BTEX Observations by UV Absorption Spectroscopy: From Research to Monitoring

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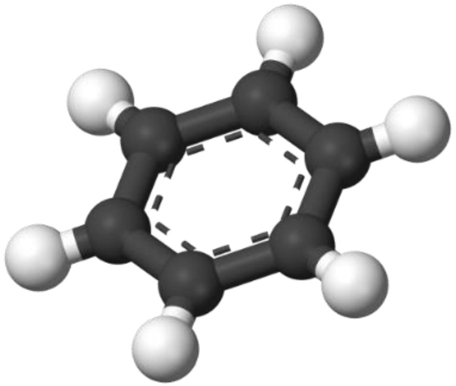
Motivation



Health Effects of Benzene (EPA)

<u>Acute</u>: Neurological effects, irritation of the eye, skin and respiratory tract

<u>Chronic</u>: Blood disorders (reduced number of red blood cells and aplastic anemia), cancer

South Coast AQMD

RULE 1180. REFINERY FENCELINE AND COMMUNITY AIR MONITORING

(a) Purpose

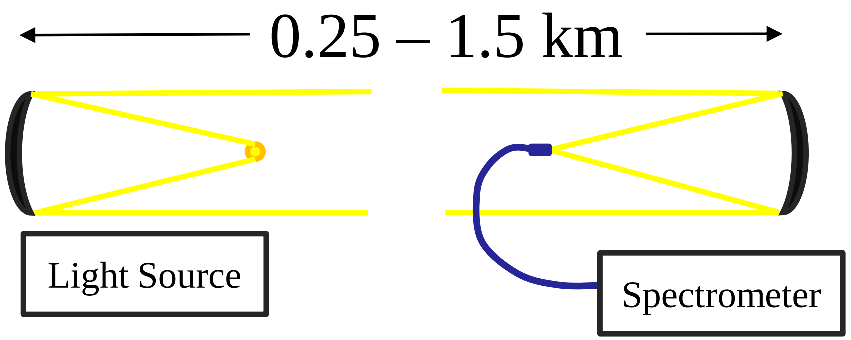
The purpose of this rule is to require real-time fenceline air monitoring systems

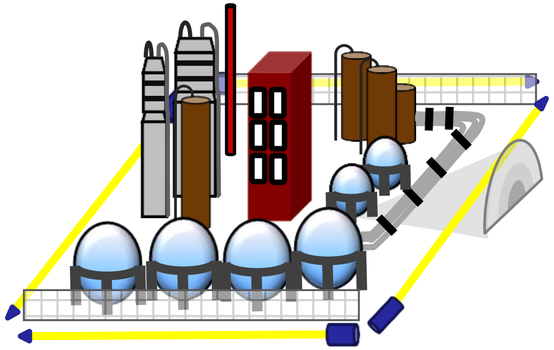
<u>Recommendation:</u>

R-A11 CARB and CAPCOA should support demonstration and implementation of ORS and spectral flux technology projects in SCAQMD and elsewhere as these technologies are validated for refinery air monitoring applications.

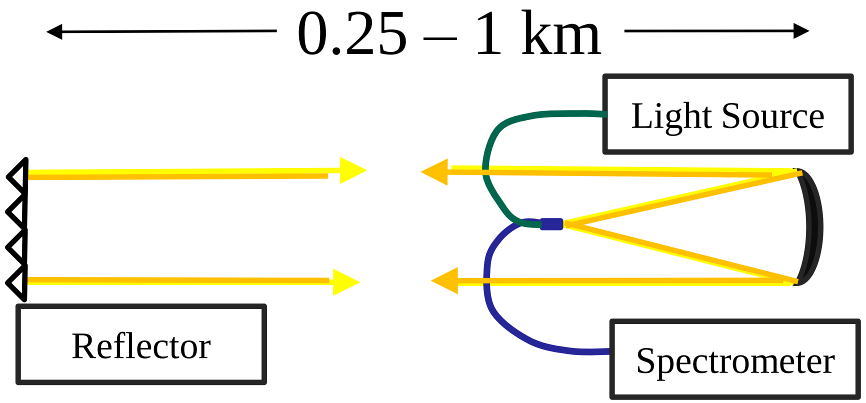
UV Absorption Spectroscopy

Bistatic Setup





Monostatic Setup

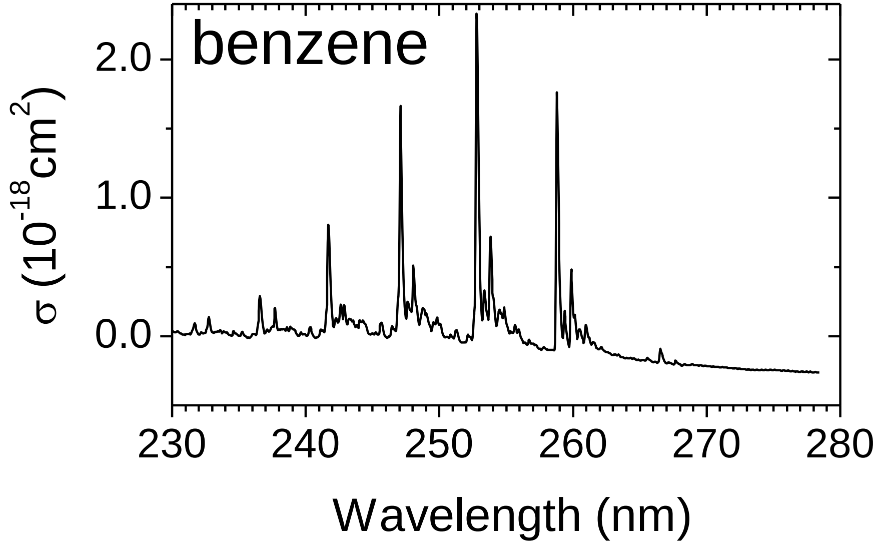


Absorption and emission are a <u>specific</u> property of a molecule

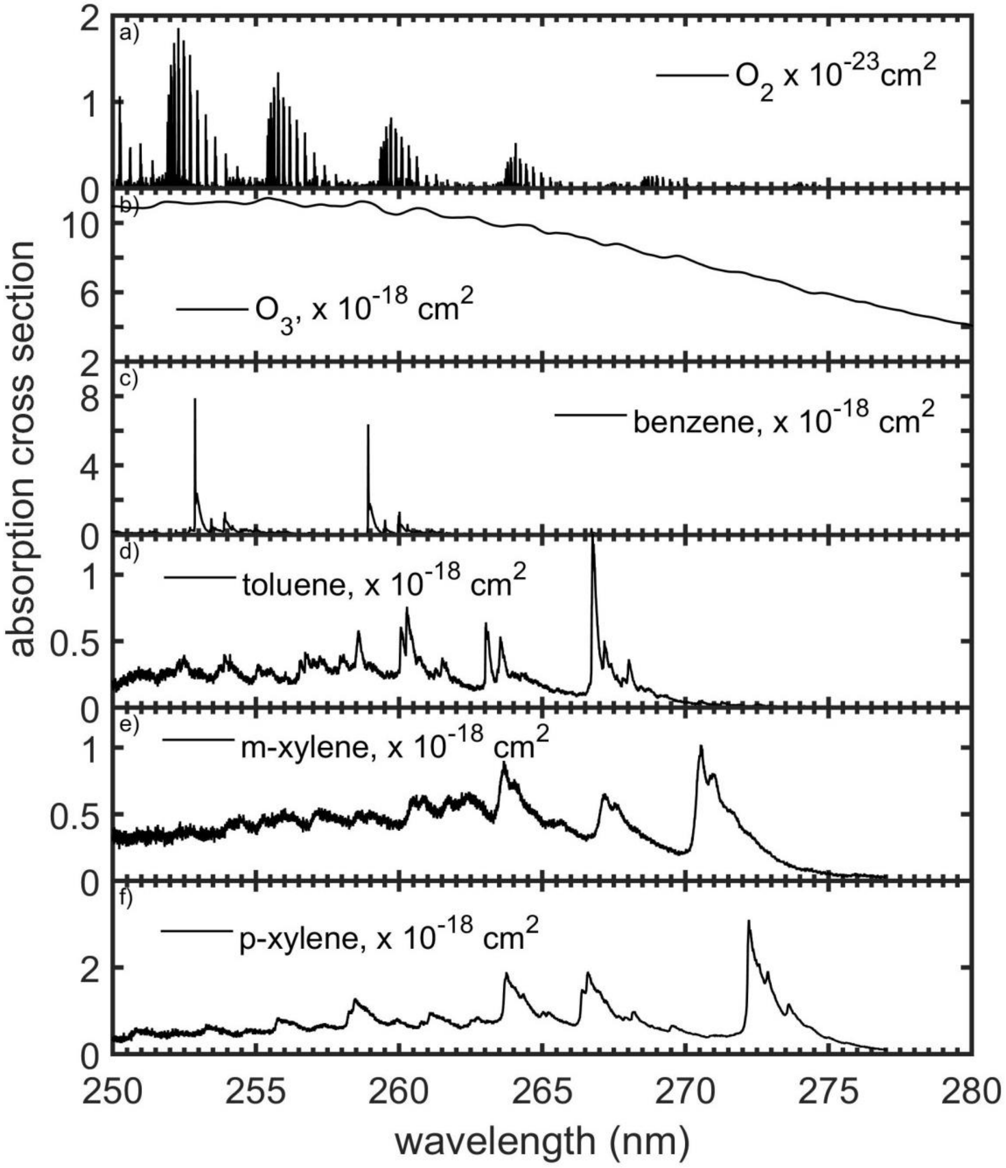
Beer's Law

$$I(\lambda) = I_0(\lambda) \times e^{-\sigma \times C \times L}$$

<u>Absorption Cross Section **σ(λ)**</u>

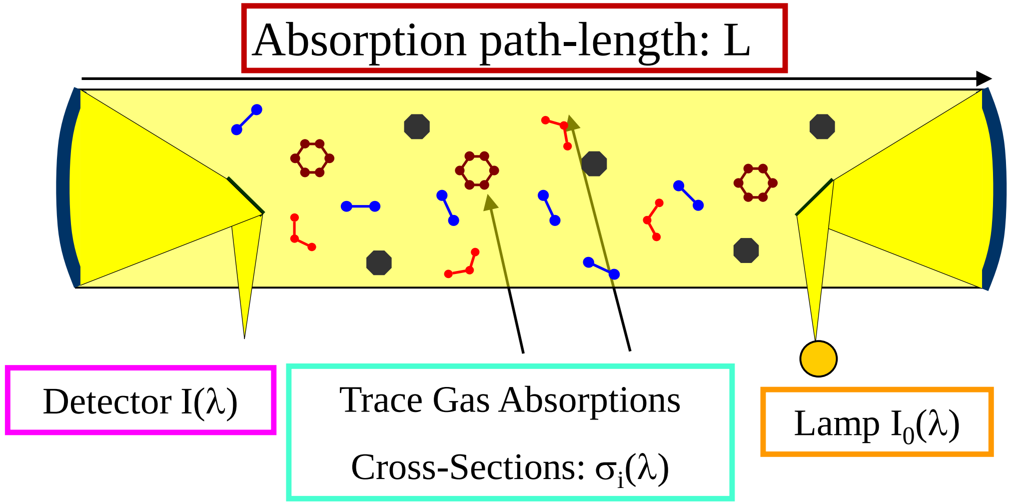


Absorptions by Aromatic Hydrocarbons



- Rayleigh (air) and Mie (particle) scattering
- Strong (saturated) narrow O_2 absorptions
- Poorly defined O_2O_2 and O_2N_2 collisional complex absorptions
- Strong temperature dependent O_3 absorptions
- Absorptions by aromatics are unique to each compound but overlap
- Turbulence
- Limited absorption path length due to Rayleigh and Mie scattering and O_3 absorptions

Differential Optical Absorption Spectroscopy



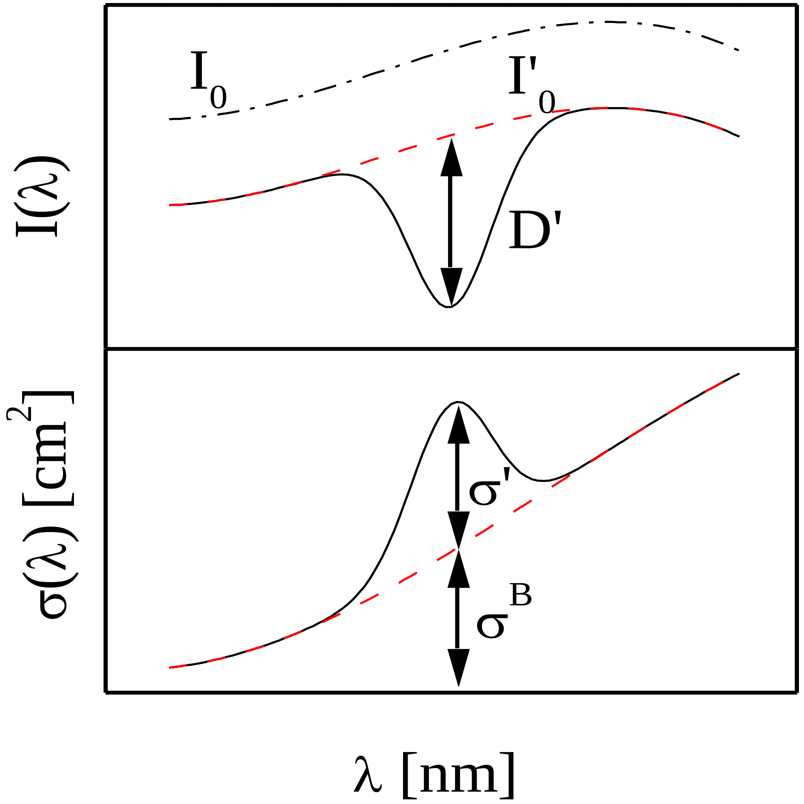
$$I(\lambda) = I'_0(\lambda)\cdot\exp\left(-C\cdot\sigma'(\lambda)\cdot L\right)$$

Modified Beer's Law

C: Trace gas concentration can be directly calculated based on path-length, and the physical constant of the absorption cross section.

DOAS: Separation of broad and narrow absorption features:

Only narrow-band depth is measured



Data Retrieval Approach

- Least squares fit of function F to $\ln(I/I_0)$:

$$F(i) = P_r(i) + \sum_{j=1}^{m} a_j \times S_j(i)$$

P_i polynomial for broad structures

S_j, reference spectra

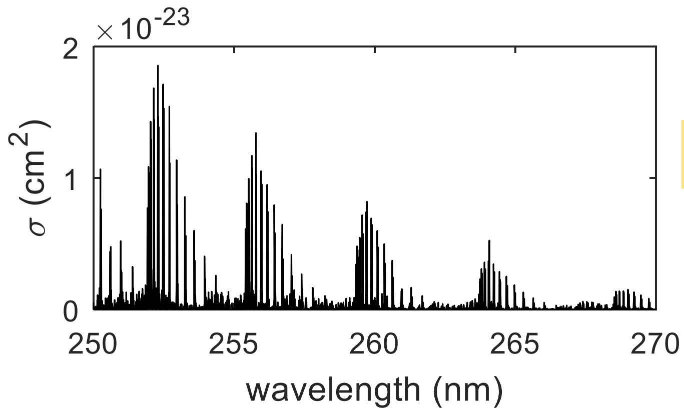
a_j scaling factors:

- Reference spectra calculated from literature high-resolution absorption cross sections.

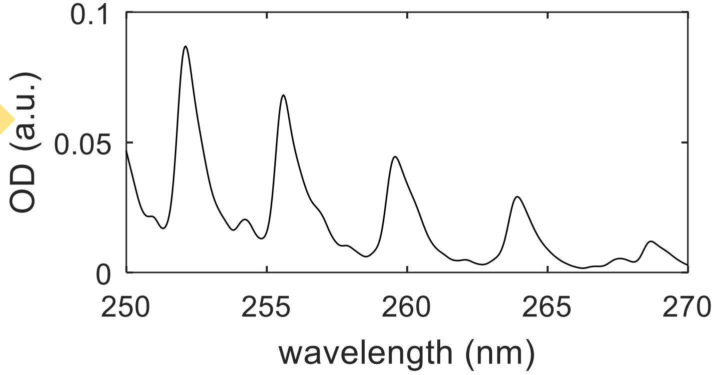
- Determination of concentration and uncertainties from retrieval.

$$\mathrm{Conc}_j = a_j / (\sigma_j \times L).$$

high-resolution cross section



Reference spectrum: $S_j(i)$



Absolute Retrieval

- All reference spectra are calculated from literature cross sections
- Lamp measured at the source
- No calibration needed

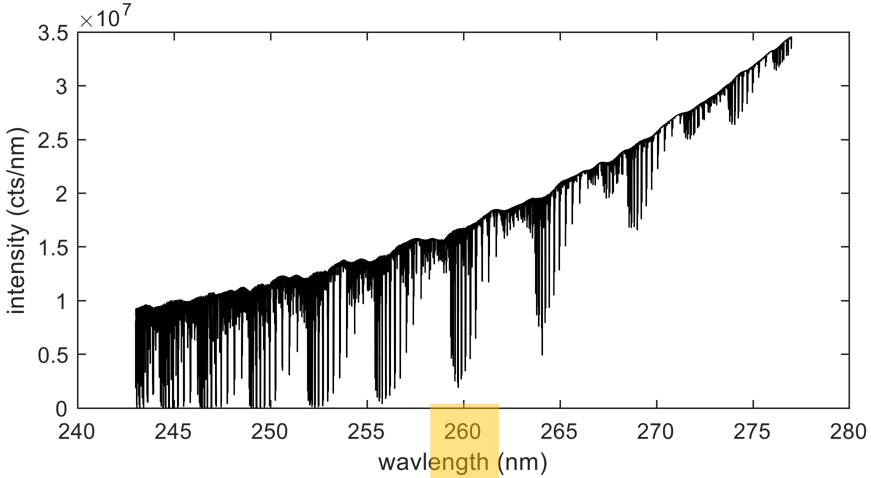
Relative Retrieval

- Use of atmospheric reference
- Trace gas reference spectra are calculated from literature cross sections
- Calibration often performed

Monte Carlo Retrieval Tests

<u>Simulation in high spectral resolution</u> (Δλ=0.001nm)

$$I(\lambda) = I_{Lamp}(\lambda) \cdot T_{instrument} \cdot \exp\left[-\left(\sigma_{Rayleigh}(\lambda) \cdot C_{air} + \sigma_{Mie}(\lambda) \cdot N_{aerosol} + \sum \sigma_i(\lambda) \cdot C_i\right) \cdot L\right] + Noise(\lambda)$$

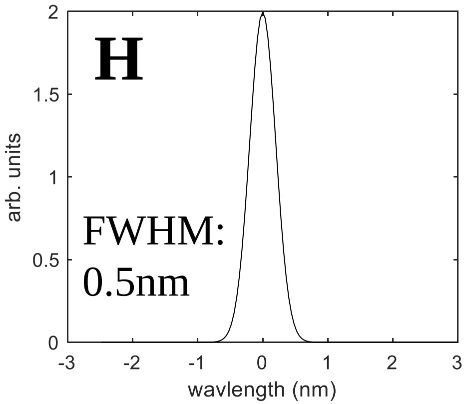


All parameters, except the benzene mixing ratio, randomly varied within atmospheric conditions

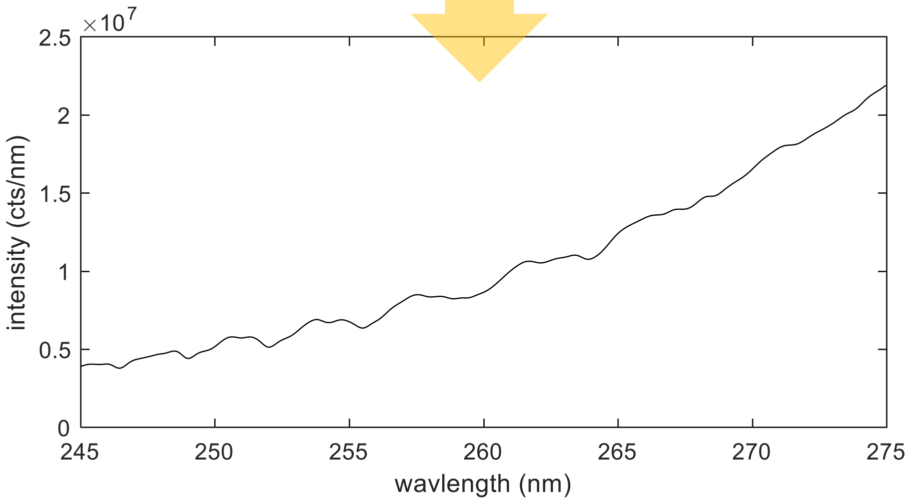
→ 1000 different atmospheric spectra

<u>Degradation to spectrometer resolution</u>

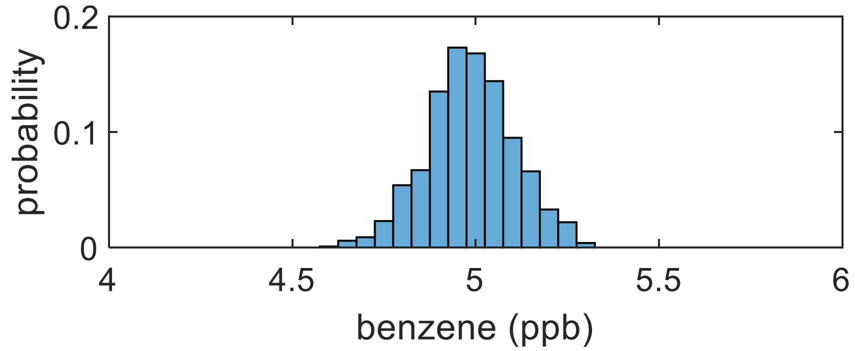
$$I^*(\lambda, L) = I(\lambda, L) * H = \int I(\lambda - \lambda', L) \times H(\lambda')d\lambda'$$



Noise added as photon noise spectrum with random number generation



Absolute vs. Relative Retrieval (5ppb benzene, no straylight)

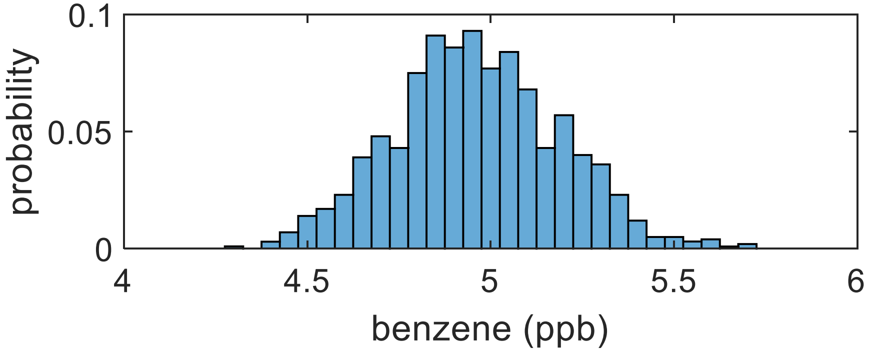


Absolute Retrieval with O_3 temperature correction

Mean: 4.98 ppb

StdDev: 0.12 ppb

meanError: 0.08 ppb (normally reported as 0.16ppb)

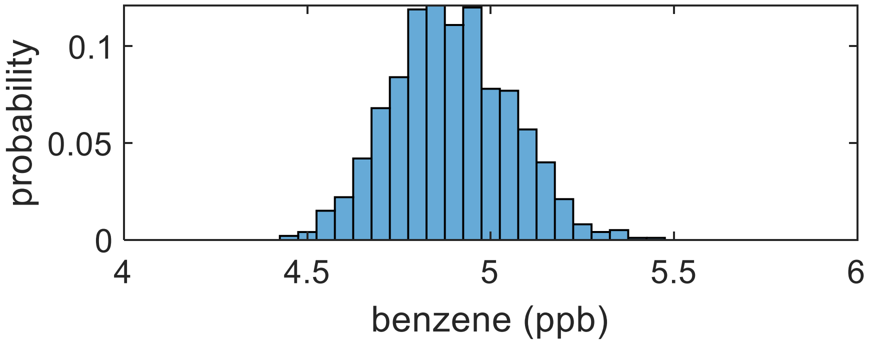


Relative retrieval with O_3 temperature correction: Reference with 0.1 ppb benzene

Mean: 4.96 ppb

StdDev: 0.23 ppb

meanError: 0.12 ppb



Relative retrieval without O_3 temperature correction: Reference with 0.1 ppb benzene

Mean: 4.89 ppb

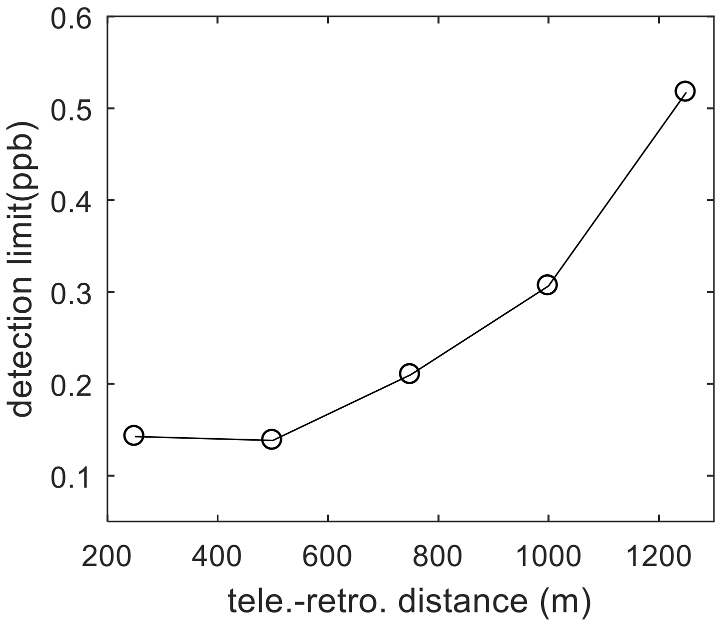
StdDev: 0.16ppb

meanError: 0.15ppb

Theoretical Retrieval Dependencies

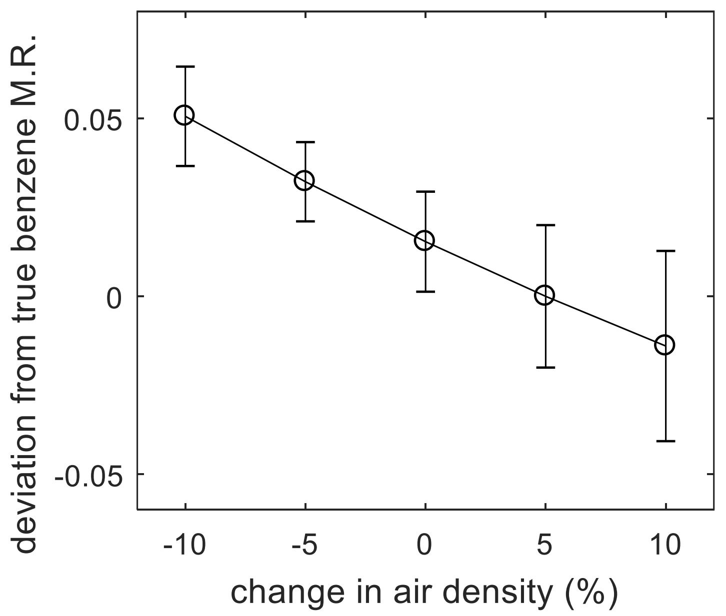
Small atmospheric transmissivity → impact on detection limit

- Up to 1.5 km total path length → little variability in sensitivity
- Strongly dependent on ozone and visibility



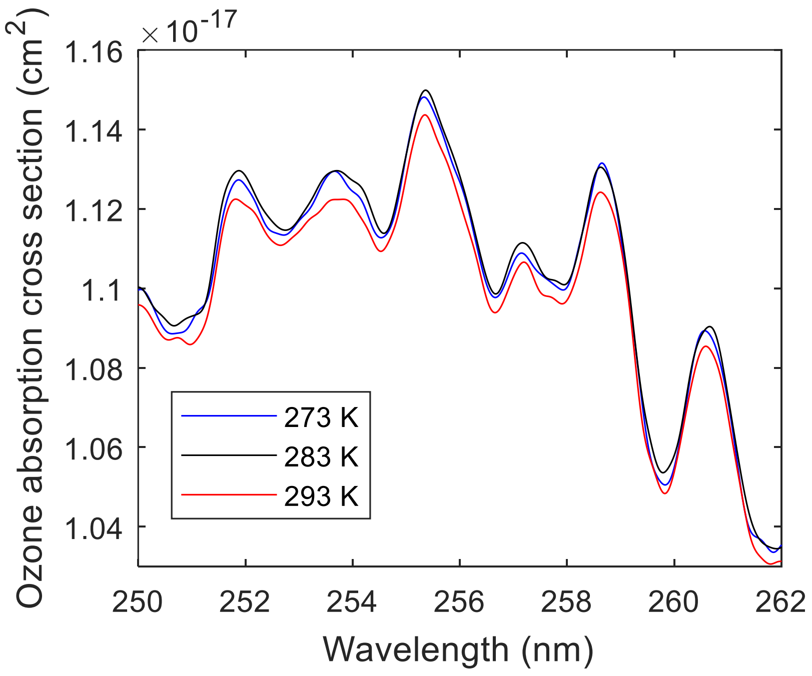
O_2 absorptions are non-linear at low spectral resolution

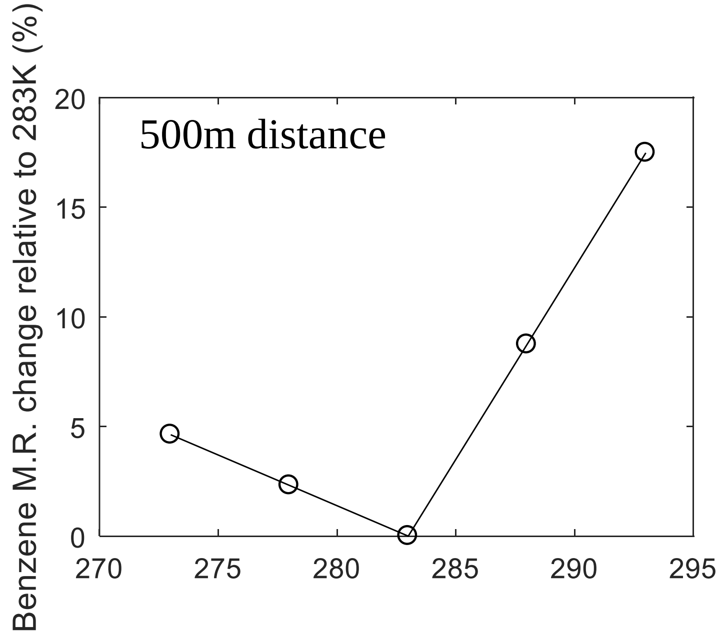
- Introduction of spectral artifacts in analysis.
- Dependence of benzene M.R. and errors on temperature and pressure.
- Corrected in absolute retrievals but not in relative retrievals

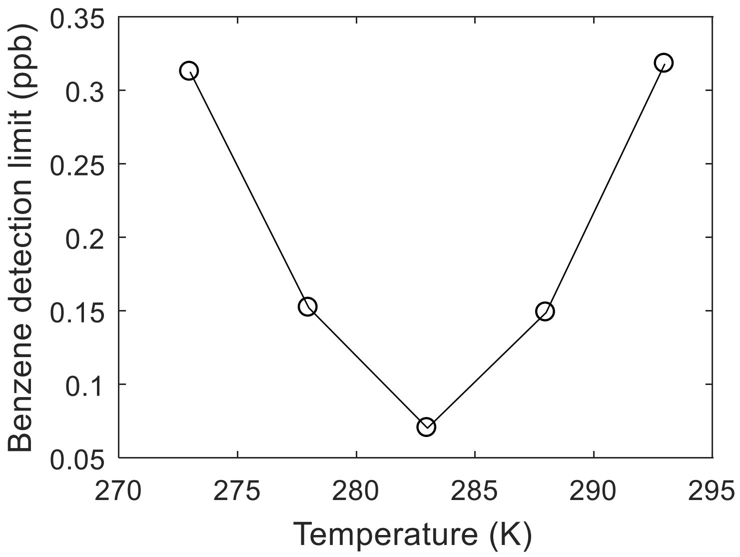


Theoretical Retrieval Dependencies

O_3 absorption is temperature dependent







- Uncorrected temperature dependence introduces biases in benzene retrieval and increases error
- Include cross sections with two different temperatures in retrieval

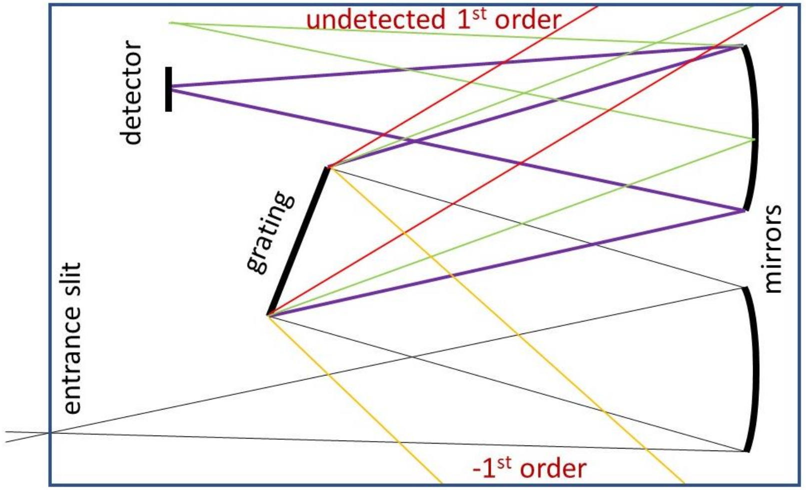
Spectrometer Straylight

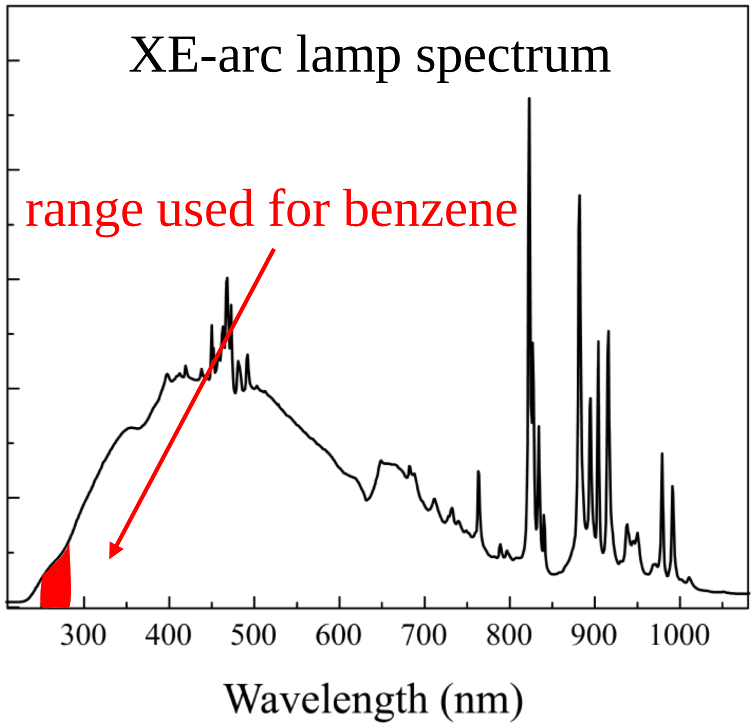
- Suppression of unmeasured wavelength by spectrometers imperfect.
- Produces a background (socket) intensity in the spectrometer

$$\mathbf{I(\lambda) = I_{stray}(\lambda) + I_0(\lambda) \times e^{-\sigma \times C \times L}}$$

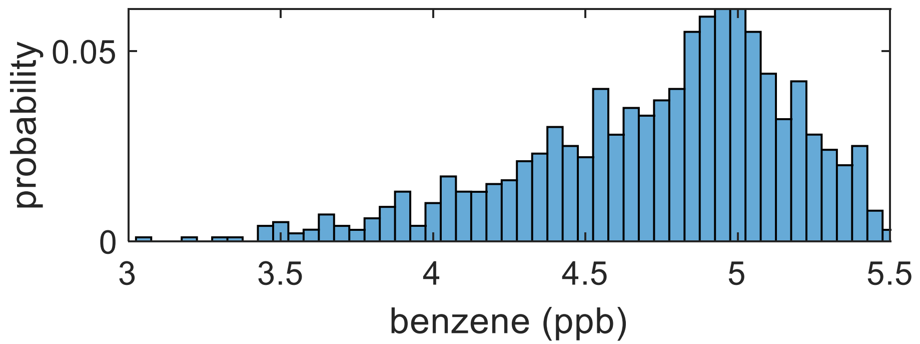
- Problems in the data retrieval
- For Xe-arc lamps (most common light source) 95-99% of incoming light needs to be suppressed

Solution
- Better spectrometer ($$$)
- Use filters
- Use different light source
- Correct during of after retrieval (difficult)





Impact of spectrometer straylight (3% of 270nm intensity, 5ppb benz)

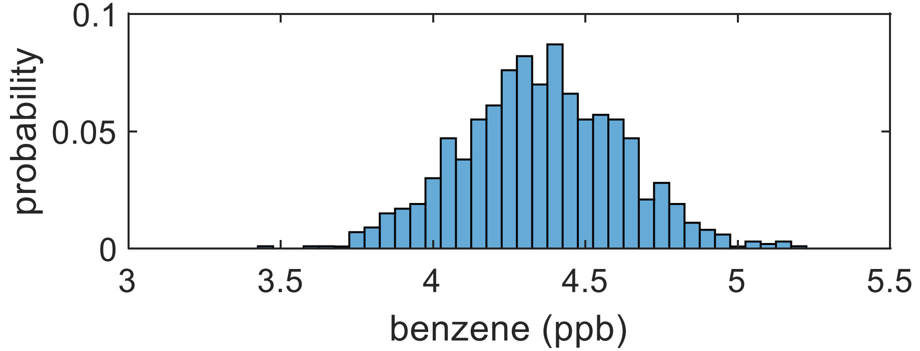


Absolute Retrieval with O_3 temperature correction

Mean: 4.74 ppb

StdDev: 0.44 ppb

meanError: 0.16 ppb (normally reported as 0.32ppb)

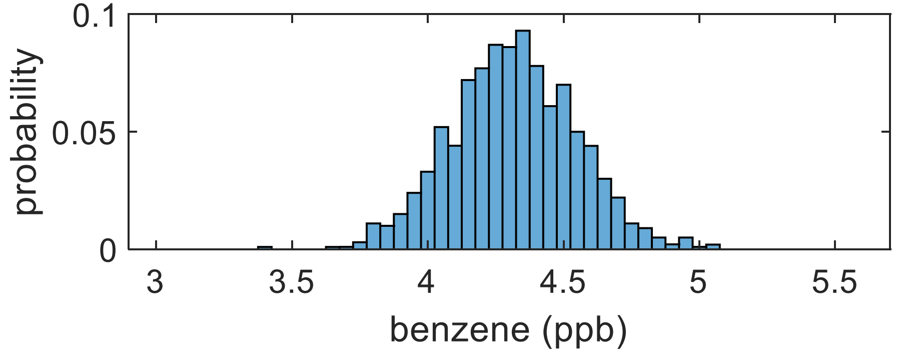


Relative retrieval with O_3 temperature correction:
Reference with 0.1 ppb benzene

Mean: **4.35 ppb**

StdDev: 0.26 ppb

meanError: 0.10 ppb



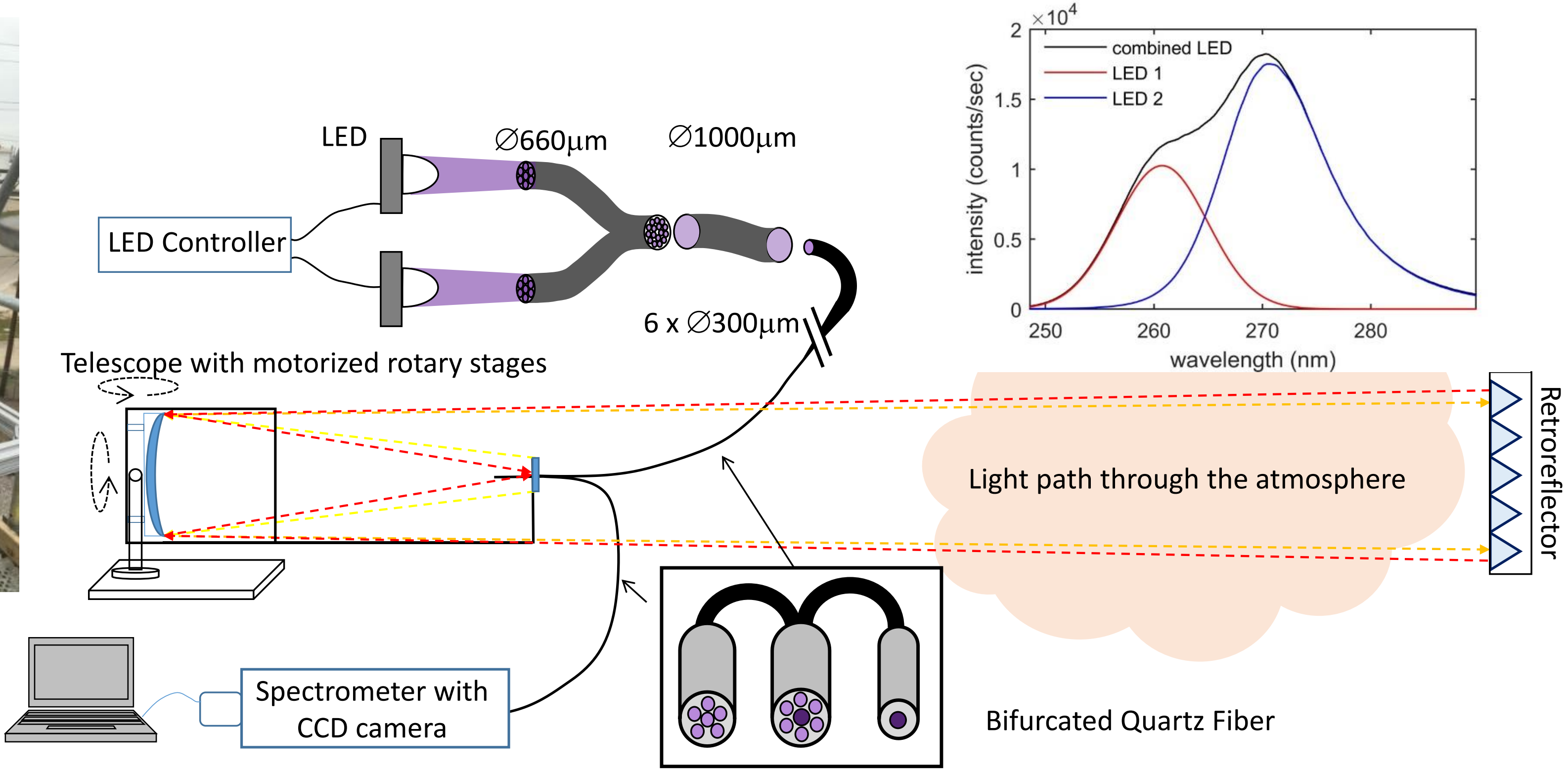
Relative retrieval without O_3 temperature correction:
Reference with 0.1 ppb benzene

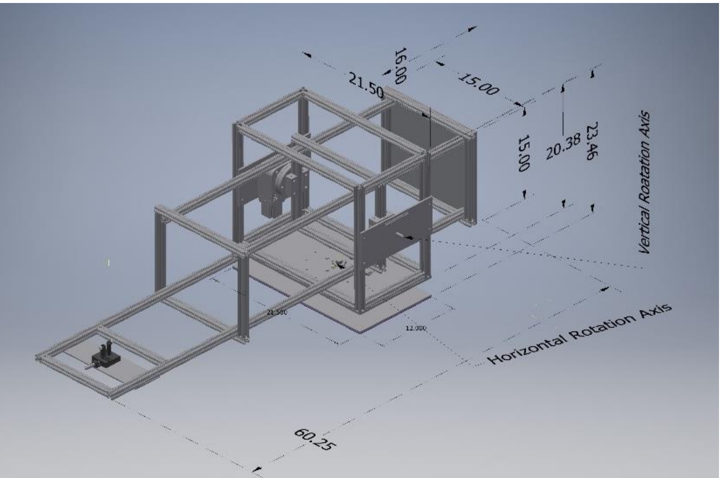
Mean: **4.31 ppb**

StdDev: 0.23 ppb

meanError: 0.11 ppb

UCLA LP-DOAS instruments

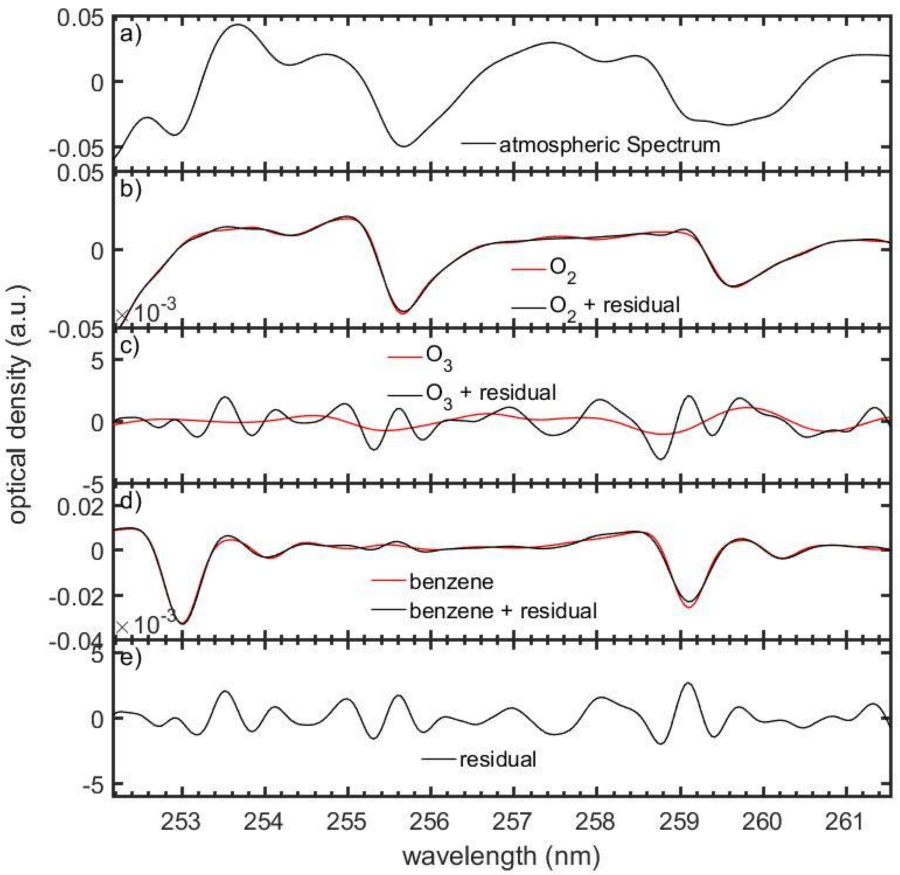


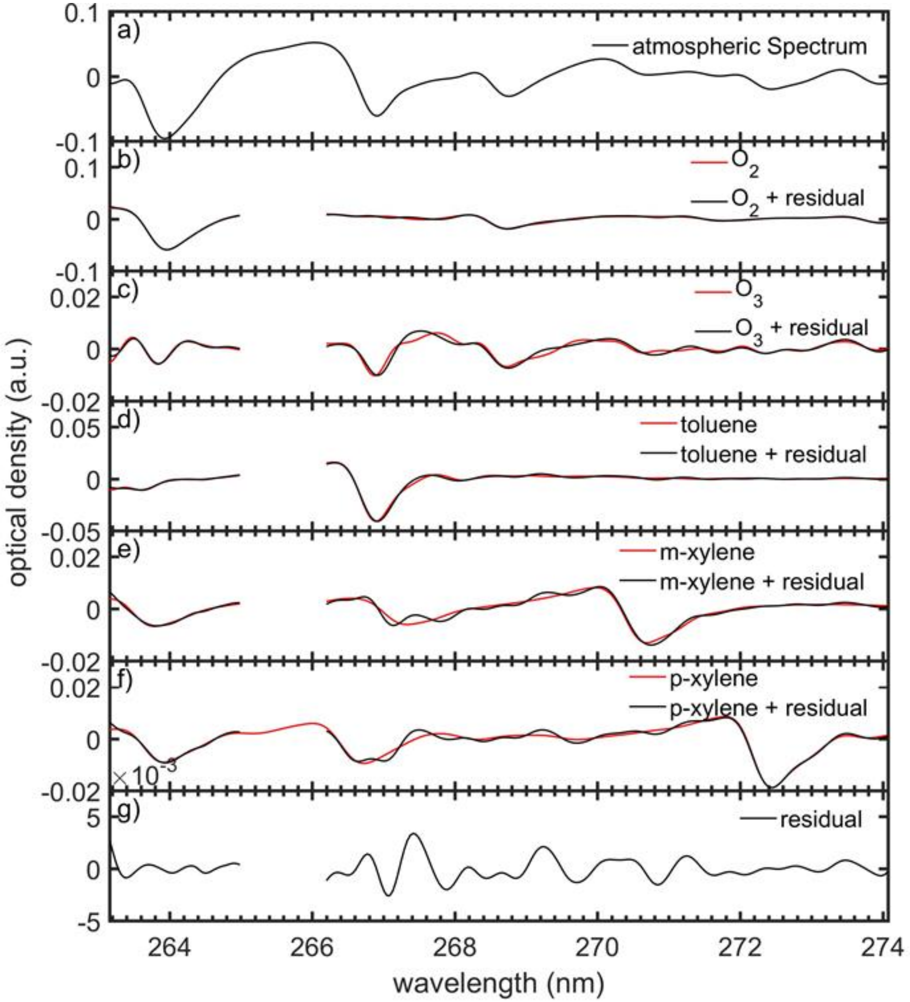


- Fiber telescope setup with wide and accurate rotation capability.
- Dual LED light source to reduce spectrometer straylight
- Research quality spectrometer/detector.
- Fully automated with near-realtime analysis capability

Stutz et al., 2016

Spectral Analysis of Field Data



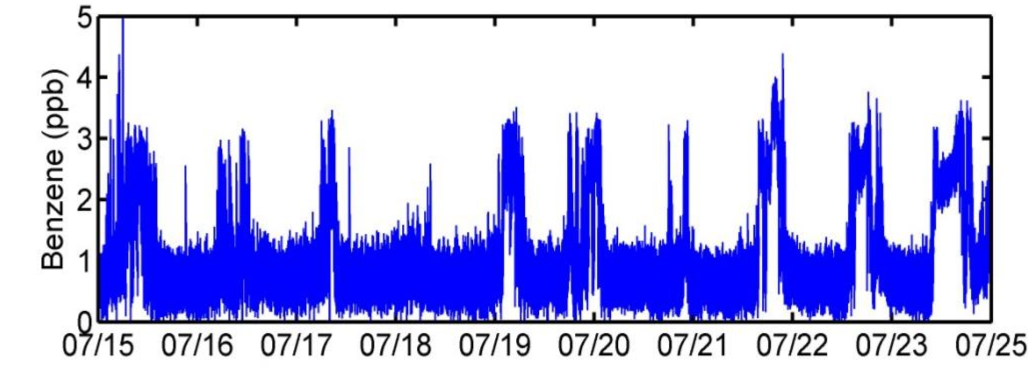


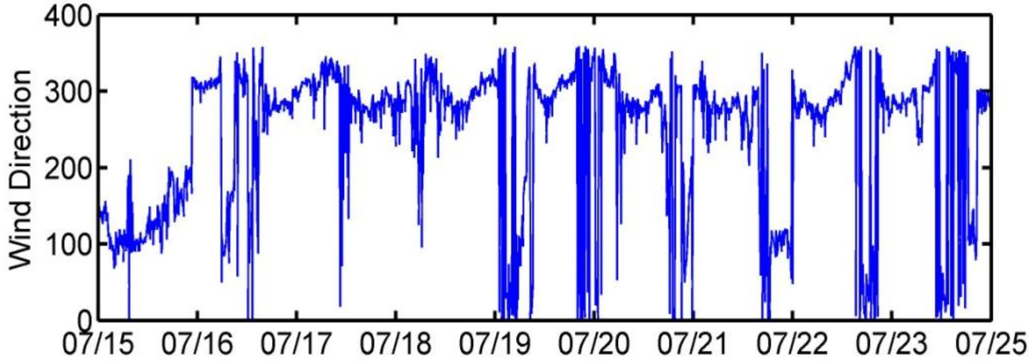
- 33 ± 0.9 ppb of benzene (270m path)

- 31.4 ± 0.8 ppb of toluene (770m path)
- 11.0 ± 0.6 ppb of m-xylene (770m path)
- 4.9 ± 0.2 ppb of p-xylene (770m path)

Stutz et al., 2016

Fenceline Application: Benzene

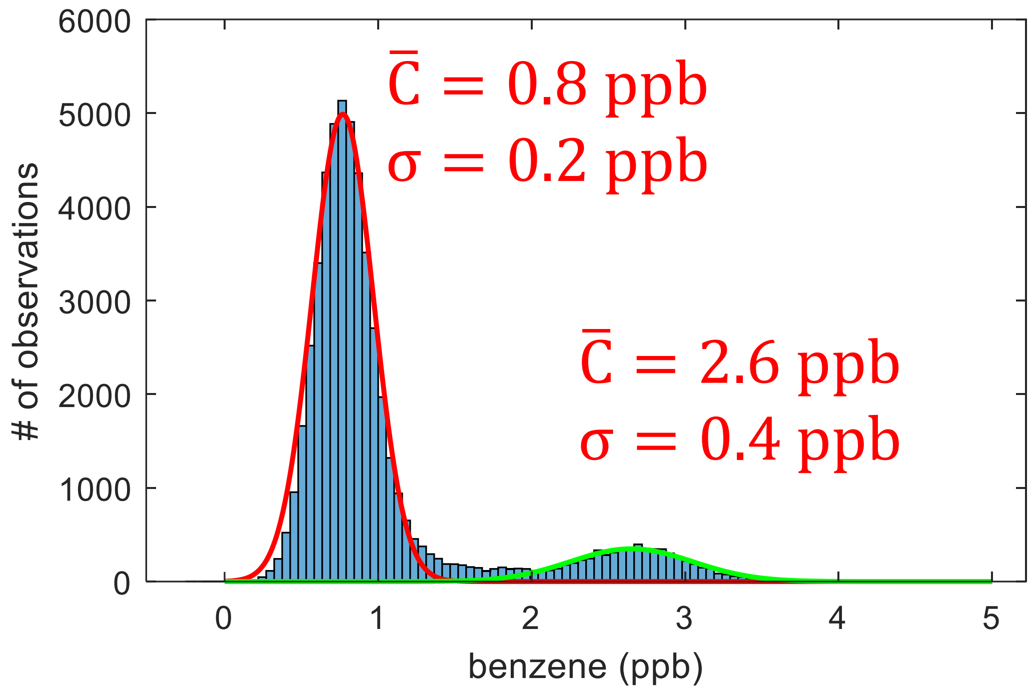




- Benzene correlated with wind direction
  - Atmospheric background ~0.8ppb
  - Facility direction ~2.6ppb
- Temporal resolution ~1min
- Fully automated operation for ~3 months

Stutz et al., 2016

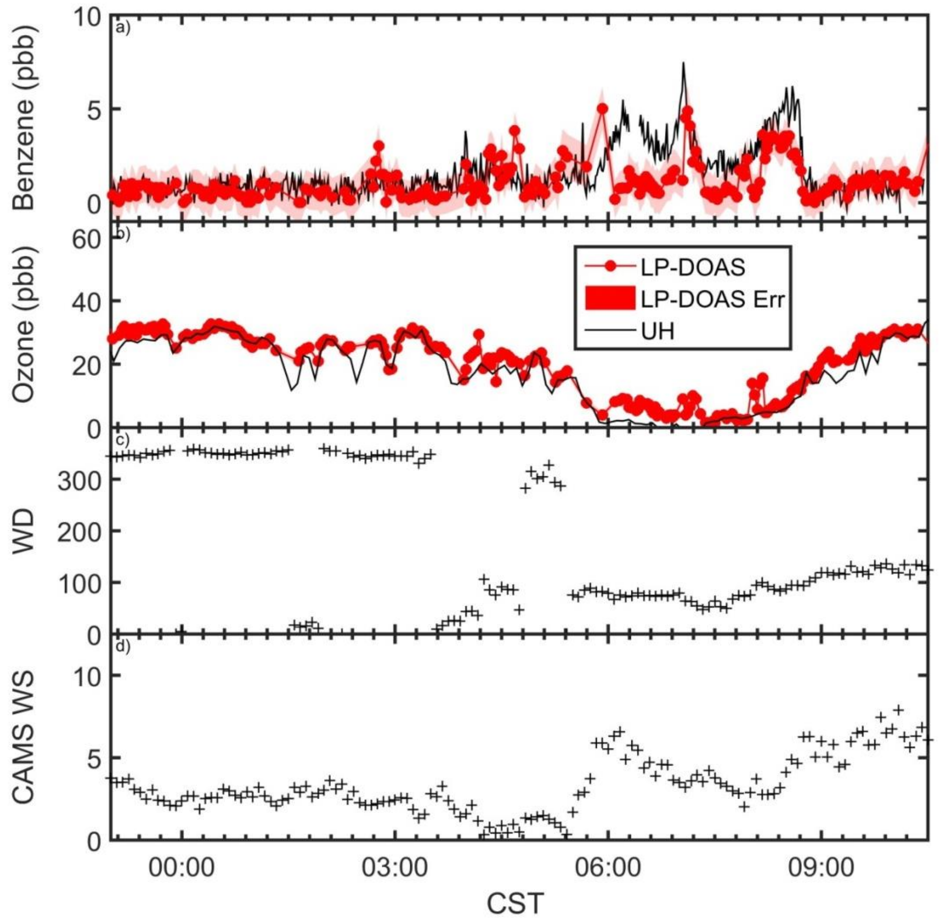
<u>Histogram of 3 months (53400) of observations</u>

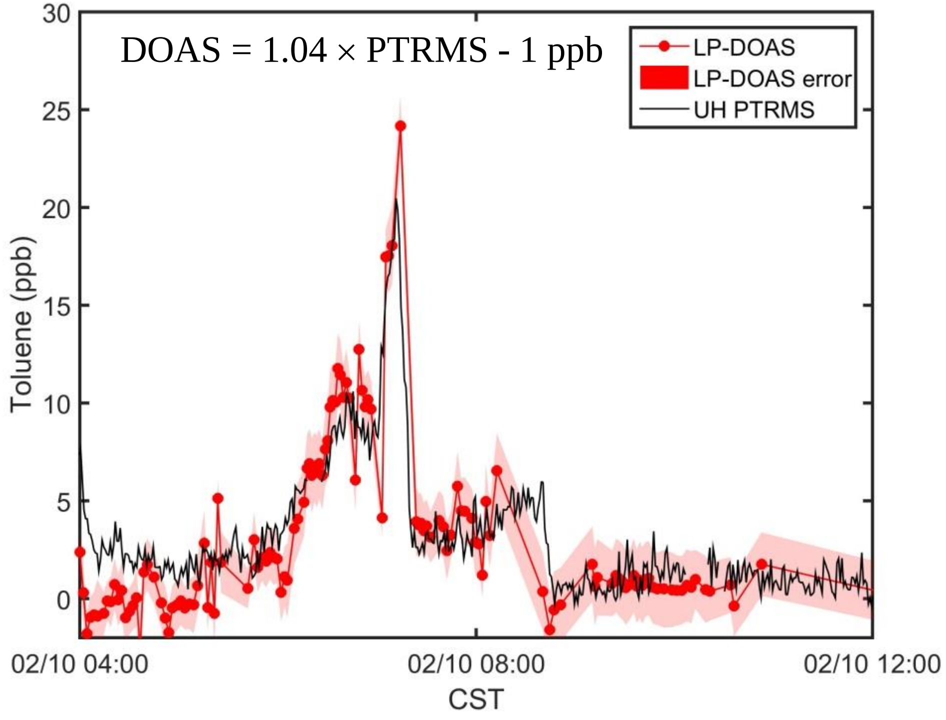


Average error: 0.3 ppb

Average detection limit ~0.4 – 0.6 ppb

Instrument Performance during BEE-TEX in Houston





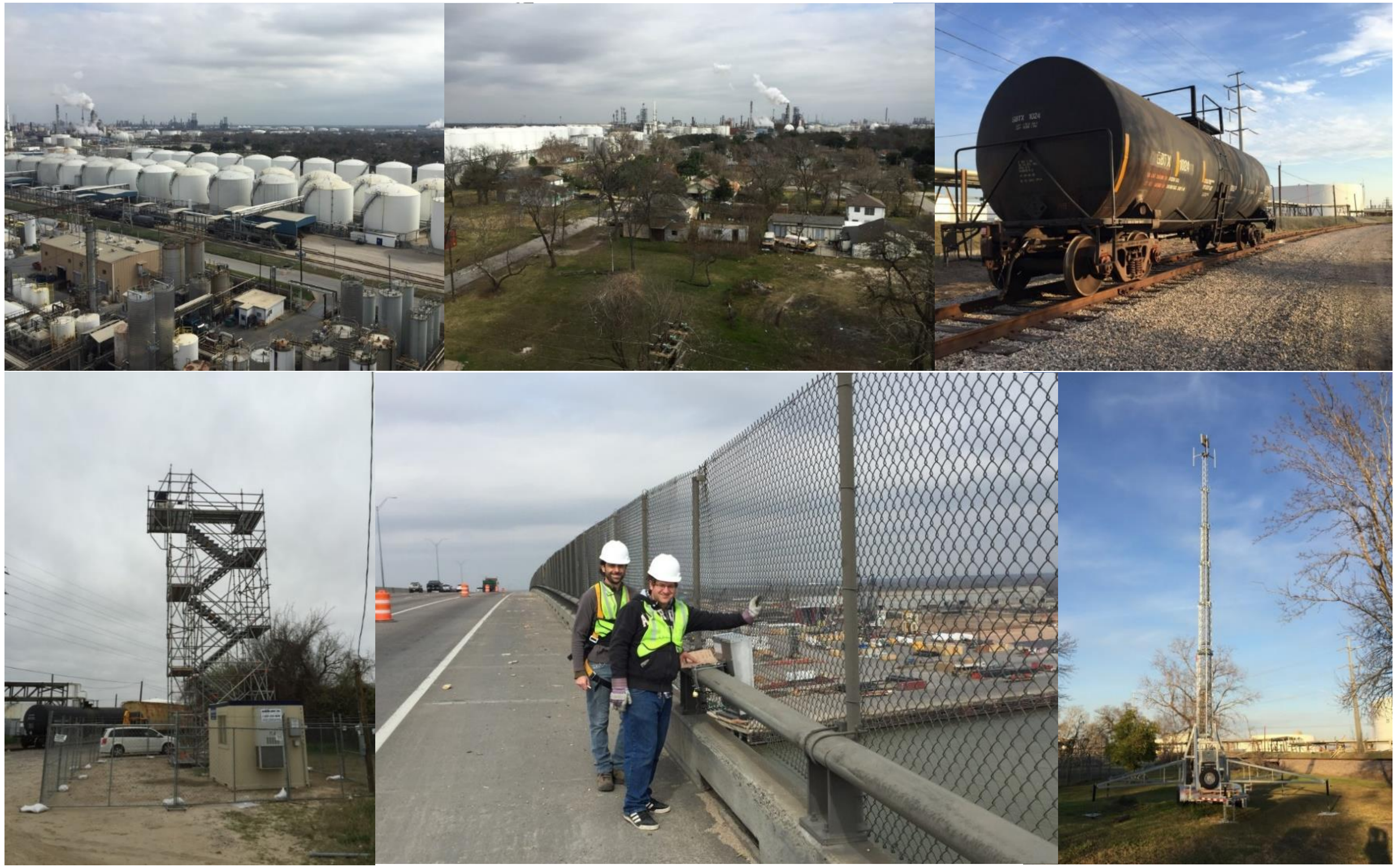
Toluene and benzene levels compare well with Univ. Houston PTR-Mass Spectrometer

Species	Average detection limit, 770m distance (ppb)
benzene	0.31
toluene	0.60
m-xylene	0.58
p-xylene	0.36

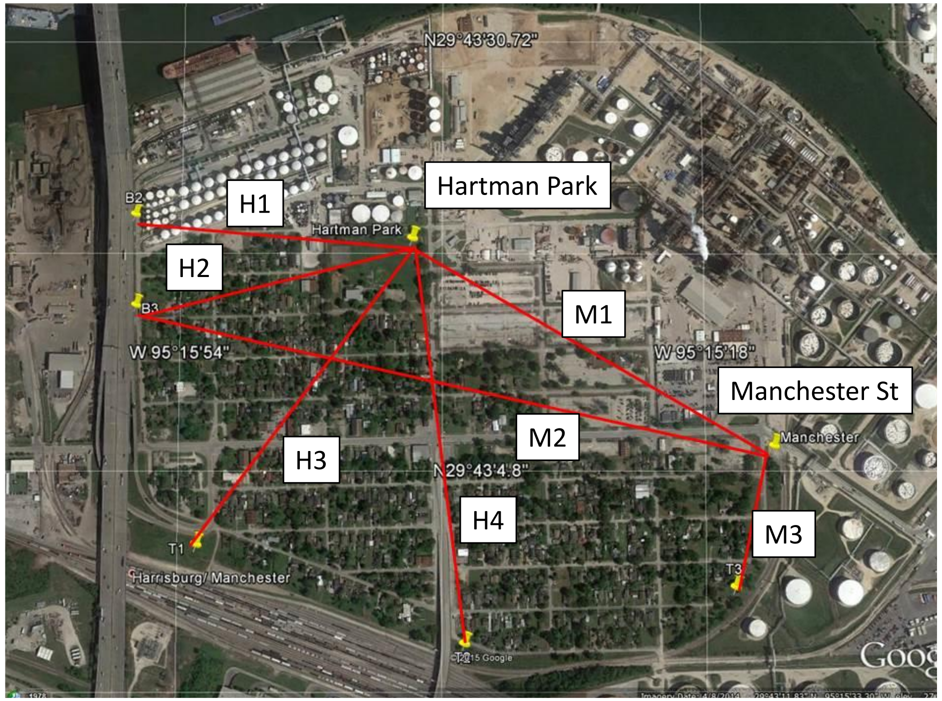
Detection limits calculated from retrieval error for each measurement

The BEE-TEX Experiment in Houston

- February 2015
- Manchester Neighborhood in the Houston Ship Channel.



BEE-TEX CAT-DOAS



	Reflector Location	Distance (m)
Manchester St. LP-DOAS		
M1	LP-DOAS scaffolding tower at Hartman Park	770
M2	Southern end of IH610 bridge	1203
M3	Telescopic tower south of LP-DOAS	270
Hartman Park LP-DOAS		
H1	IH610 bridge	513
H2	Southern end of IH610 bridge	526
H3	Telescopic tower at the exit ramp of the IH bridge	689
H4	Telescopic tower near the Central St. bridge	740

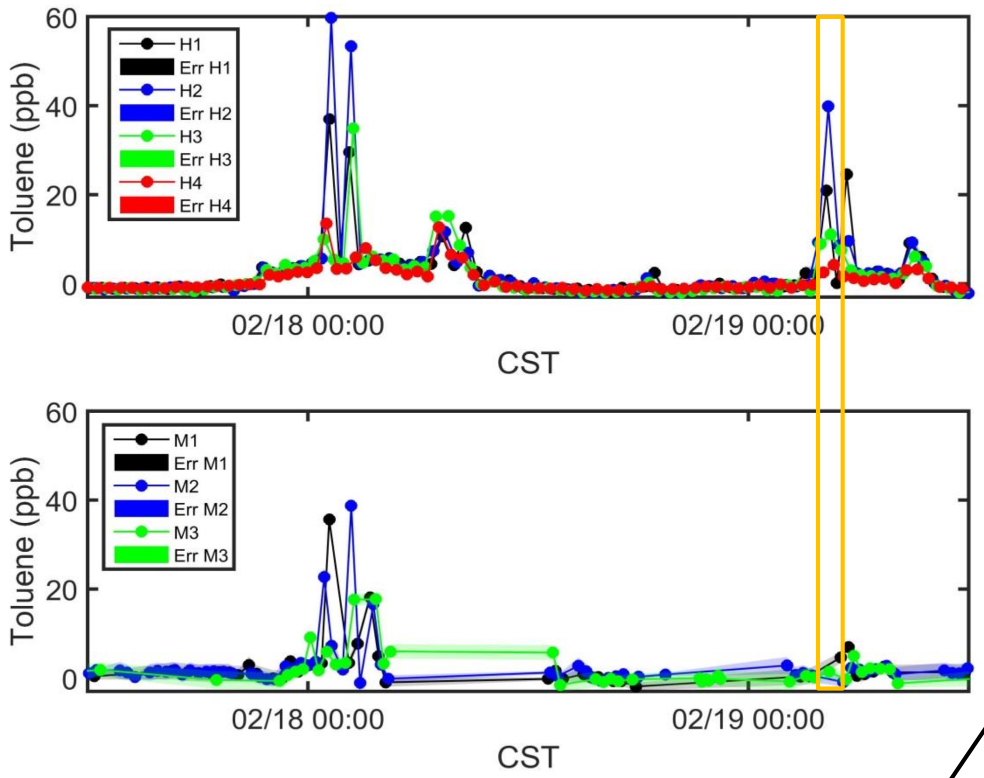
Observations

- From 2/9 – 2/28/15
- Two LP-DOAS instruments
- 7 light paths from 270 -1203m length

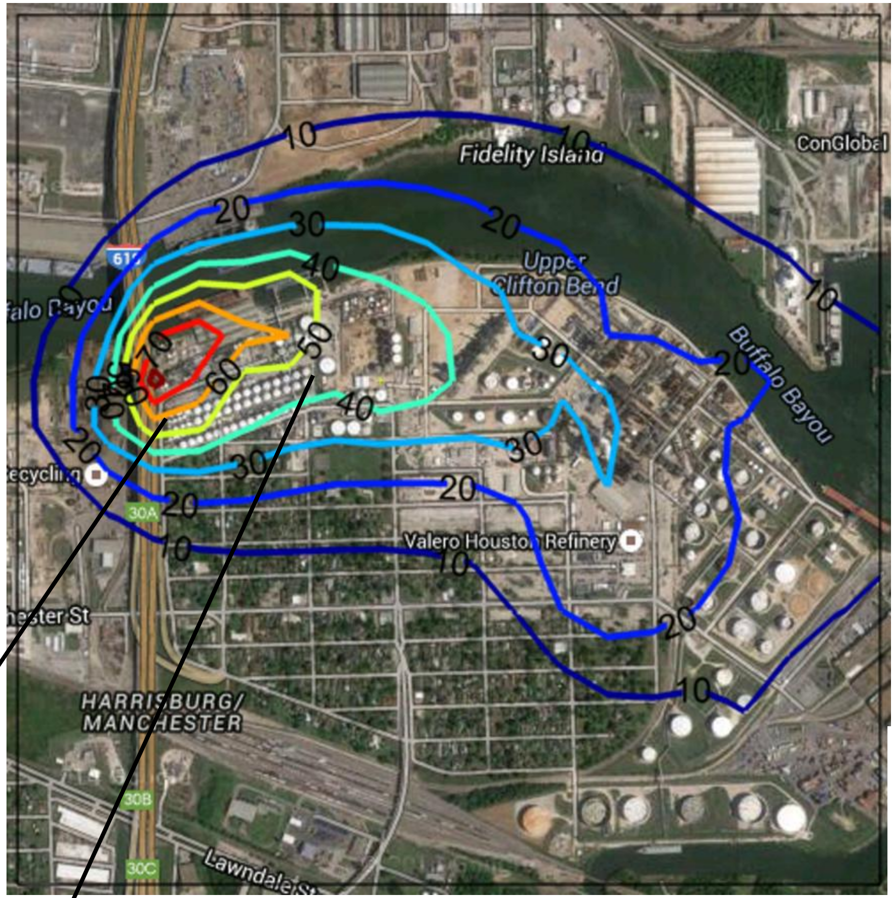
Analysis / 2D Reconstructions

- Real-time computer aided tomography (CAT) retrievals of 2D concentration fields
- Re-analysis using high-resolution HARC 3D Eulerian air quality model (QUIC-based) with adjoint 4Dvar data assimilation (Olaguer et al., 2017)

Toluene Plume 2/19 Reconstruction



Stutz et al., 2016

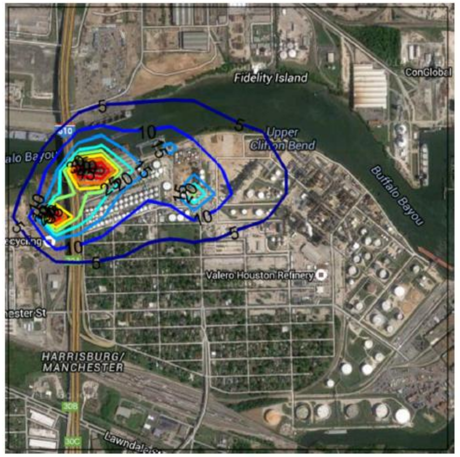


Reconstruction

2/19 4:00 am

LP-DOAS reconstruction agrees well with reconstruction from mobile lab observations

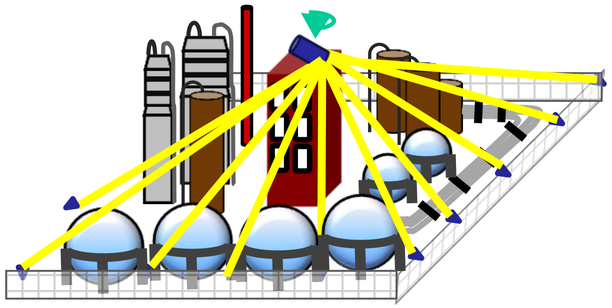
Olaguer et al., 2017



Mobile Lab-based Reconstruction

What is next? The Optical Tent

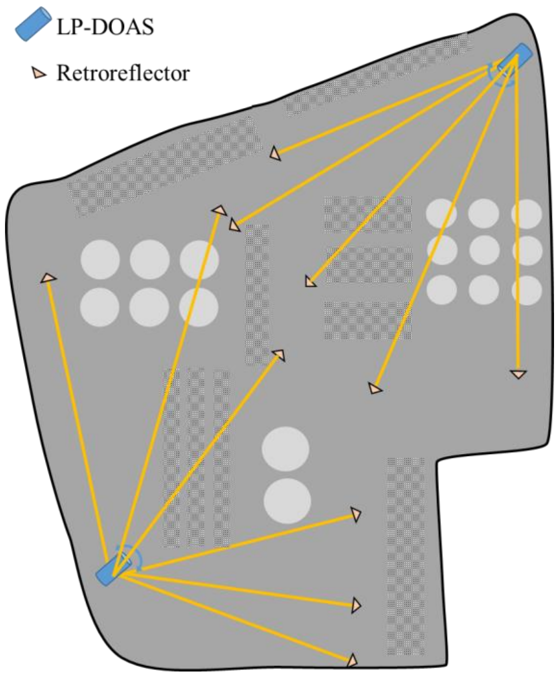
- Bring 2D sensing capability into a petrochemical facility
- Measurement of benzene, toluene, xylene's, etc.
- Provide near-realtime observations to alert facility of emission events.
- Provide guidance on location of emissions



Optical tent will shorten time between release event and mitigation

⇩

Reduced emissions



Optical Tent in Refinery

- Two LP-DOAS instruments + 10-12 light paths cover entire facility.
- BTEX detection limits similar to previous field deployments ~0.5 - 1 ppb.
- Integration with fenceline systems and facility operation.

Conclusions

- State-of-the-art LP-DOAS systems provide reliable observations of benzene, toluene, xylene's
  - Theoretical benzene detection limits around 0.25 – 0.5 ppb
  - Practical detection limits ~ 0.3 – 0.6 ppb for benzene, and 0.3 – 1 ppb for other BTEX compounds
  - UCLA LP-DOAS compares well with other methods for benzene and toluene

- 2D CAT-DOAS approach successfully demonstrated during the BEE-TEX experiment in Houston.
  - Successful BTX measurements on light paths longer than 1.5 km.
  - Reconstruction of concentrations fields (near-realtime and re-analysis)
  - Identification of emission sources

- Optical tent will bring 2D capability inside facilities.
  - Alarm system to warn facility operators of release events
  - Provide guidance for location of emission source

Acknowledgement

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Houston Advanced Research Center

South Coast Air Quality Management District