Atmospheric Model Evaluation that leads to a better understanding of the factors that control ozone concentrations in the lower troposphere

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**Approach:**
Field experiments that emphasize processes in order to evaluate components of the Modeling System:

- Emissions of Precursors
- Chemical Production and Loss
- Transport and Dispersion of Precursors and Ozone
- Loss by Surface Deposition

**Example:**
Rapid ozone formation in Houston
Ozone Formation in the Oxidation of Hydrocarbons in the Presence of Nitrogen Oxides

**Ozone Production Efficiency**: OH reacts with CO, VOCs <-> OH reacts with NO2

**Secondary Products** like CH2O and PAN reflect on hydrocarbon chemistry
Houston regularly violates the 120 ppbv 1hour ambient ozone standard. Peak concentrations are over 200 ppbv. Regulatory photochemical transport models can not reproduce the peak concentrations. ==> Development of a reliable emission control strategy is difficult.

Maximum 1hr O3 of TNRCC network and O3 maxima during Electra flights During Texas Air Quality Study 2000.
What does set Houston apart from other urban areas?

Ambient reactive hydrocarbon concentrations over Houston are much larger than expected for typical automotive urban emissions.

Airborne hydrocarbon measurements over Houston and other urban air sheds.
Rapid and efficient formation of ozone in plumes from petrochemical industries
Co-located anthropogenic NO\textsubscript{x} and alkene emissions

Aircraft data from the 2000 Texas Air Quality Study, TexAQS
28 August 2000
NCAR Electra TEXAQS 2000 Flight
color coded according to Ozone for altitude below 1000 m
Model NO\textsubscript{x} emissions agree with 1999 TNRCC inventory

TNRCC inventory underpredicts Alkene/NO\textsubscript{x} molar ratios by factors of 50 to 200

Sweeny: \(\text{ENO}_x = 15 \text{ kmole/h}\)
Freeport: \(\text{ENO}_x = 30 \text{ kmole/h}\)

Area source of isoprene

Sweeny: \(\text{C}_2\text{H}_4/\text{NO}_x = 3.6, \text{ C}_3\text{H}_6/\text{NO}_x = 2.0\)
Freeport: \(\text{C}_2\text{H}_4/\text{NO}_x = 1.5, \text{ C}_3\text{H}_6/\text{NO}_x = 0.5\)
Model with measured ethene, propene to NO\textsubscript{x} emission ratios reproduces measured CH\textsubscript{2}O and CH\textsubscript{3}CHO.

CH\textsubscript{2}O is formed in the oxidation of ethene and propene
CH\textsubscript{3}CHO is formed in the oxidation of propene.
Model with measured ethene, propene to NO$_x$ emission ratio reproduces rapid formation of Ozone and PAN.

Oxidation of propene in presence of NO$_x$ leads to formation of PAN

Approximation: PAN = (NOy - NOx - HNO3)
TexAQS 2000 measurements indicate that NOx, HNO3, and PAN are the major components of NOy. Measurements of PAN by GC every 3 min.
CH₂O is formed more rapidly than Ozone

CH₂O has a shorter lifetime than Ozone

No significant direct emissions of CH₂O or CH₃CHO seen in the measurements

ENOX = 30 kmole/h, EC2H4 = EC3H6 = ENOX
wsp = 4m/s, emit at 10 am
F(isoprene) = 5.2E15 molec m-2 s-1 at 30 C, noon
Chemical Transformation:

Highest Ozone and CH2O values are always associated with petrochemical plumes

Reactivity is due to petrochemical emissions of light alkenes

Questions in 2006:

What are the consequences of the change in the emissions from point sources since 2000?
Large differences in ozone yield observed

Transects equally oxidized -
(NOx/NOy) $\sim 0.20$
Electra 08/28/00 flight data

- Houston urban yield similar to other cities studied
- Power plant yield similar to other low-VOC plumes
- Coalesced plume from Ship Channel petrochemical industry emissions similar to isolated refineries
Aircraft and ground monitors measured high Ozone (>200 ppb) on 30 August, 2000.
Update of emission factors of olefin processing facilities according to measurements / model of isolated facilities.

**Photochemical transport model captures high, localized ozone concentrations in the plume from industrial complexes.**

Photochemical transport model: Georg Grell and Stuart McKeen
Measurements of secondary species can provide critical tests for photochemical model systems:

Results of Texas Air Quality Study 2000:
Measurements of photochemical products such as \( \text{CH}_2\text{O} \) and \( \text{CH}_3\text{CHO} \) were critical in establishing the important role that light alkenes, i.e. Ethene and Propene, play in the rapid and efficient formation of ozone in the Houston air shed.

Other examples:
Ambient measurements of Methylviyl ketone and Methacrolein, MPAN and PPN to PAN ratios reflect the role of biogenic isoprene emissions.

Alkylnitrate measurements can provide a photochemical signature of alkane chemistry.
Questions and Goals of 2006 Texas Air Quality Study II:

What are the consequences of reductions of NOx emissions from point sources since 2000?

What are the sources of the VOC emissions from petrochemical facilities? Are they intermittent or continuous?

Have the VOC emissions changed since 2000?

What are the requirements to meet the 8 hr ozone standard in near non-attainment areas of eastern Texas?
Regional Transport to NE Texas
What are the implications for the 8hr O3 standard

Example: 3 September, 2000
High regional CO and
Ozone concentrations higher than 80 ppbv.

Accumulation of CO emissions during transport in the PBL leads to high CO over NE Texas.