

# Critical Issues for Ozone Research in East Texas

Jay Olaguer

Air Quality Program Manager

Houston Advanced Research Center

# TERC Strategic Research Plan

- FY2008-2009 update to SRP finalized by SAC in November 2007 and approved by TERC Board on December 13, 2007.
- Final version of SRP incorporated comments from various stakeholders, including:
  - City of Houston
  - EPA Region 6
  - Former TCEQ Commissioner, Ralph Marquez
  - Texas Association of Business
  - Mothers for Clean Air

# SRP Framework Issues

- The ozone productivity of the Houston SIP model may be low due to insufficient **new radical sources**. This depresses simulated control strategy effectiveness.
- The emissions inventory in HGB may still undercount **VOC/HRVOC emissions**. (Must also not lose sight of NOx inventory issues.)
- New **modeling episodes** for HGB and DFW based on better data may respond differently to control strategies than previous SIP model episodes.
- Long-range **transport** may be more critical to ozone exceedances, especially if the federal ozone standard is lowered by EPA.

# Other Considerations

- Need to spend adequate resources on **continued analysis** of TexAQS II data. This includes:
  - Improving and disseminating **2006 emissions data**;
  - Improving **meteorological inputs** to TexAQS II analyses.
- Need **closer examination** of some important issues identified in recent analyses of TexAQS II data:
  - More finely targeted **measurements of key species** (e.g., HCHO, HONO, NO<sub>y</sub>, and olefins) and their sources;
  - Development of **heterogeneous chemical mechanisms** in air quality models based on lab and field studies.
- Continue to identify and evaluate possible new **control strategies**, and assess the effectiveness of old ones.

# New Radical Sources: Formaldehyde (HCHO)

- Friedfeld et al. (2002) deduced from correlations of HCHO with CO and O<sub>3</sub> that **~37% of Houston HCHO is primary.**
- During TexAQS I (2000):
  - Ground-based instrument at HRM-3 detected 0.15 - **47 ppb** HCHO, with mean of 4.5 ppb (Dasgupta et al., 2005).
  - Midnight HCHO peak of 15 ppb on 9/18/00 with **NO<sub>x</sub> spike and O<sub>3</sub> titrated down to zero.**
  - Airborne TDLAS saw HCHO routinely **10-20 ppb above background** when O<sub>3</sub> > 120 ppb, and sometimes over 30 ppb (Wert et al., 2003).
- Vizuete et al. (2006) assumed 1% of flare mass is HCHO in Houston SIP model and found **peak O<sub>3</sub> enhanced by up to 30 ppb.**
- More evidence to be presented from Baylor aircraft and TRAMP experiments during TexAQS II.

# Possible Undercounted Sources of Formaldehyde

- Flares in Houston Ship Channel Facilities
  - Super-stoichiometric conditions in SNL burner yielded similar concentrations of HCHO, ethene and propene in refinery fuel flue gas (Seebold et al. , 2004) .
  - CFD model studies indicate flare destruction efficiency may be significantly reduced (below assumed 99%) by over-steaming and cross-winds > 1 m/s (Castineira and Edgar, 2006ab).
- Other Industrial Processes
  - Refinery emissions (catalytic cracking, coking, gas combustion) of HCHO may be undercounted by millions of lbs per year (EIP, 2007) .
  - Fugitive emissions are largely unknown.
- Diesel Engines
  - Some studies indicate HCHO/CO ratios as high as 4%.
- Reactions between O<sub>3</sub> and Industrial Olefins
  - TexAQS II observations (e.g., SOF) indicate olefin and other VOC emissions may be underestimated by an order of magnitude or more.
  - Errors due to titration of O<sub>3</sub> by combustion NO<sub>x</sub> sources falsely co-located with non-combustion olefin sources, or artificial dilution by vertical mixing.

# New Radical Sources: Nitrous Acid (HONO)

- Primary HONO from mobile sources, with ratios of  $\text{HONO}/\text{NO}_x = 0.3\%$  to  $0.8\%$  compared to ambient ratios of up to  $4\%$ .
- Possible missing sources of HONO in SIP models:
  - Heterogeneous  $\text{NO}_2$  to HONO conversion on:
    - Urban canopy (surface source)
    - Particulates (volume source)
  - Photolysis of gas-phase ortho-nitrophenols (volume source).
- Lei et al. (2004) assumed  $\text{NO}_2$  to HONO conversion on soot in a 3-D model for 2003 Houston episode and found changes in daytime ozone of up to 12 ppb.

# New Radical Sources: Focused Field Study

- Study of Houston Atmospheric Radical Precursors (SHARP)
  - Overall study to focus on the sources of the key radical precursors HCHO and HONO, including possibly undercounted industrial olefins.
  - Distinguish between primary and secondary sources.
  - Not intended to duplicate TRAMP.
  - May involve surface, tower, and aircraft measurements.
  - Probable date: Apr 2009 with some preliminary work in Oct 2008.
  - Sub-experiments: SOOT and FLAIR.
- Surface-induced Oxidation of Organics in the Troposphere (SOOT)
  - Laboratory and field measurements to quantify particulate influences on HONO and reactive nitrogen (NO<sub>y</sub>) through heterogeneous reactions.
- Formaldehyde and olefins from Large Industrial Releases (FLAIR)
  - DOAS, SOF, aircraft, and in-situ measurements of primary formaldehyde and olefins from the Houston Ship Channel.

# Emissions and Controls

- Sources of VOCs need better characterization: oil-water separators, cokers, etc.
- Top-down studies needed to reconcile 2006 TexAQS II data with emissions inventories.
- TARC has recommended two flare emissions and control studies for TERC funding.
- Effects of diesel engine PM control technology on NO<sub>x</sub> emissions are of national interest.

# New Episodes and Transport

- Need to incorporate new data from TexAQS II intensive, including use of meteorological and chemical data assimilation to improve models.
- A critical meteorological modeling issue is vertical mixing within the PBL.
- Data from the 2005 Southeast Texas Transport Study (SETTS) and the 2006 DFW Stationary Front experiment have yet to be analyzed.

# Relation to the SIP

- Projects continuing the analysis of TexAQS II data will most likely contribute to the HGB ozone SIP modeling, such as:
  - Examining PBL mixing impacts on inventory reconciliation and ozone chemistry (e.g., response to primary HCHO);
  - Testing simple schemes for urban canopy formation of HONO.
- SHARP projects will contribute to weight-of-evidence arguments.
  - Illuminating paths to attainment besides addressing a possible NO<sub>x</sub> shortfall;
  - Control of olefins vs. aldehydes;
  - Sensitivity studies involving radical precursors.
- All TERC projects will be useful for any Mid Course Review SIP between 2010 and 2019.

# Budget Constraints

- \$4.9 million available for air quality research in FY2008-2009.
- 25 proposals submitted to SAC worth a total of \$6.6 million.
- Distribution of proposals:
  - Radical Precursors (11): \$3.04 million
  - Emissions and Controls (9): \$2.34 million
  - Modeling of New Episodes (3): \$1.05 million
  - Transport (2): \$0.20 million