MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

Inverse Modeling of Episodic Measurements for Conventional and Real Time Applications

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Introduction

- Ambient air measurements based on optical, chemical ionization, or other contemporary monitoring techniques make **real-time observation** a reality.

- These measurements can now be interpreted either off-line or in real time using **inverse methods for source attribution and emissions quantification**.

- This presentation demonstrates examples of inverse modeling of conventional and real-time measurements based on either **Gaussian dispersion** models or **3D microscale grid models** for pollutant transport and/or chemistry.

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Example 1: Ethylene Oxide from a Sterilization Facility

- Ethylene oxide (EtO) is a global commercial chemical (~20 Mt/yr) that is often used to sterilize medical equipment.
- EtO is a known carcinogen; it can cause breast and blood cancers. Michigan's Initial Risk Screening Level (IRSL) is 0.0002 µg/m^3 (annual average) corresponding to a cancer risk of 1-in-a-million.
- Largest medical sterilization facility in Michigan reported fugitive emissions of EtO, whose AERMOD-simulated annual average impacts at nearby residences were up to 0.3 µg/m^3.
- EGLE (then known as MDEQ) conducted 24-hr Summa canister sampling at 16 sites around facility followed by TO-15 analysis (refined to eliminate interference from trans-2-butene).

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Ethylene Oxide Phase II Sampling

MARCH 27 - 28, 2019

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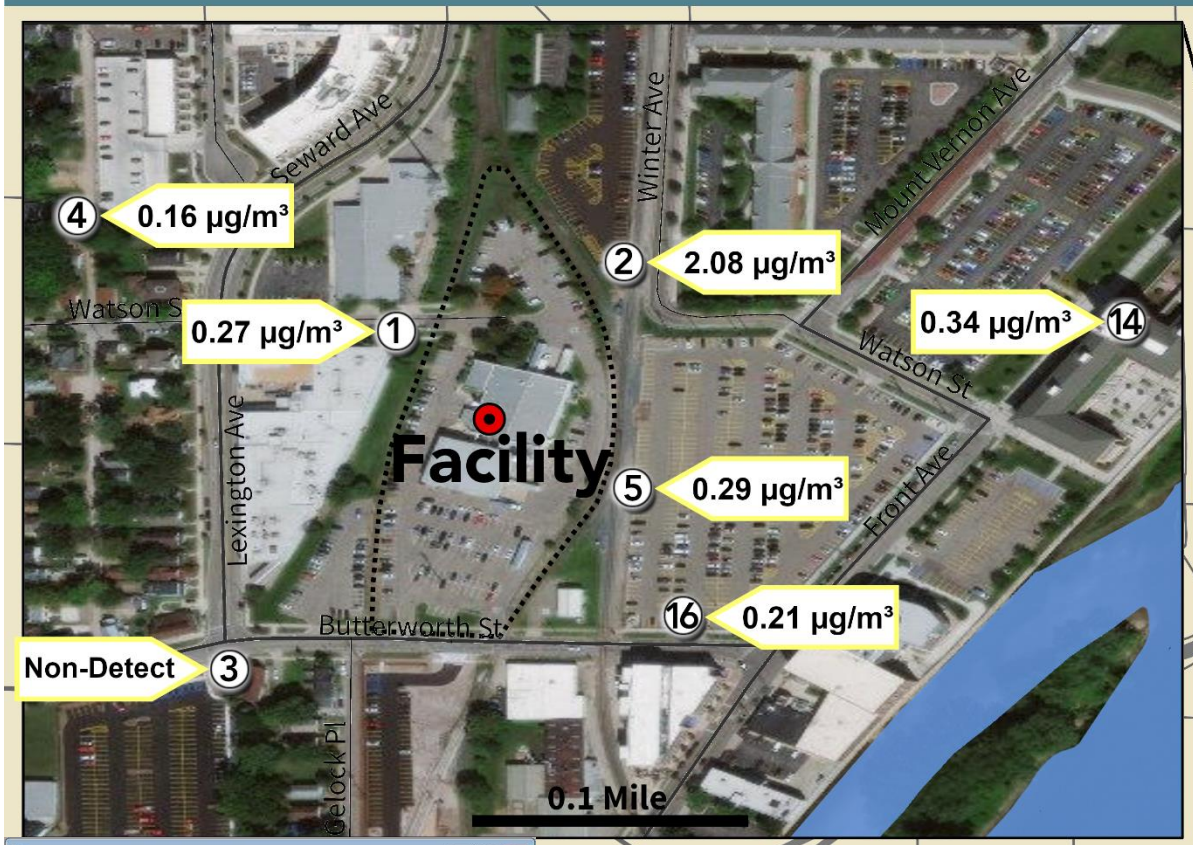

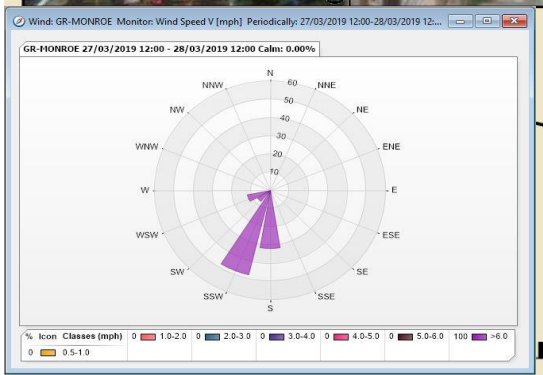

Inverse Modeling Method: Steady State Gaussian Plume

Solve for *B* and *Q* using linear regression (for positive values of *x* only):

Measured EtO concentrations

Background EtO concentration

Fugitive emission rate

$$C(x,y) = B + Q \times D \quad \textbf{(1)}$$

EtO atmospheric half-life is roughly 105 days

$$D = \frac{exp\left(-\frac{y^2}{2{\sigma_y}^2}\right)}{\pi U \sigma_y \sigma_z} \quad \textbf{(2)}$$

$$\sigma_y = \frac{0.16x}{(1+0.0004x)^{0.5}} \quad \textbf{(3)}$$

$$\sigma_z = \frac{0.14x}{(1+0.0003x)^{0.5}} \quad \textbf{(4)}$$

where:

x = distance from facility emission point along average wind direction (= 204°)
y = perpendicular distance from x-axis
U = average wind speed (= 4.47 m/s)
σ_y = horizontal urban dispersion parameter for neutral stability (Briggs, 1973)
σ_z = vertical urban dispersion parameter for neutral stability (Briggs, 1973)

Inferred Ethylene Oxide Parameters (*based on 12 downwind sites*)

- ***Inferred EtO emission rate*: 594 lbs/yr**
- Reported emissions based on indoor GC measurements and mass balance: **420 lbs/yr**
- ***Inferred EtO background*: 0.247 µg/m^3**
- Average upwind measurement: **0.177 µg/m^3**
- Background EtO concentration in Chicago measured by Ramboll (2019): **0.24 µg/m^3**

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Example 2:
Refinery Emissions of Reactive Formaldehyde

- **Primary formaldehyde** may be more important in urban ozone formation than originally thought due to its ability to generate an initial pool of radicals (Olaguer et al., 2009, 2014).
- The **Study of Houston Atmospheric Radical Precursors (SHARP)** took place in 2009. It brought advanced remote sensing and mobile monitoring techniques to measure primary formaldehyde.
- **Imaging Differential Optical Absorption Spectroscopy** (I-DOAS) and mobile **Quantum Cascade Laser** (QCL) measurements were made outside the fence line of the third largest refinery in the U.S.
- An advanced **3D microscale Eulerian chemical transport model** was later developed to serve as a data interpretation engine for real-time measurements from SHARP and other field campaigns. (Olaguer, 2011; 2012a,b; 2013; Olaguer et al., 2013; 2016a,b; 2017)

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High Resolution 3D Eulerian Air Quality Model

- Neighborhood scale 3D Eulerian grid model with its own **chemical mechanism for near-source applications** (48 gas phase reactions).
- **Very fine resolution** (20 s, 200 m horizontal) for simulating highly reactive species.
- Model has both **forward and adjoint** modes.
- Uses calculus of variations to perform **4D data assimilation and inverse modeling**.

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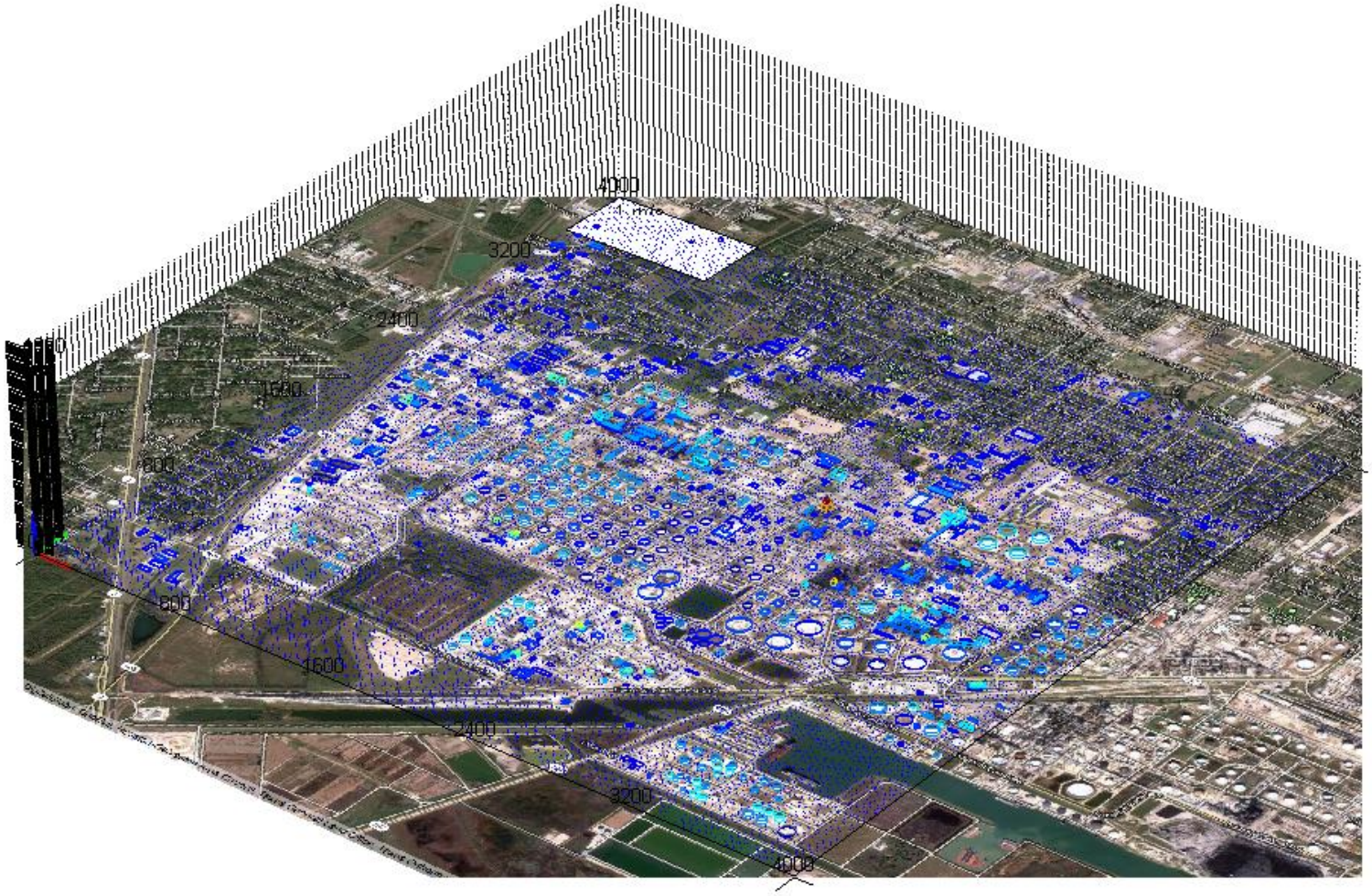
High Resolution Urban Wind Model



QUIC model used to simulate wind based on 3D LIDAR building morphology

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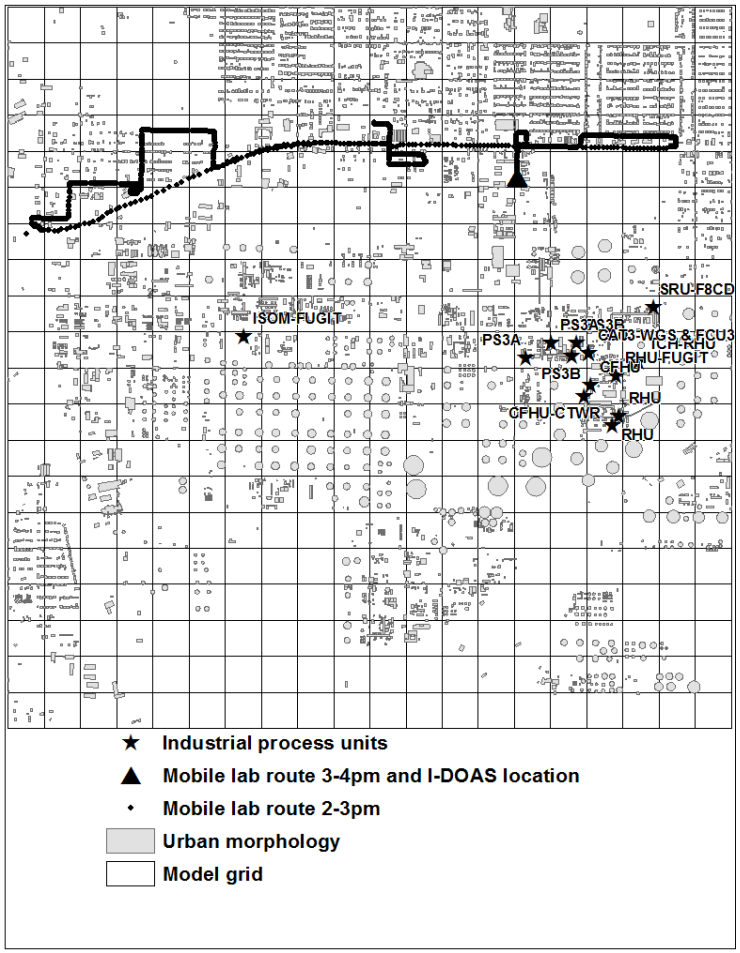
Formaldehyde Source Attribution for a Texas City Refinery



- Winds from QUIC model
- Inverse modeling based on mobile QCL measurements
- Emissions attributed primarily to fluidized cat cracking and desulfurization operations
- Formaldehyde emissions agree with I-DOAS remote sensing measurements (18 kg/hr)

Olaguer et al. (2013), *J. Geophys. Res.-Atmos.*, *118*, 11,317–11,326.

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Example 3: Underground Pipeline Leaks of Benzene

- **Benzene and other Toxics Exposure Study (BEE-TEX)** occurred during February 2015 in the Houston Ship Channel.

- Three mobile labs equipped with **Proton Transfer Reaction—Mass Spectrometry** (PTR-MS), plus GPS and meteorological measurements.

- **Real time source attribution and emissions quantification** (within 1 hr of measurements) based on high-resolution inverse modeling with a **3D microscale Eulerian grid transport model**.

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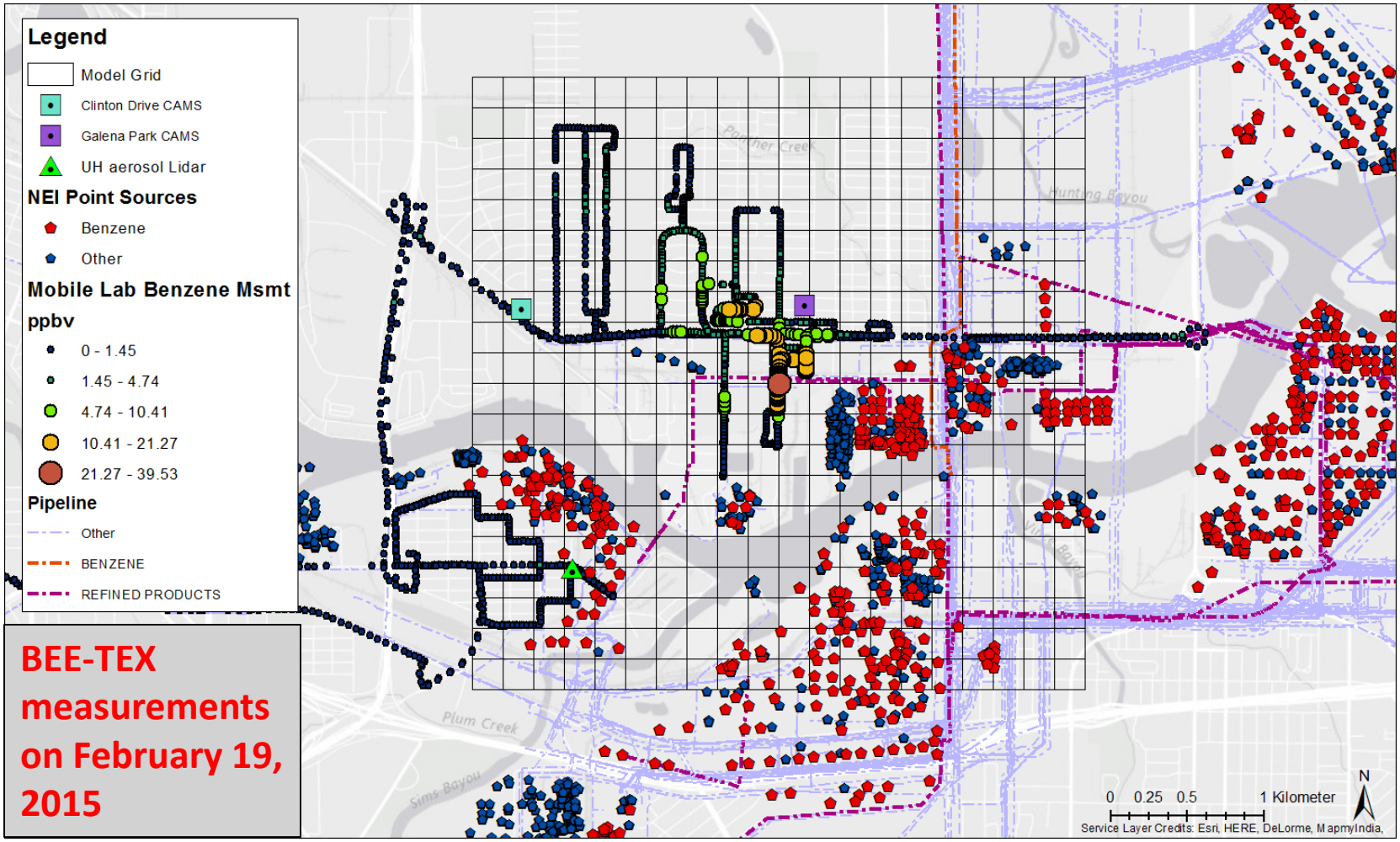
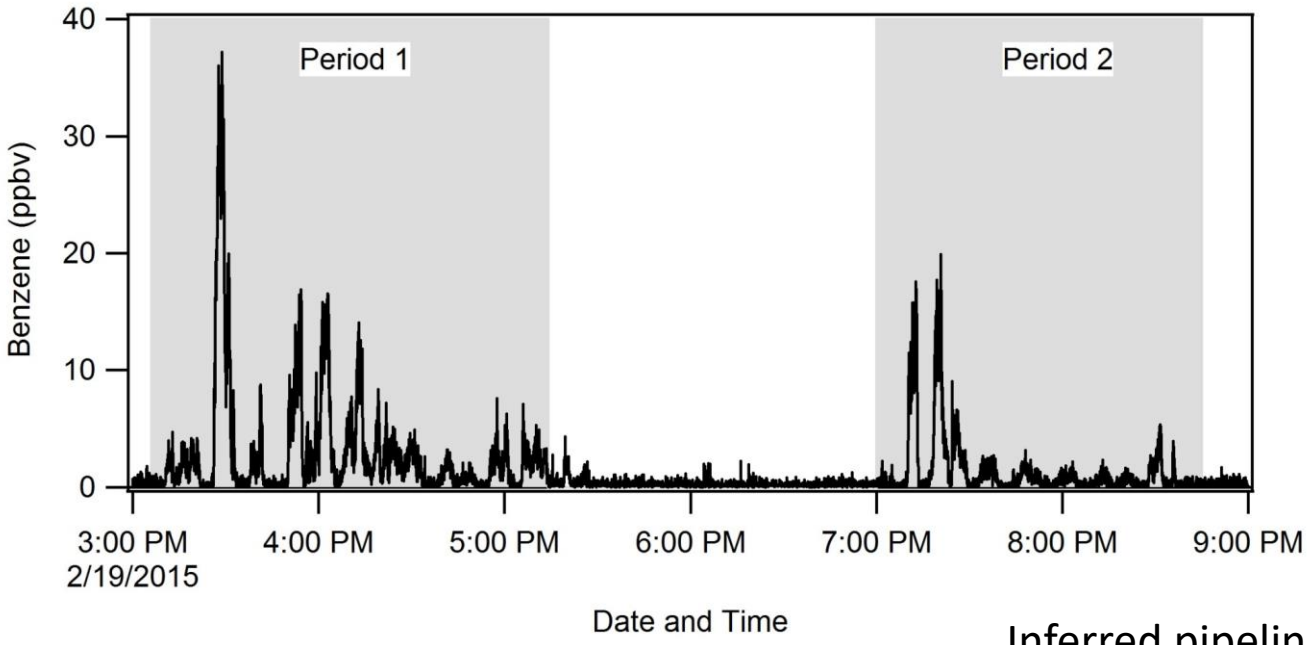
Pipeline Network, Point Sources, and Mobile Lab Measurements of Benzene in Galena Park, Texas



BEE-TEX measurements on February 19, 2015

BEE-TEX Mobile PTR-MS Measurements



Tanker at Kinder Morgan port terminal from 8:52 AM – 3:19 PM

Barges at Kinder Morgan port terminal from 4:23 PM – 6:41 PM

Inferred pipeline segment emissions were below the detection limit of helicopter-mounted IR cameras.

Feb 19, 2015 Galena Park Benzene Total Domain Emissions (kg/hr)

Time Period	Point Sources	Pipelines	Total Emissions
Afternoon	16.43	34.73	51.16
Evening	5.59	10.69	16.29
2011 NEI	8.27	0	8.27

Olaguer et al. (2016), *J. Air Waste Manage. Assoc.*, *66*, 164–172.

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Current and Future Work at EGLE

- New Python-scripted Gaussian plume inverse model with complex terrain capability for initial application to EPA mobile cavity ring-down spectroscopy measurements of CH_4 and H_2S at landfills.

- Inverse modeling of fugitive emissions from underground pipelines (natural gas, crude oil, refined product) in the Detroit metropolitan area based on mobile real-time measurements.

- Incorporation of inverse modeling results into very fine resolution air quality model runs for ozone attainment demonstration in the Southeast Michigan nonattainment area.

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