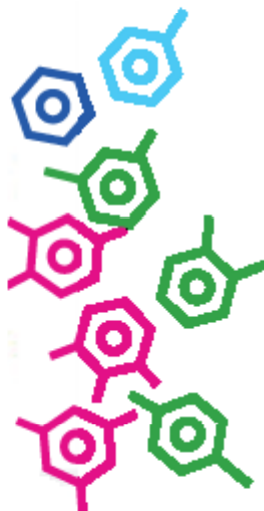




**BE**n**Z**En**E**  
**and other**  
**Toxics**  
**EX**posure  
**Study**



# The BEE-TEX Study

A Proposed Project  
Concept

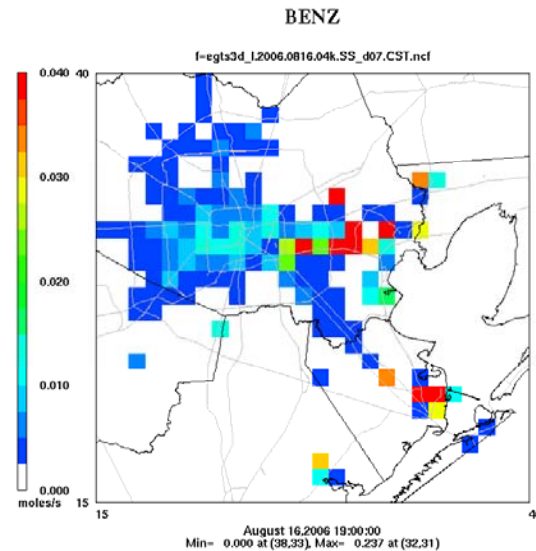
Jochen Stutz (UCLA),  
Scott Herndon (Aerodyne),  
Jay Olaguer (HARC)

# The Goal

- Facilitate the establishment of **cost-effective**, state-of-the-art **neighborhood-scale monitoring** networks in the Houston Ship Channel and other potential areas of **high toxic emissions** around the country.
- Use them in the improvement of **emission inventories**, the conduct of **epidemiological studies** for air toxics, and ultimately the **enforcement** of regulations.

# Basic Description

- The Benzene and other Toxics Exposure (BEE-TEX) Study is a two-part, 3<sup>1</sup>/<sub>2</sub>-year field study of **human exposure** to and **source attribution** of the air toxics: benzene, toluene, ethyl benzene and xylenes (BTEX).
- The study will be conducted in the Houston Ship Channel where **intense industrial sources** of BTEX are located in **close proximity to residential neighborhoods**.



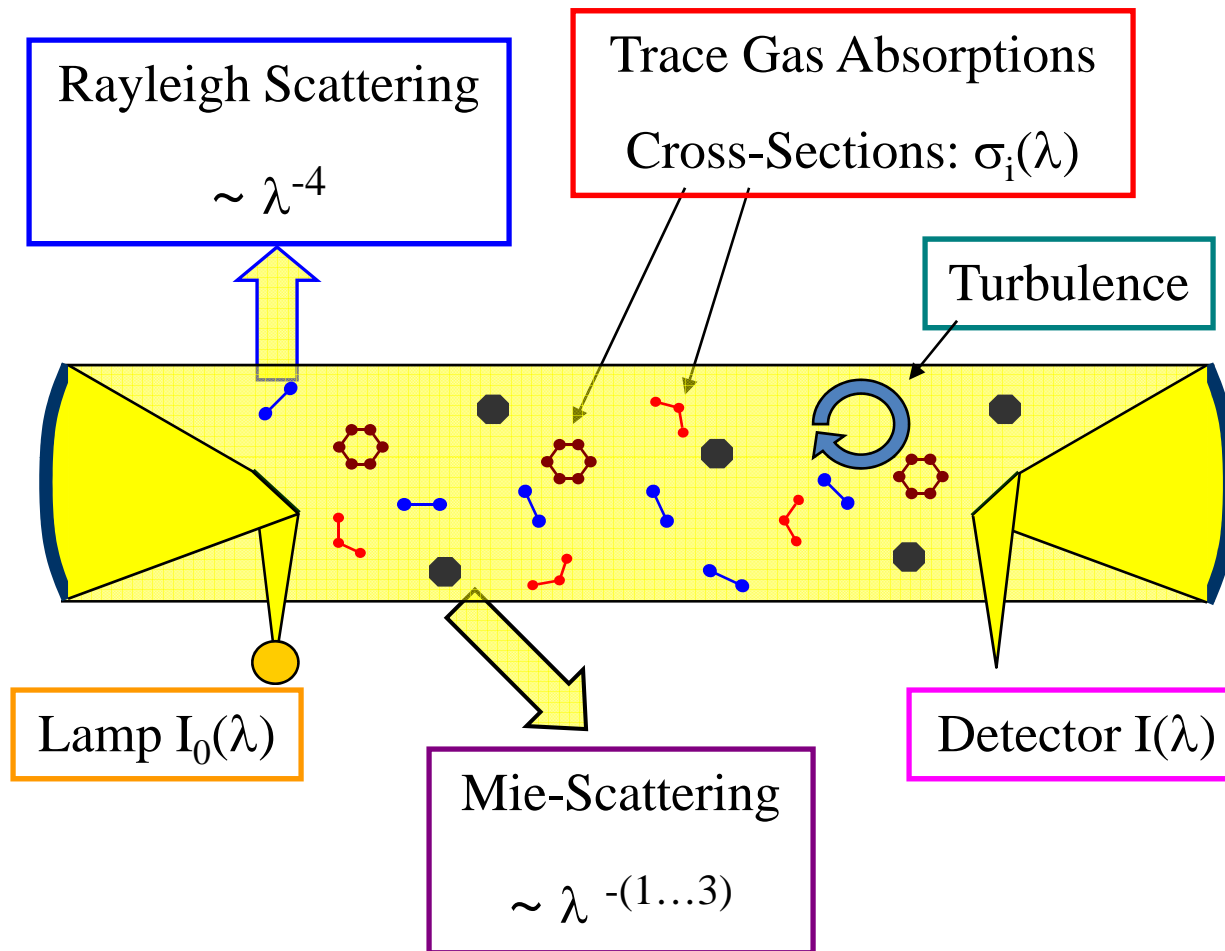
Benzene  
Emissions  
in UH  
CMAQ  
Model



# Study Design Elements

- Differential Optical Absorption Spectrometry (DOAS) remote sensing
- Computer-Aided Tomography (CAT)
- Ambient breathing zone measurements using both stationary and mobile techniques
- Meteorological data (CAMS, sondes, sodar, lidar, etc.)
- Inverse plume modeling for source attribution
- Personal exposure monitoring
- Dispersion, atmospheric transformation, and human exposure modeling

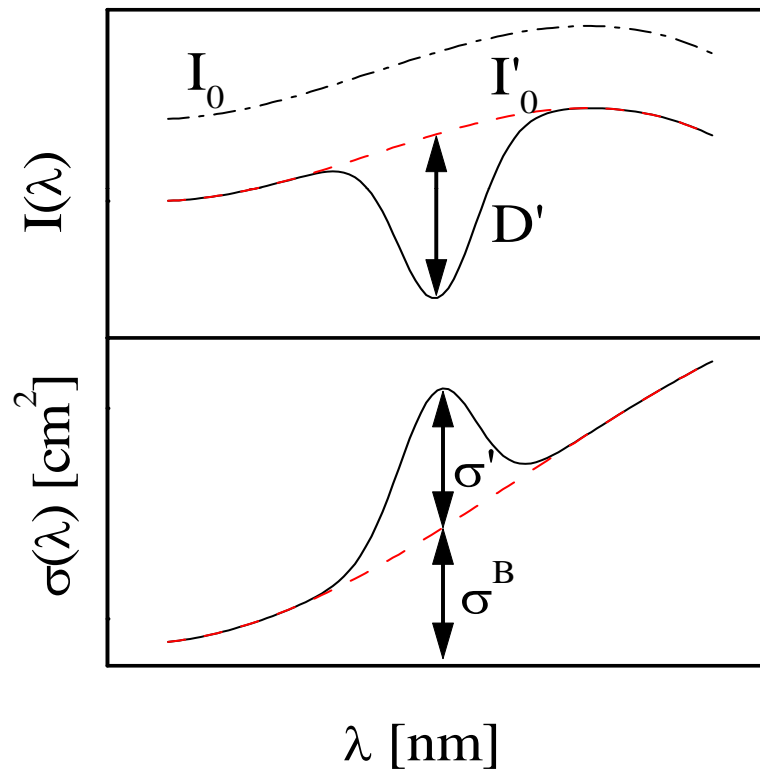
# Absorption Spectroscopy in the Atmosphere



## Lambert-Beer's Law

$$I(\lambda) = I_0(\lambda) \times \exp\left(\sum \sigma_i(\lambda) \times C_i \times L + \sigma_{\text{Ray}}(\lambda) + \sigma_{\text{Mie}}(\lambda)\right) \times T(\lambda)$$

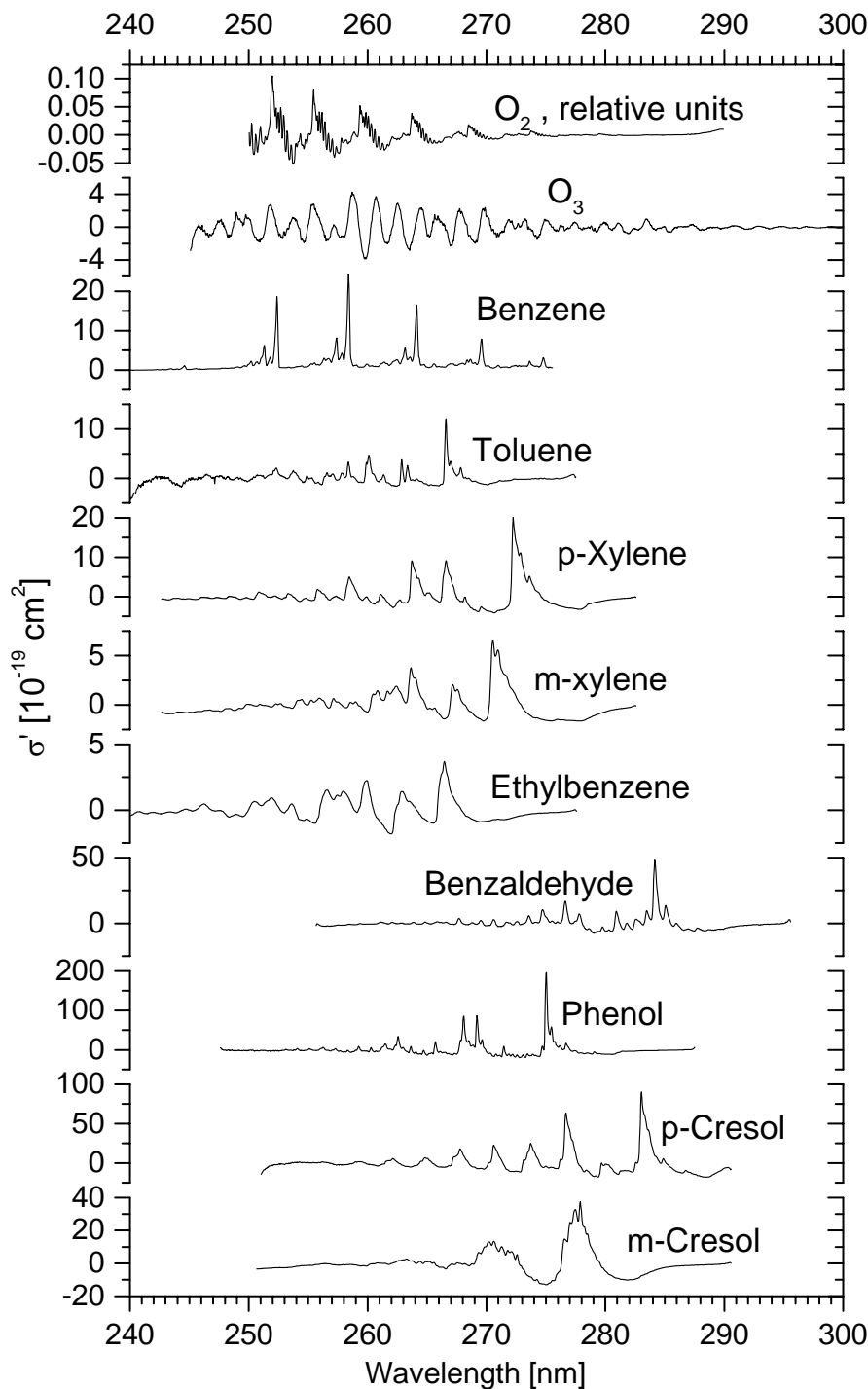
# Principle of Differential Optical Absorption Spectroscopy (DOAS)



Identification and quantification  
of trace gases by their unique  
narrow band absorption in the  
open atmosphere

$$D' = \ln \left( - \frac{I(\lambda)}{I'_0(\lambda)} \right)$$

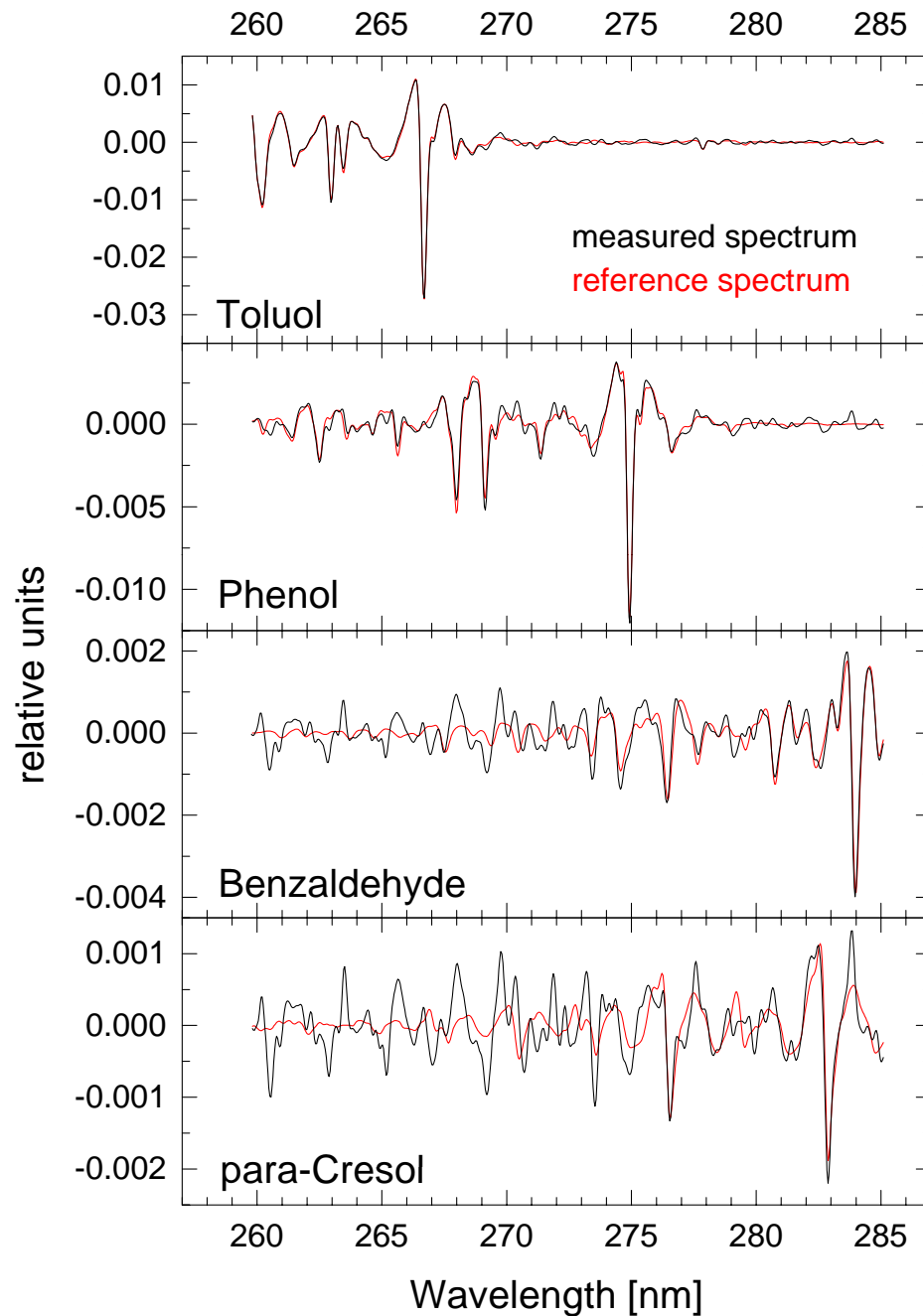
$$\sigma(\lambda) = \sigma^B(\lambda) + \sigma'(\lambda)$$



# Measuring BTEX with DOAS

- Aromatic hydrocarbons show structured absorption spectra between 250-290 nm.
- Absorption spectra identify each compound like a fingerprint.
- DOAS can measure total amount of substance over a 0.5 – 2km path using an artificial UV light source.

# DOAS Analysis



- Apply narrow-band band-pass.
- Least squares fitting of known absorption cross sections to identify and quantify trace gases.
- Calculation of uncertainty of each individual measurement.

Example in Traffic Tunnel  
Ackermann 2000

# Detection Limits of Some Aromatics

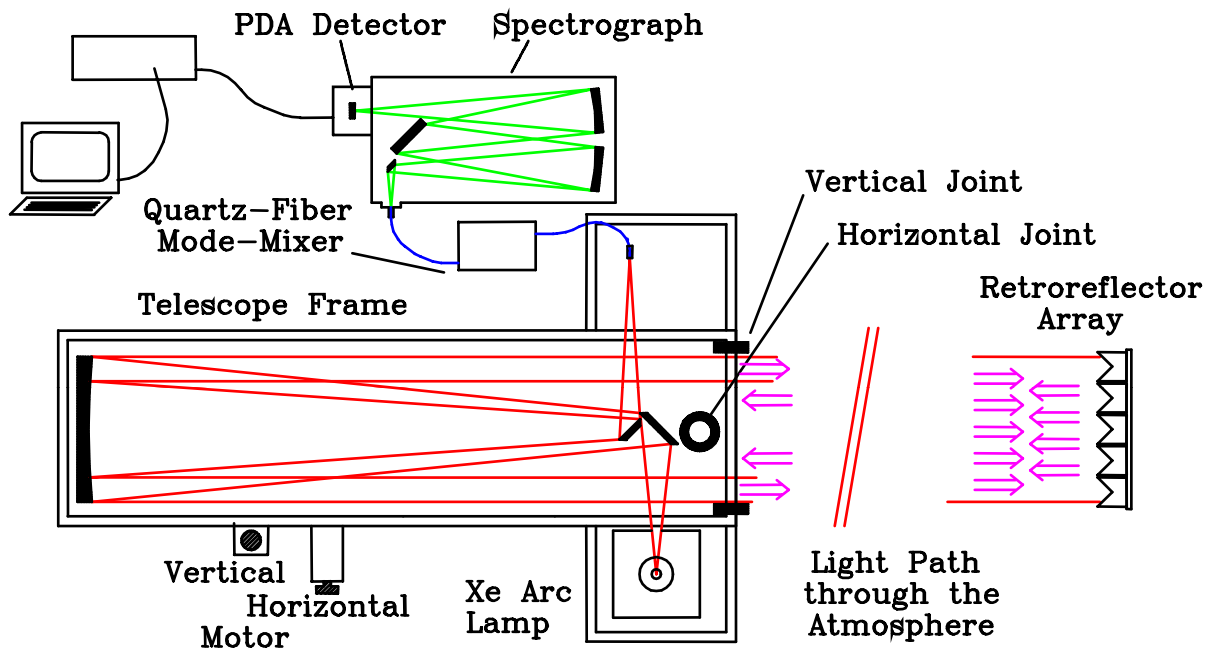
Species	Wavelength interval nm	Approximate differential absorption cross section $10^{-19}$ cm <sup>2</sup> /molec.	Detection limit on 500m light path and 0.0005 minimum detectable O.D. ppt
Benzene	250-270	21.9	180
Toluene	250-280	12.8	310
Xylene (o/m/p) <sup>b</sup>	250-280	2.1/6.6/20.3	2000/650/210
Phenol	260-290	198	20
Cresol (o/m/p)	250-280	20.1/31.8/87.2	200/135/50
Benzaldehyde	280-290	44	90

# Advantages of DOAS

- Absolute Method → a calibration is not necessary
- “Touchless” method → no sampling artifacts
- No trace gas interferences. Compounds are uniquely identified.
- Determination of uncertainties from absorption spectrum.
- Re-analysis of measurements is always possible, i.e. to double-check results or if new trace gases are identified.
- Simultaneous measurements of many aromatics
- Measure vertical/horizontal trace gas distributions  
→ CAT-DOAS

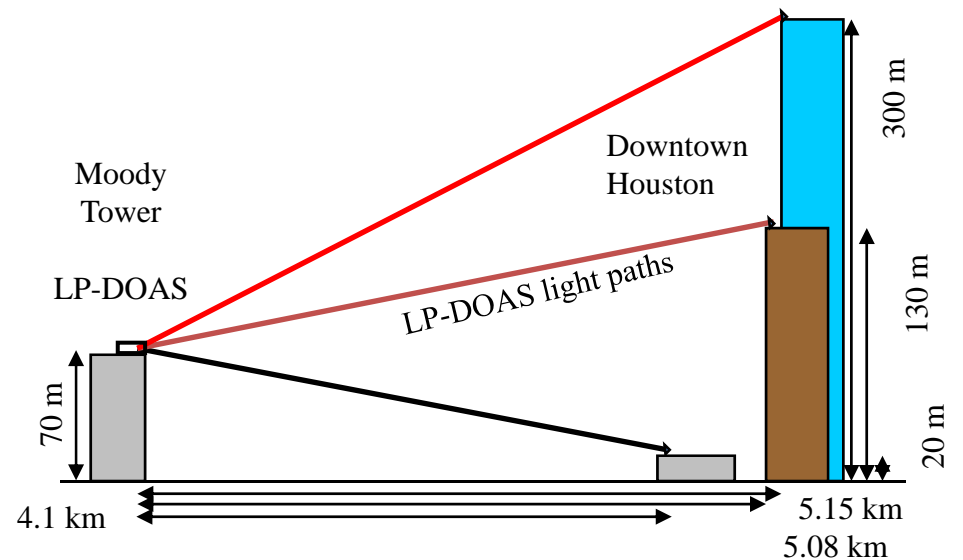
DOAS takes a “spectral photograph” of the atmospheric composition

# Long Path DOAS Instrument



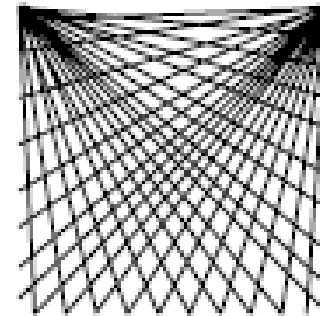
## Current Setup:

- Scanning in horizontal and vertical.
- Currently up to 3 retroreflectors.
- Automated and remotely controlled

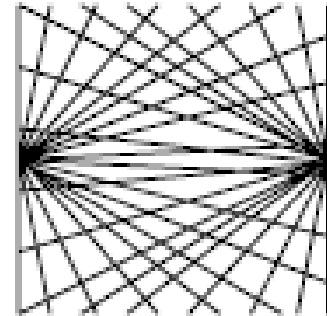


# Computer-Aided Tomography

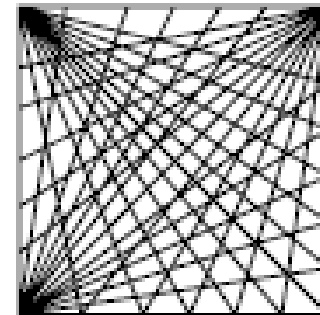
- Two to four DOAS instruments with multiple reflectors or light sources can cover an area of up to 2x2km.
- Crossing light paths allow the application of the CAT approach to derive concentration fields over an entire neighborhood.
- Different light-path arrangements are possible, depending on the sampling conditions.



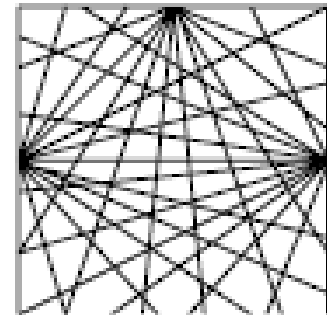
a) 2T90°



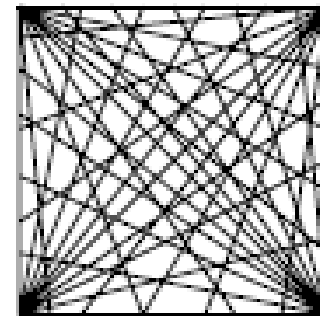
b) 2T180°



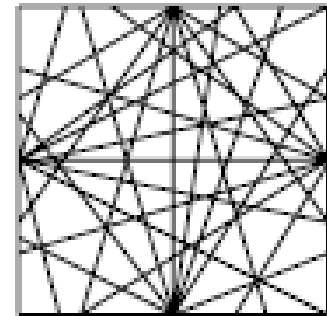
c) 3T90°



d) 3T180°



e) 4T90°



f) 4T180°

# Advantages of CAT-DOAS

- Remote sensing over long distances ( $> 1$  km) allow the observation of intense industrial sources far away from the fence line.
- Continuous day and night monitoring over long periods of time with little maintenance, if equipment is designed properly.
- Potentially more cost-effective for studies of human exposure and health impacts of BTEX on neighborhood scales than in-situ monitoring or short-range remote sensing.

# UCLA: Project Activities / Goals

- Development of a dedicated, highly automated, and stable LP-DOAS instrument for BTEX CAT-DOAS (+ adaptation of existing LP-DOAS).
- Testing of instrument and data analysis.
- Testing of CAT algorithms based on previous work in the literature and determination of best light-path configuration.
- Deployment of during the 2010 field intensive (initially with ~20 paths).
- Validation of method using Aerodyne measurements.

## Long-term goal:

Duplication of new LP-DOAS to allow measurements on more light paths and thus a higher spatial resolution.

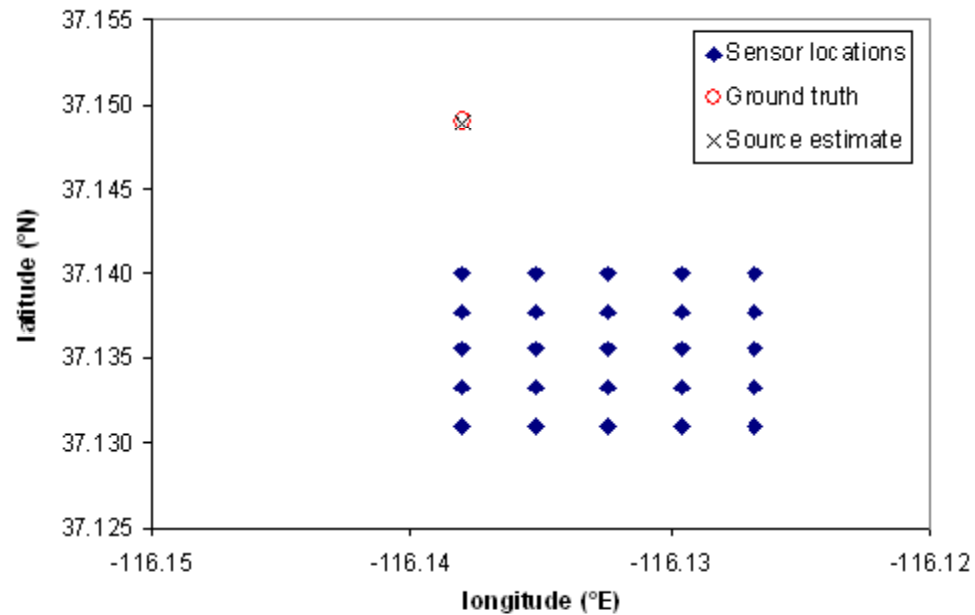
# Relation to Human Exposure

- Perform ancillary measurements in the breathing zone below CAT-DOAS elevation to derive transfer functions for use in human exposure modeling.
- Local TCEQ or HRM auto-GC measurements.
- Stationary GC-FID/PID BTEX analyzers for continuous monitoring (15 min cycle).
- Fast (1 s cycle) mobile PTR-MS measurements will allow ground level pollutant concentration maps in receptor neighborhoods.

# Source Attribution

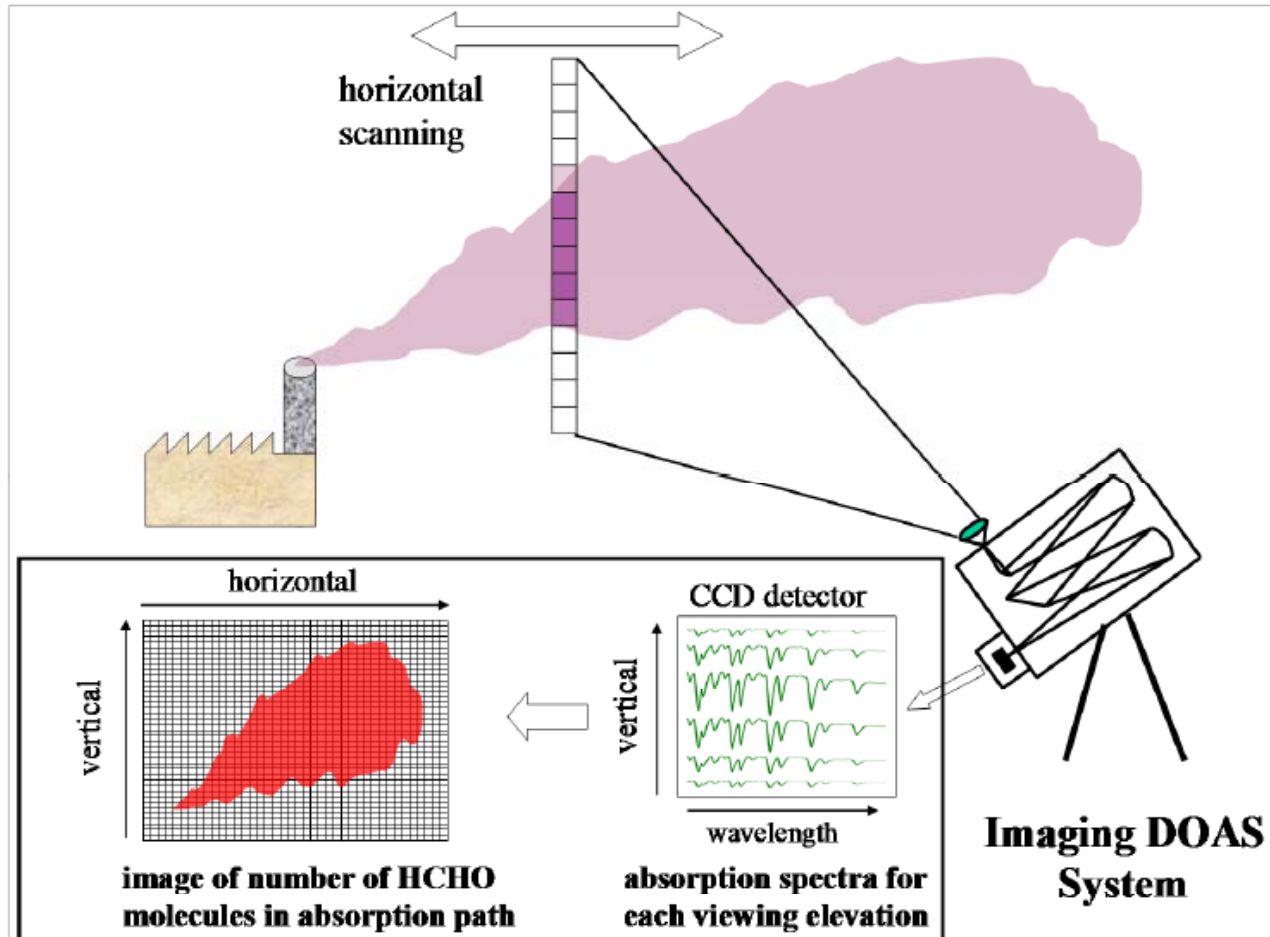
- Use an inverse plume model (SCIPUFF + adjoint method) to derive emission source strengths and locations from CAT-DOAS concentrations.
- Use an imaging DOAS (I-DOAS) to “see” combustion plumes by measuring HCHO.
- Use an IR Camera to “see” non-combustion plumes (e.g., large storage tank leaks).
- Use observed plume spread and meteorological data (CAMS, sondes, sodar, aerosol lidar) to constrain inverse model turbulent transport.

# Aerodyne Inverse Plume Model



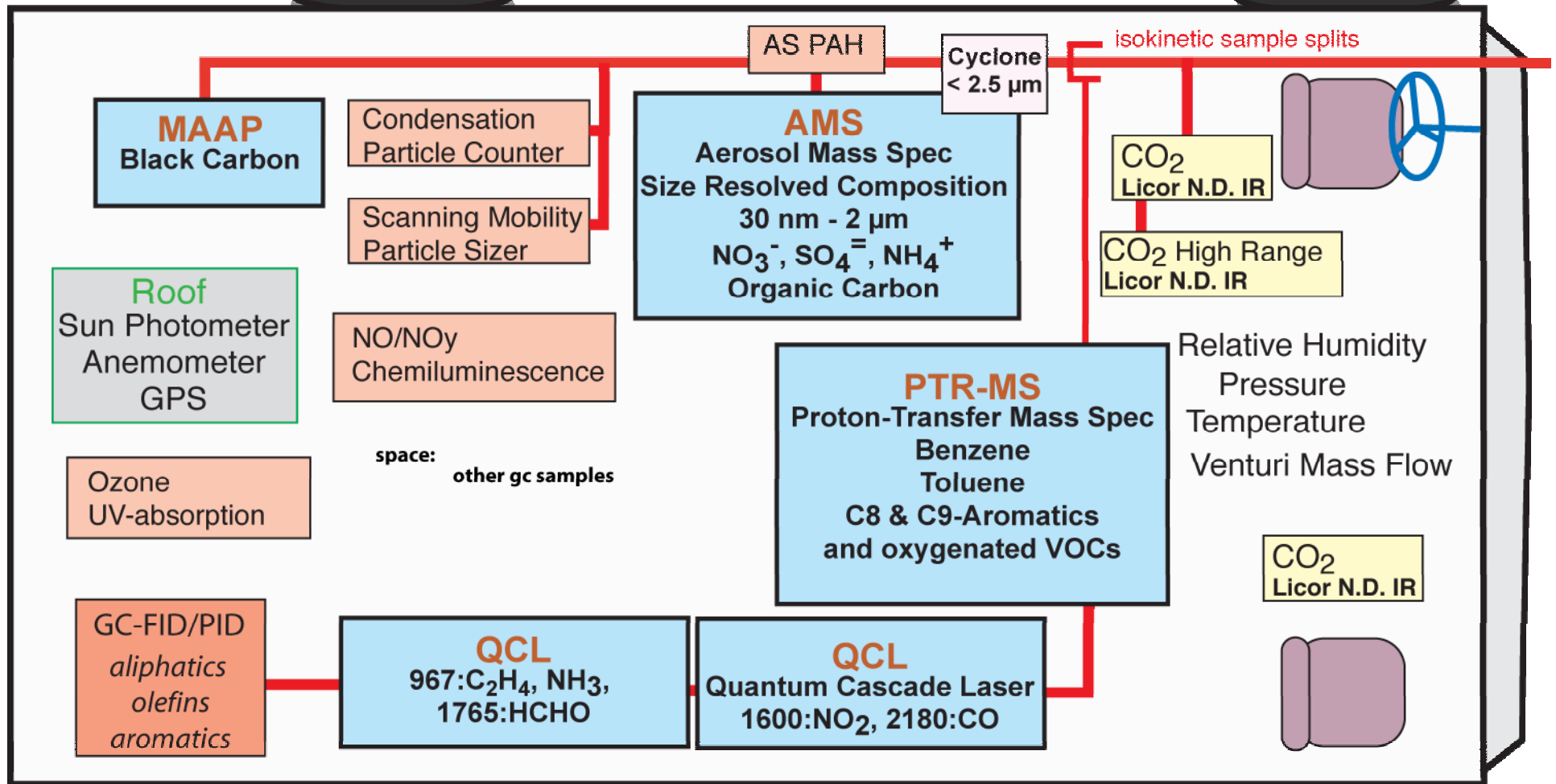
	Source Estimate		"Ground Truth"
	Ideal data	Noisy data	
Mass (kg)	52.9	53.6	54.0
Release Time (p.m.)	11:21	11:21	11:21
Release Duration (hrs)	0.15	0.15	0.15

# Imaging DOAS (I-DOAS)





# BEenzenE and other Toxics EXposure study



# BEETEX Phase I

## ARI Plume Inversion Work

- Extend current inverse modeling capabilities to handle line-of-sight data
  - Current capability requires spatially and temporally resolved concentration measurements
- Apply inverse modeling capabilities to
  - derive:
    - emission rates, durations, locations, as well as number of sources that are most likely responsible for observed concentration fields
  - given:
    - “Coarse” MET data from local CAMS stations
    - Line-of-sight concentration data from DOAS measurements

# Leverage expertise from...

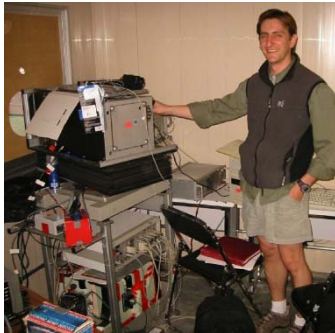
- **Daewon Byun**

- Prof. Atmospheric Sciences, Univ. of Houston
- Atmospheric Science, Air Pollution, Meteorology Air Quality Study
- Led development of CMAQ model (Community Multiscale Air Quality)

- **Adrian Sandu**

- Assoc Prof. Computer Science, Virginia Tech.
- Numerical Methods, High Performance Computing, Sensitivity Analysis, Inverse Modeling, Applications of Computational Science

# DOAS in Mexico City 2003 (MIT)



**DOAS-1**  
L= 860m  
H= 16m

- Benzene, Toluene, Styrene
- m-xylene, p-xylene, ethylbenzene
- Benzaldehyde, Phenol, pCresol
- Naphtalene
- HCHO, Glyoxal (DOAS-2)



CENICA

East

South

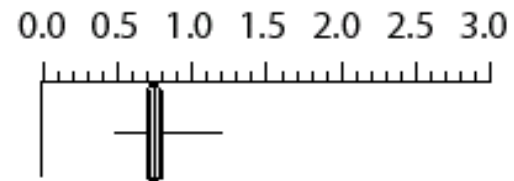
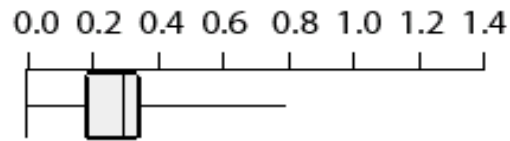
South-West

# DOAS and ARI Mobile Lab comparison of Toluene and Benzene emission ratios

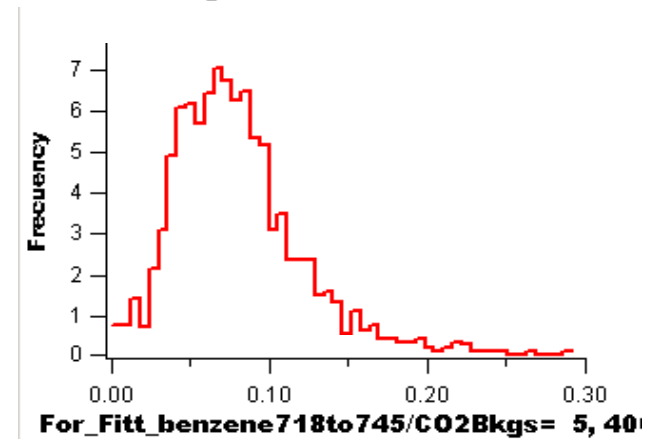
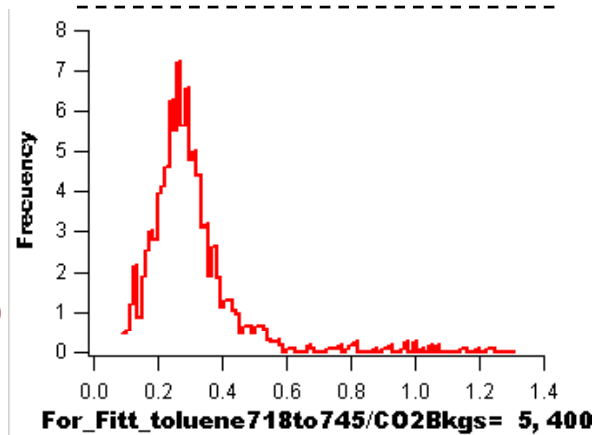
Toluene

Benzene

DOAS



ARI  
Mobile Lab



# Infrared Camera



*The color photo of this barge shows what the human eye sees. The black and white photo shows the Hawk detecting a hydrocarbon leak. Photo by Leak Surveys, Inc.*

# Personal Exposure Monitoring

- Adopt the successful elements of the Houston Exposure to Air Toxics (HEATS) study.
- Pay special attention to recruitment to enable sound statistical sampling of exposures.
- Pay special attention to the quality and calibration of potential instruments.
- Test novel techniques such as use of cultured human lung cells as exposure indicators.

# Air and Exposure Modeling

- Use a standard model such as APEX to simulate human exposure to BTEX in various microenvironments based on time-activity data from neighborhood participants.
- Compare simulated exposures from both observed and modeled concentrations.
- Use a combination of MM5/WRF, CMAQ and plume dispersion models to simulate chemical fate and transport.

# Potential Project Participants

- UCLA will build and operate CAT-DOAS.
- Aerodyne Research, Inc. will provide mobile lab and perform inverse plume modeling.
- HARC will provide stationary BTEX measurements and operate IR camera (non-TERC funding).
- UNC will perform cultured lung cell studies.
- Mickey Leland NUATRC will coordinate personal exposure monitoring aspects of study.
- Ted Johnson will apply human exposure model.
- UH will provide meteorological measurements and apply meteorological and air quality models.

# Possible Timing

- Pilot Study (6/2009 – 12/2010)
  - Select neighborhood site(s)
  - Build, test, and operate pilot CAT-DOAS network
  - Conduct ancillary measurements and derive transfer functions for human exposure model
  - Perform source attribution
- Intensive Field Study (1/2011 – 8/2012)
  - Recruit neighborhood participants
  - Conduct indoor, outdoor, and personal monitoring
  - Conduct air and human exposure modeling

# Estimated Costs and Potential Funding Sources

- Estimated Costs
  - Phase 1 (Pilot Study): \$1,000,000
  - Phase 2 (Intensive): \$3,000,000
- Potential Funding Sources
  - TERC CIAP (\$750,000)
  - Health Effects Institute (\$250,000)
  - USEPA, TCEQ, etc.