Chemical Processing of a Land-Lake Breeze Effect: Study of Non-methane Hydrocarbons in Chicago

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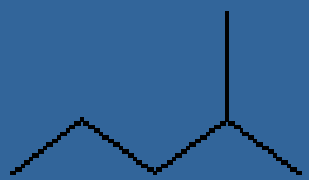
Outline

- Non-methane hydrocarbons (NMHCs)
  - Define
  - Role in air pollution
- Area of Study: Chicago
  - Land-Lake breeze
  - Hypothesis
- NMHC air samples
  - Collection methods
  - Analysis
- Preliminary Results
  - Conclusions
- Future Work
- Acknowledgements

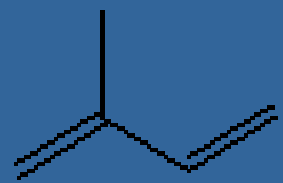
NMHCs

- Non-methane hydrocarbons
- C_2-C_{12} chains
- Single, double, and triple bonds
- Aromatics
- Examples:

2-methylpentane

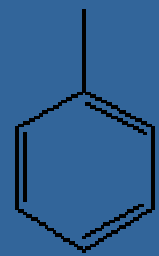


isoprene



propane

toluene



NMHCs: Importance in Ambient Air Relating to NO_x and Ozone

- NO_2 is broken down to NO by radiation from the sun. One way ozone forms is from the collision of atomic oxygen and molecular oxygen, releasing energy to a third body, M. Ozone is consumed when NO is oxidized back into NO_2. This is a natural sink for O_3.

$$NO_2 + h\upsilon \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O_3 + NO \rightarrow NO_2 + O_2$$

- NMHCs are oxidized by hydroxy radicals (·OH) which form various peroxy radicals. These peroxy radicals oxidize NO to NO_2 without destroying ozone, i.e. O_3 accumulates. O_3 is a pollutant in the troposphere and a major factor in smog.

$$NMHC + \cdot OH \rightarrow RO_2 + HO_2$$
$$RO_2 + NO \rightarrow NO_2 + O_2 + \cdot OH$$
$$HO_2$$

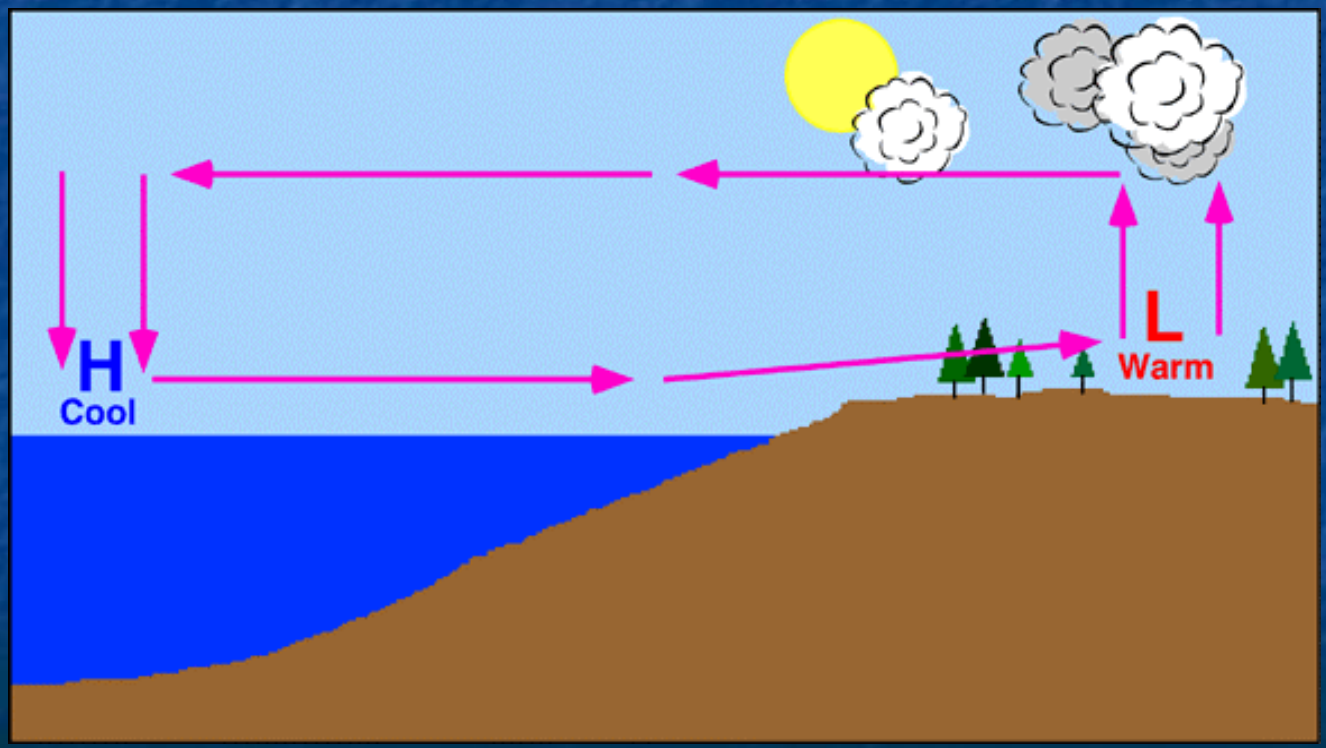
Example: ethene

$$C_2H_4 + \cdot OH + 2O_2 \rightarrow HOCH_2CH_2O_2\cdot$$
$$HOCH_2CH_2O_2\cdot + NO \rightarrow NO_2 + \cdot OH + O_2 + RO + OHRO$$

Area Site: Loyola University in Chicago

Land-Lake (Sea) Breeze

- Land heats more quickly than water
- Warm air mass moves out and cools over water
- Creates a thermal flow
- Daytime effect, peaks midday



Source: Michael J. Pidwirny, Ph.D., Dept of Geography, Okanagan University College, 2000.

http://www.geog.ouc.bc.ca/physgeog/contents/7o.html

Hypothesis

The edge of a land-lake breeze returning to land creates an acute, high concentration of chemically processed pollutants.

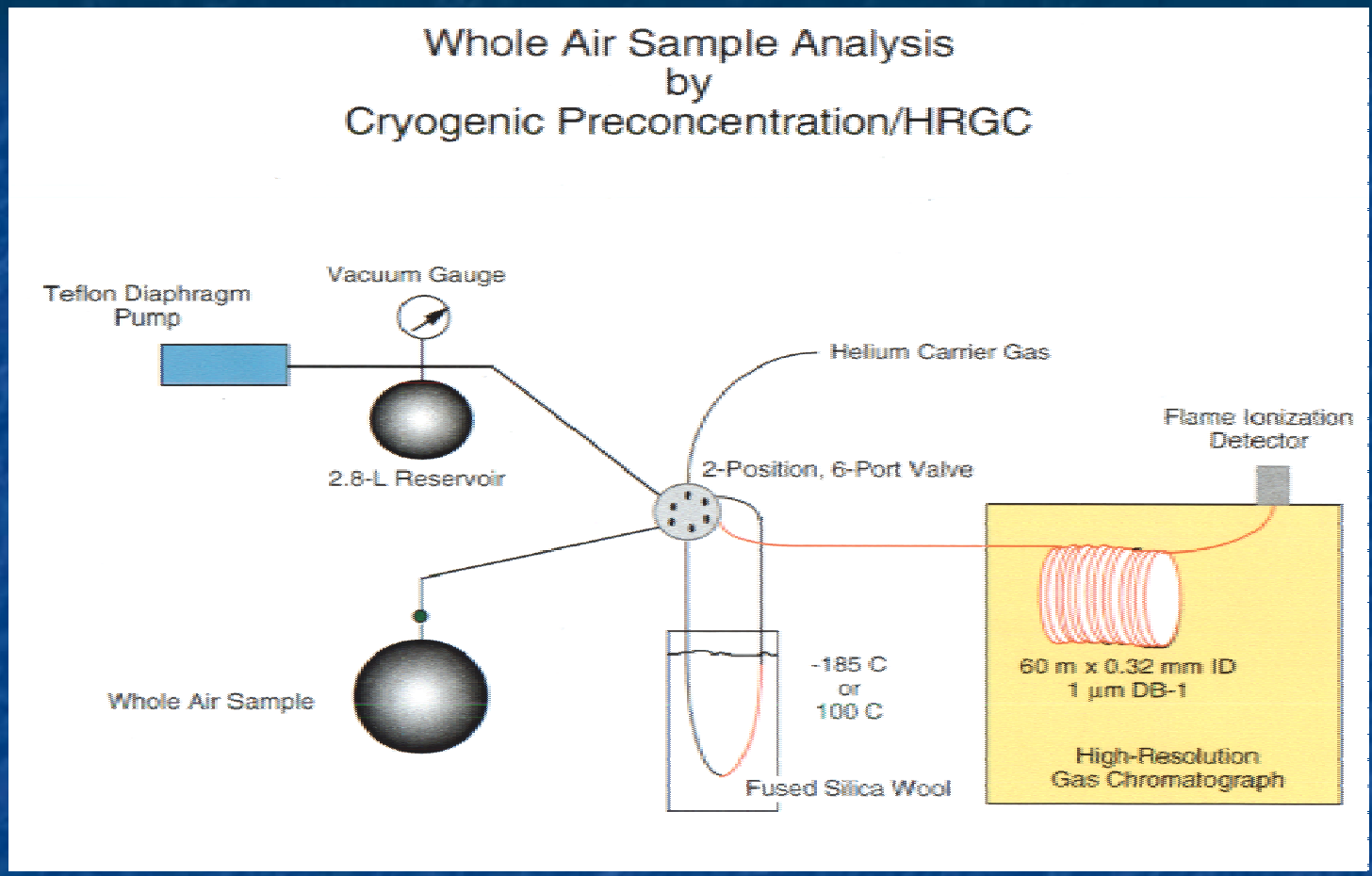
NMHC Air Samples

- Collection Site
  - Loyola University Chicago Air Monitoring Station (LUCAS)
  - Elevation: 60 m
  - 21 sampling days in 2002; July 16-August 16
  - 11 sampling days in 2003; July 15-29

NMHC Measurements

- Collection:
  - automated 10 canister sampler
- Frequency:
  - 5 minute samples collected every hour from 0700 to 1000 LT
  - 12 minute samples collected continuously from 1100 to 1300 LT

NMHC Measurements

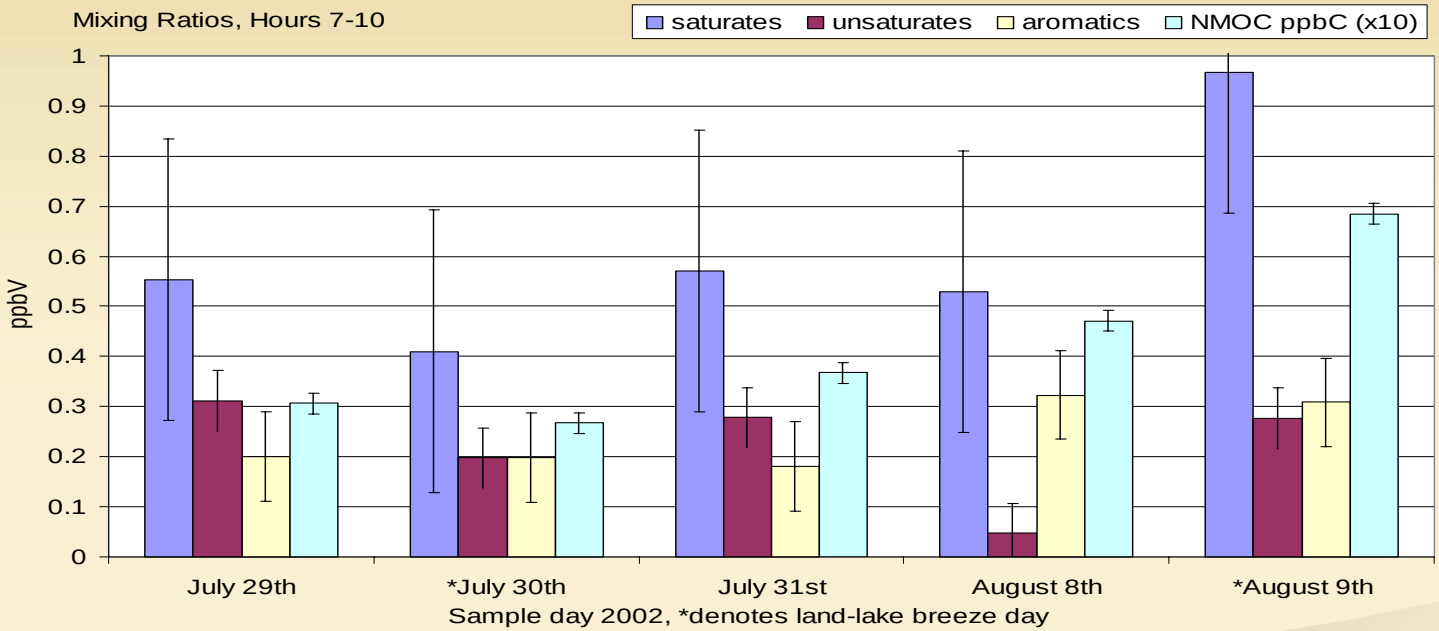


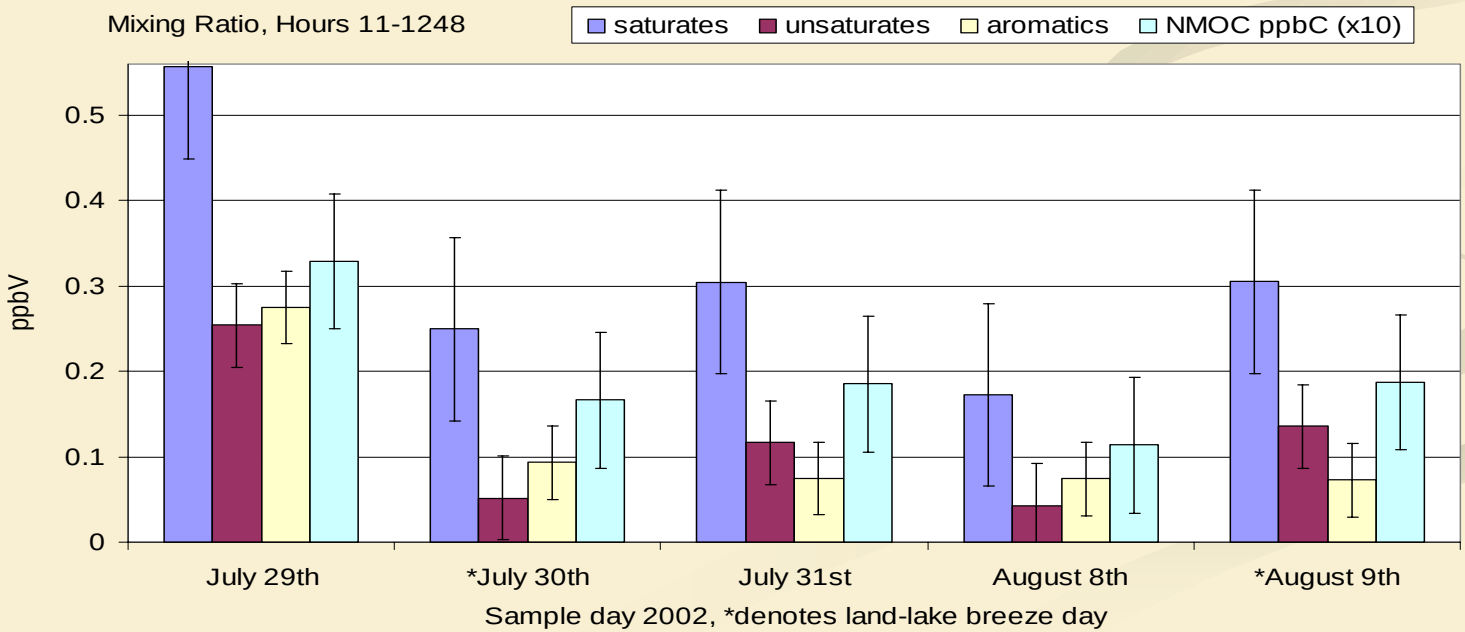
- Analysis:
  - At ANL by cryogenic pre-concentration/high-resolution gas chromatography with flame ionization detection

Preliminary Results

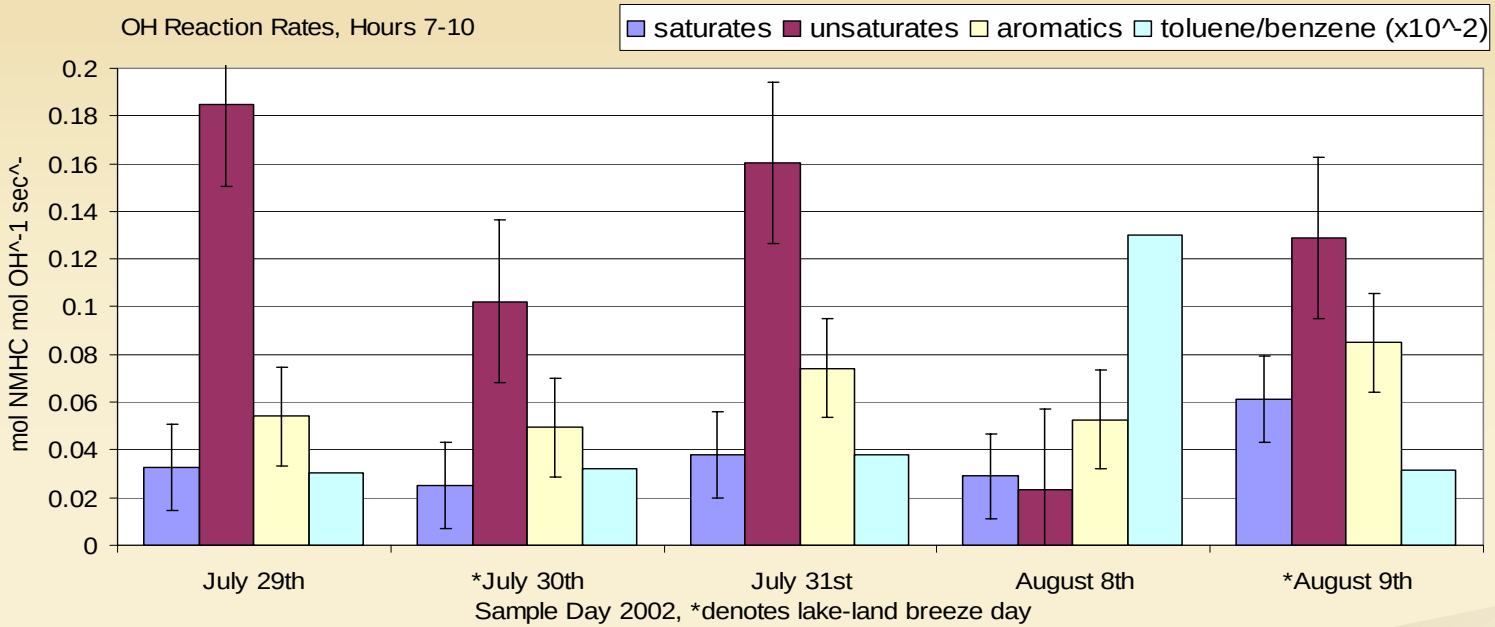
- 2 land-lake breeze days in summer 2002 during sampling period: July 30th and August 9th
- Analyzed chromatograms and calculated concentrations and reaction rates for 5 days in 2002
  - July 29th, 30th, 31st, and August 8th and 9th; August 10th data not available

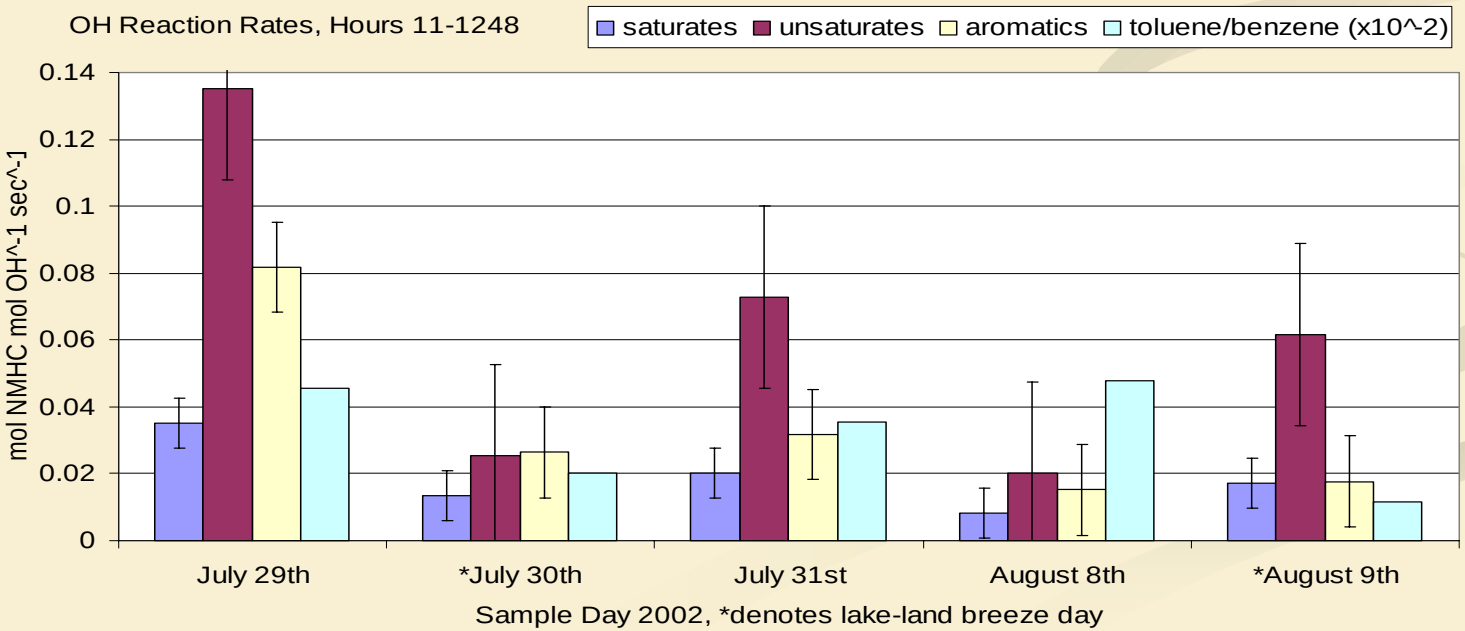
Mixing Ratios: Early Morning and Mid-Day





OH Reaction Rates: Early Morning and Mid-Day





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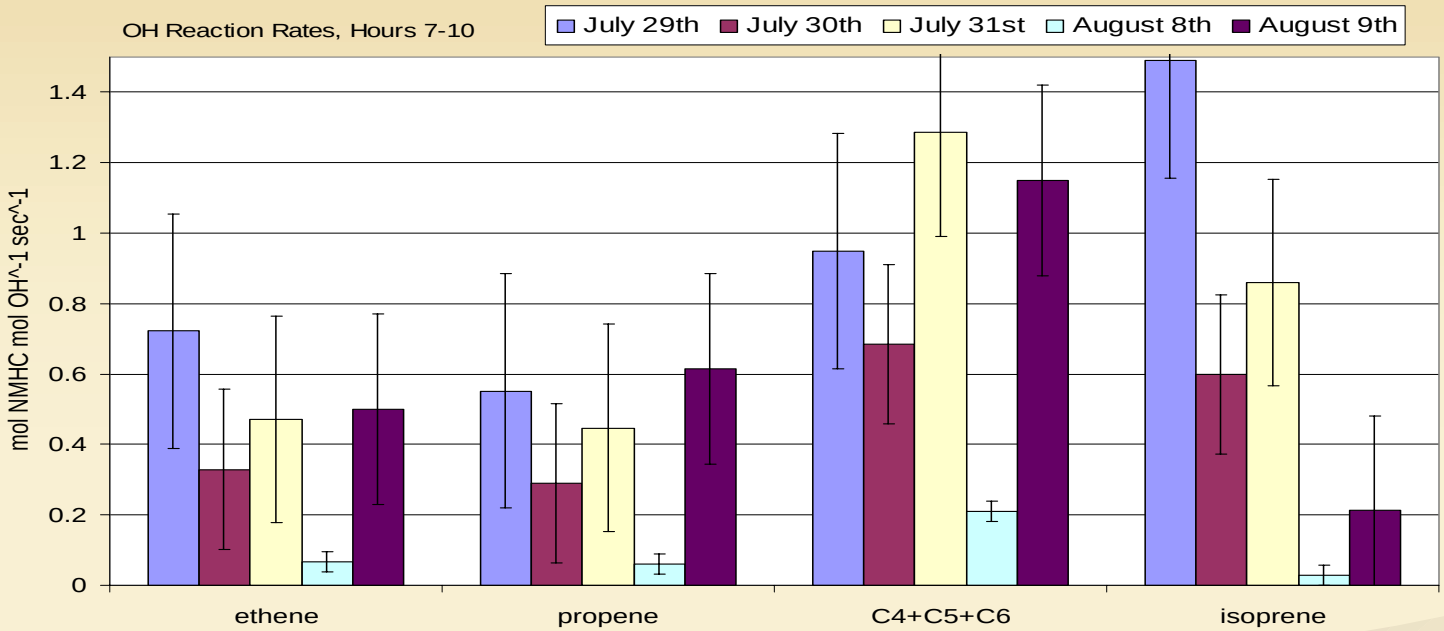
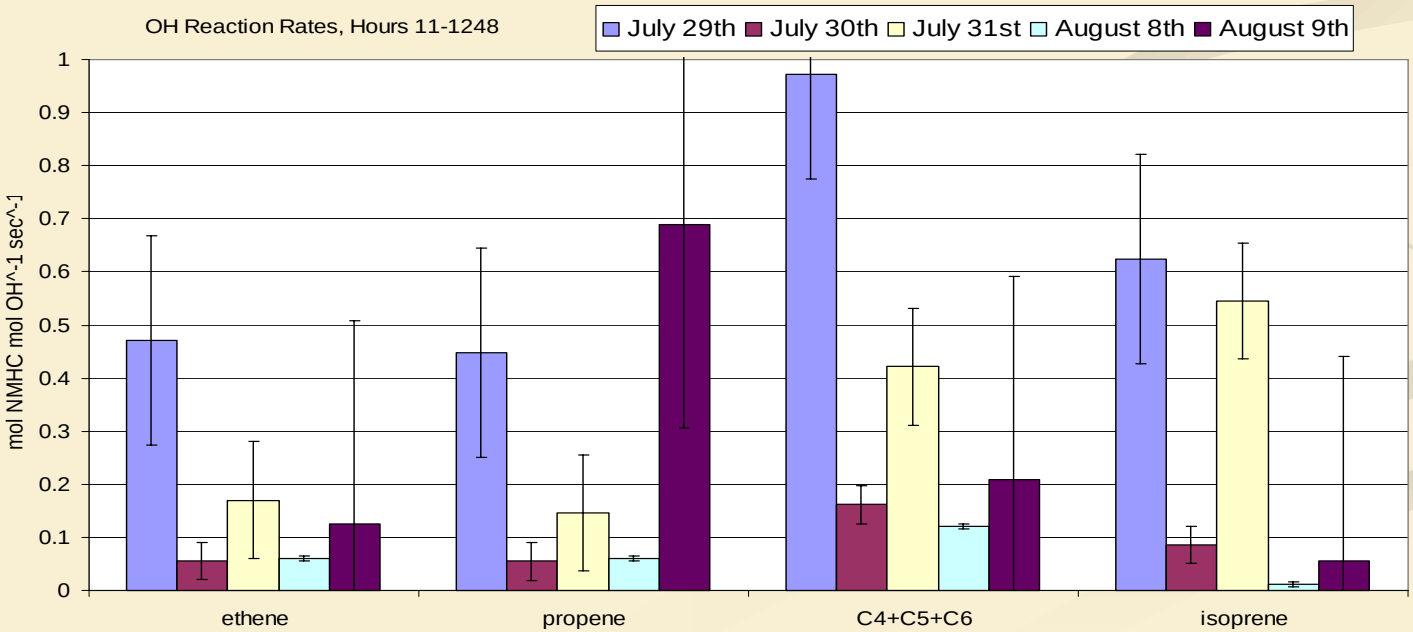
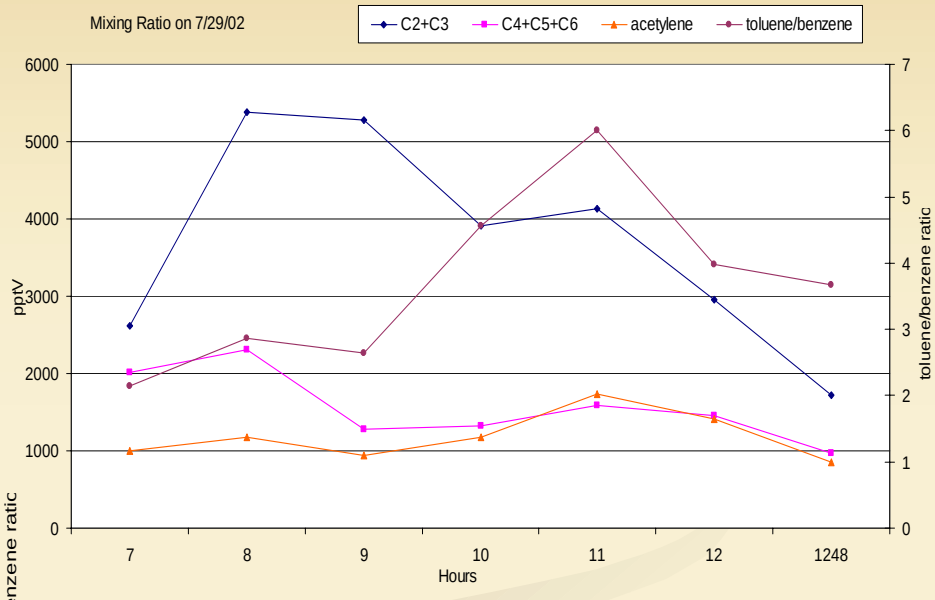


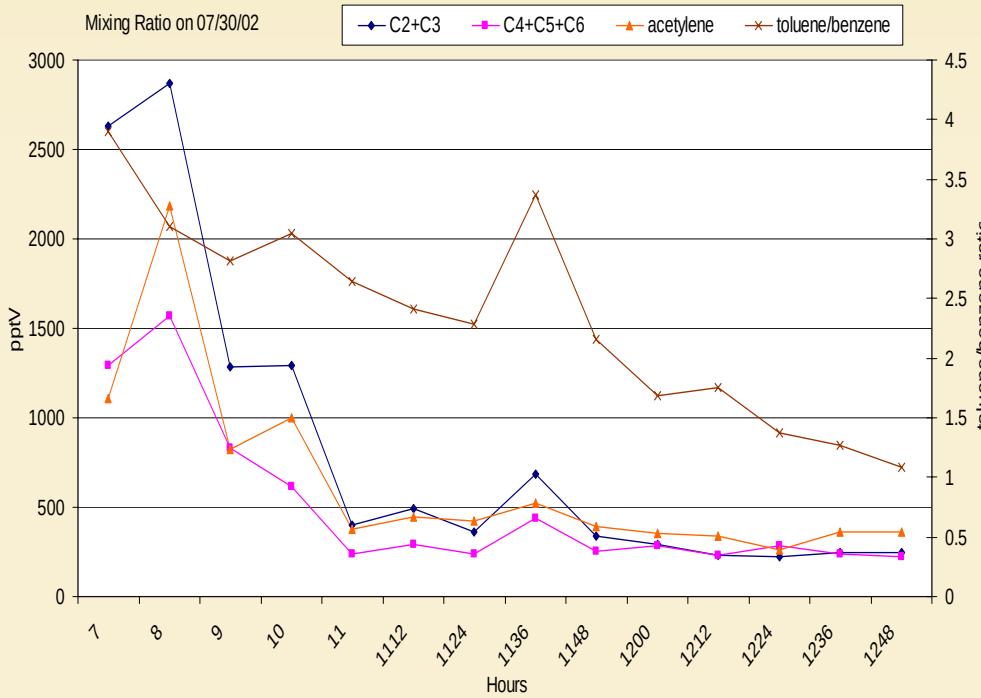


Mixing Ratio by the Hour

July 29th

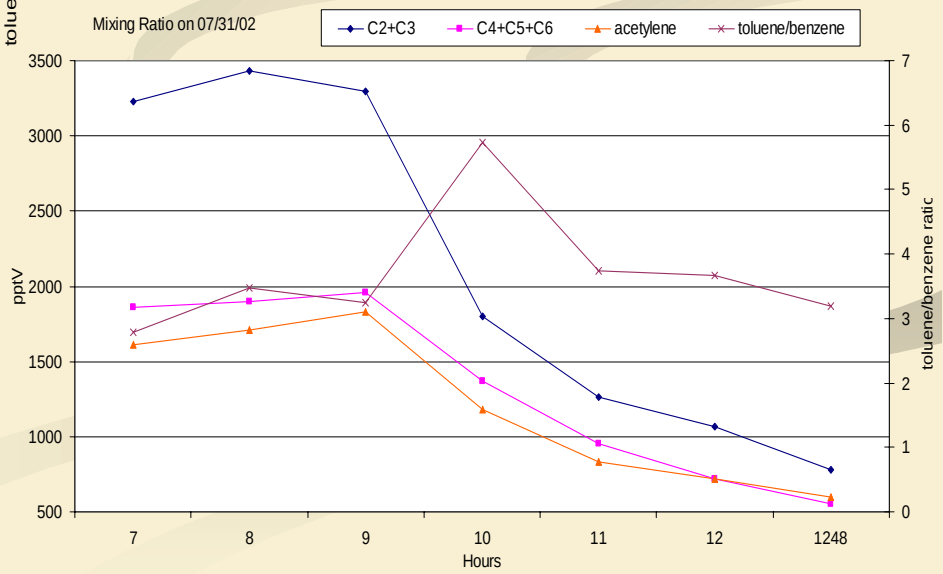


July 30th*

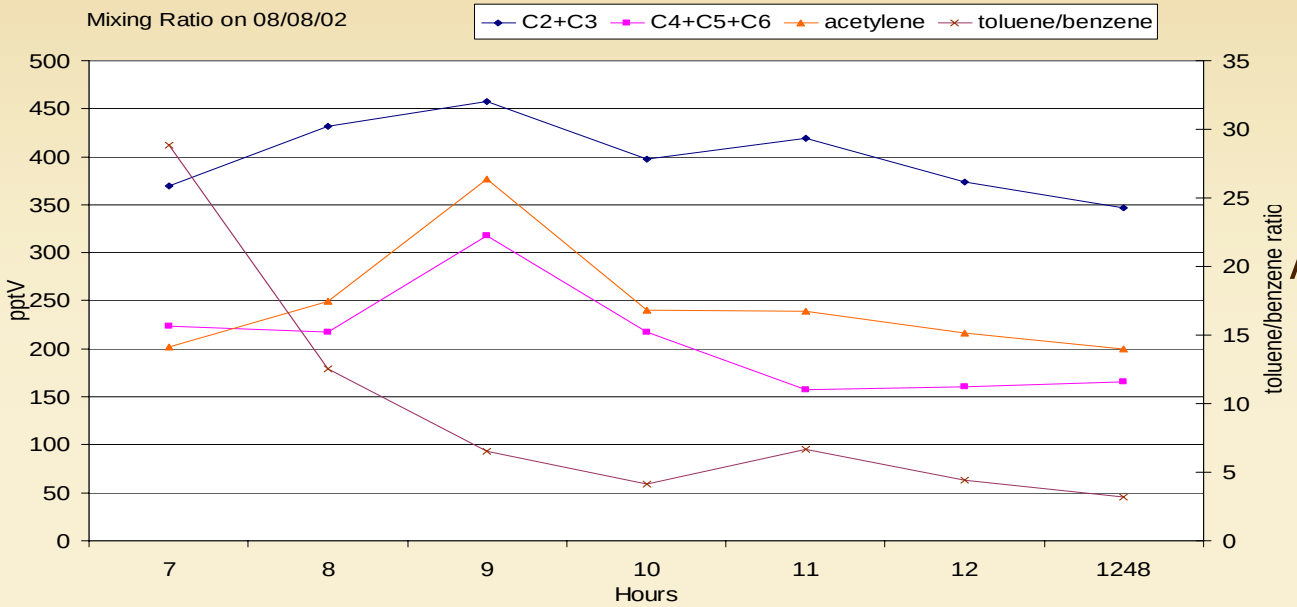


*Land-Lake Breeze Day

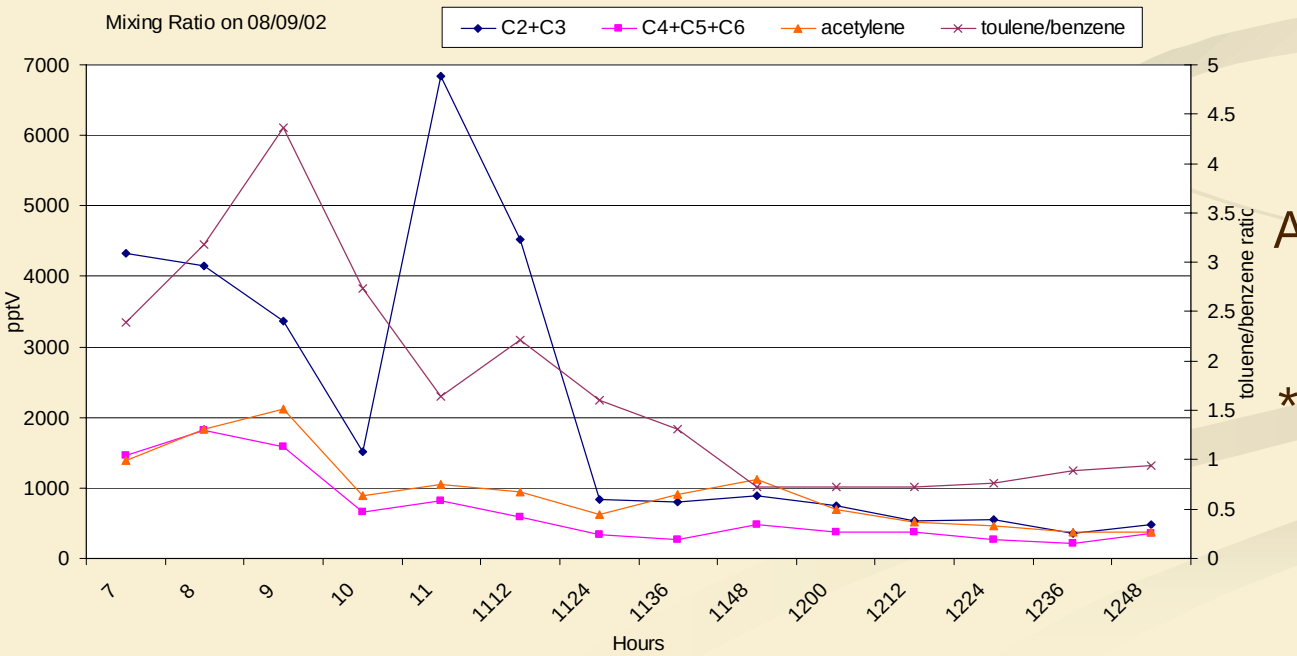
July 31st



Mixing Ratio by the Hour



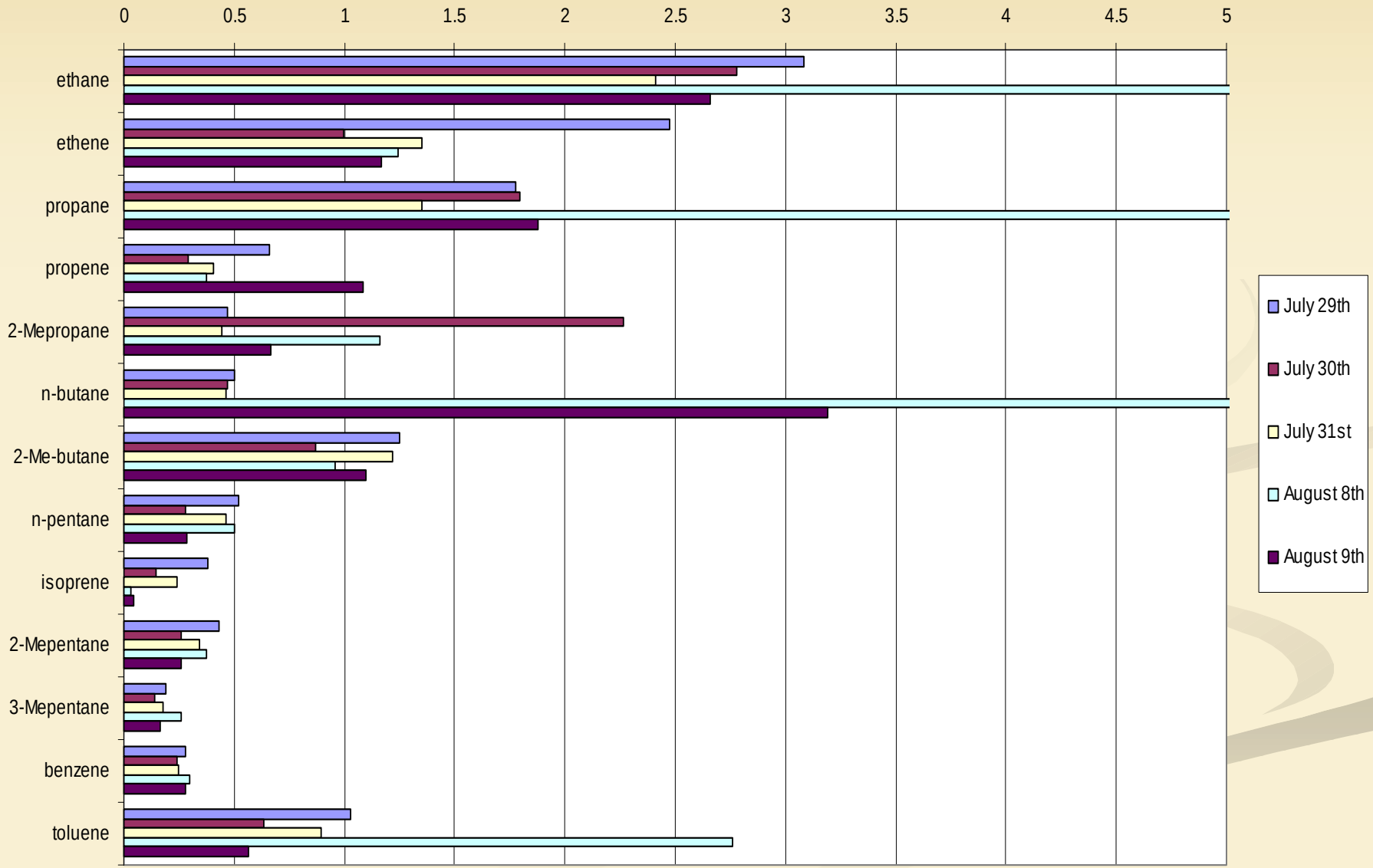
August 8th



August 9th*

*Land-Lake Breeze Day

Ratio to Acetylene



Future Work

- Analyze data from summer 2003 land-lake breeze days
- Continue to collect samples at LUCAS during the summers
- Collect and analyze air samples from east side of lake while still sampling at LUCAS

Acknowledgements

- Paul Doskey, GCEP mentor
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