Ozone Production in 5 Urban Areas: Why does Houston have the Highest Ozone Concentration in the U.S.?

Atmospheric Sciences Division, Brookhaven National Laboratory

Highest O_3 is in Houston

The Problem:

Health: Damages lung tissue & reduces function
Vegetation: Reduced crop & forest yields
Material: Damages rubber

The Regulations:

Clean Air Act: 1 hour average O_3<120 ppb
Emission Controls for NO_x and VOCs

The Reality:

1/3 of U.S. lives in non-attainment areas
Only a modest improvement over last 30 years

U.S. Monitoring Data, last 5 years

Rank	Ozone (ppb)	City	County
1	251	Deer Park	Harris
2	244	Crestline	San Bernadino
3	239	San Bernadino	San Bernadino
4	236	Calexico	Imperial
5	234	Houston	Harris
6	234	Crestline	San Bernadino
7	232	Houston	Harris
8	231	Houston	Harris
9	230	n/a	Harris
10	230	Houston	Harris

Highest O_3 is in Deer Park, a suburb of Houston
Data from U.S. EPA

Ozone Production Rate: $P(O_3)$

Calculations
Constrained Steady State Box Model

- **Inputs from G-1 Observations**

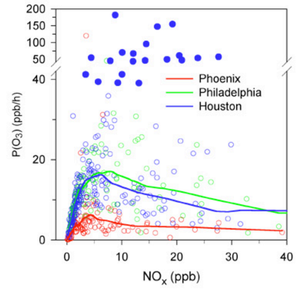
  O_3, NO, VOCs, CO, HCHO, H_2O_2, ROOH, SO_2, temperature, dew point, pressure, solar intensity

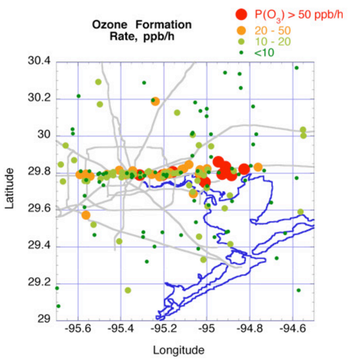
  # calculations ≈ # VOC samples

- **Outputs**

  Radical concentrations: OH, HO_2, RO_2's, NO_2
  Rates: Ozone production rate = $P(O_3)$
  VOC reactivity: Rate of reaction with OH

O_3 Production Rate in Houston >> Other Cities





Texas Air Quality Study: TexAQS2000

The Most Comprehensive Urban Air Quality Study To-Date

People:

Over 200 scientists from:
DOE Atmospheric Sciences Program (incl. chief scientist); NOAA Aeronomy and ETL; NCAR; Texas National Resources Conservation Commission; City of Houston; Universities

Surface Sites:

Augmented monitoring, 3 EPA aerosol supersites (U. Texas); TexAQS supersites at LaPorte Airport (NOAA) and 66th floor of Williams Tower (DOE)

Aircraft:

"Comprehensive:" DOE G-1 & NOAA/NCAR Electra
Source categorization: Baylor Twin Otter
O_3/Aerosol Lidar: NOAA/ETL DC-3

Laporte Airport

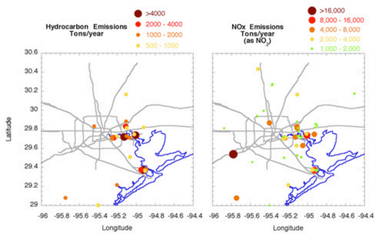
O_3, NO_y/NO_x, PAN, CO, radicals, DOAS for HONO NO_3 and aldehydes, Doppler Lidar for winds, aerosol composition & microphysics, O_3/Aerosol Lidar, Proton Transfer MS for HC, etc.

Williams Tower 62nd Floor

O_3, NO_y/NO, PAN, CO, SO_2, etc., Single particle MS, APS/MS for HNO_3, HONO, etc., aerosol microphysics, aerosol composition.

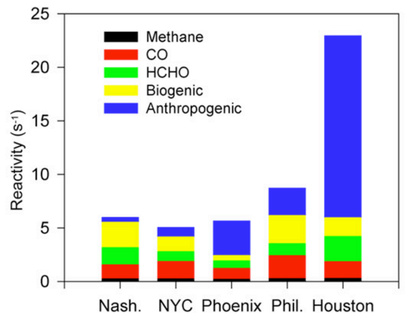
Volatile Organic Compounds: VOCs

Point Sources of O_3 Precursors



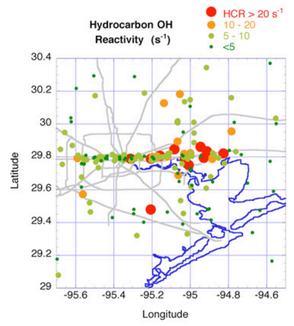
Major point sources of VOC and NOx along the Houston Ship Channel and to the south near Texas City.

VOC Reactivity in Houston >> Other Cities



High VOC reactivity causes high $P(O_3)$

- *Industries in and around Houston Ship Channel appear to be a major source of hydrocarbons for ozone formation*



Geographic distribution of hydrocarbon reactivity from all G-1 measurements.

5 City Study with G-1 Aircraft

DOE G-1

O_3, $NO_y/_x$, SO_2, CO, HCHO, H_2O_2, VOC's, continuous aerosol composition, aerosol number concentrations, size distributions (3-1000 nm).

A Library of Results on O_3 and Aerosols in 5 Cities

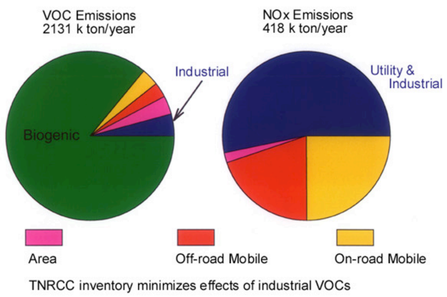
City	# Flights			$P(O_3)$		Max O_3
	Total	O_3>100	O_3>120	50th%	90th%	
Nashville, 95	17	7	3	6	15	146
NYC, 96	13	4	0	4	15	119
Phoenix. 98	24	1	0	4	8	101
Nashville, 99	4	2	1	-	-	133
Philadelphia, 99	20	6	1	11	22	147
Houston, 2000	18	12	9a	11	39	211

[a] 8 flights with O_3 > 150 ppb

"The locales in which we have chosen to conduct these experiments represent very different environments for ozone formation and transport. Conducting experiments in these different venues is a deliberate strategy on our part because we believe that these contrasts constitute important tests of our understanding of the composite meteorological/chemical processes that lead to O_3 formation." From the ACP proposal that supports this work at BNL.

Emissions

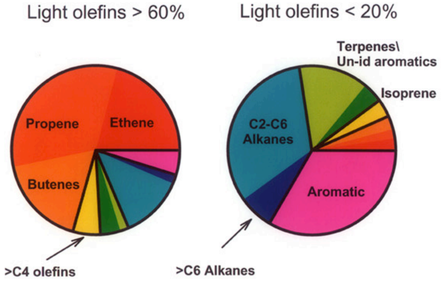
Houston/Galveston Non Attainment Area



TNRCC inventory minimizes effects of industrial VOCs

VOC Species

Two Types of High Reactivity G1 VOC Samples



Observed VOCs don't agree with emission inventory

Conclusions

Petrochemical Industry makes Houston Unique

- VOC reactivity much greater than other cities

  Biogenic compounds – secondary importance
  Highest values near industrial Ship Channel
  VOC compounds consistent with refining
  Emission inventory is underestimating high reactivity VOCs

- Ozone production rate much greater than other cities

  Very high $P(O_3)$ occurs in air with high VOCs

- Houston's high O_3 caused by industrial VOC emissions

Kleinman, Daum, Imre, Lee, Nunnermacker, Springston, Weinstein-Lloyd, and Rudolph, Geophys. Res Lett. 29, 10.1029 (2002) and C&EN News of the Week, June 10, 2002