/ion trap mass spectrometry (GC/ITMS) in chemical impact (CI) and EI modes. Products in both the gas and aerosol phases will be derivatized with O-(2,3,4,5,6-pentafluorobenzyl) hydroxyl-amine hydrochloride (PFBHA: Yu et al. (1997a,b); Liu et al. (1999a,b)) for carbonyls. Organic Nitrates and PAN Volatile alkyl nitrates and peroxyacetyl nitrate (PAN) will be measured by gas chromatography with electron capture detector (ECD).

Formaldehyde is measured continuously, using the automated Dasgupta-diffusion-tube sampler to obtain aqueous formaldehyde, which is then mixed with buffered 2,4-pentanedione and measured with fluorescence (Dasgupta et al., 1988) .