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Testing of Cerex Open-Path Ultraviolet Differential Optical Absorption Spectroscopy Systems for Fenceline Monitoring Applications

A&WMA Air Quality Measurement Methods and Technology - March 15-17, 2016, Chapell Hill, NC – Extended Abstract # 12

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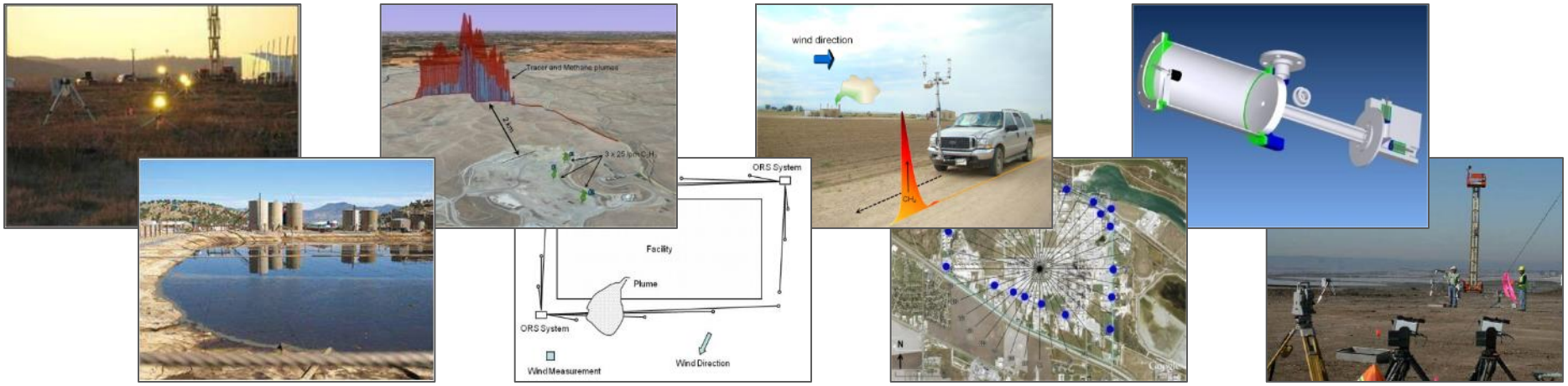
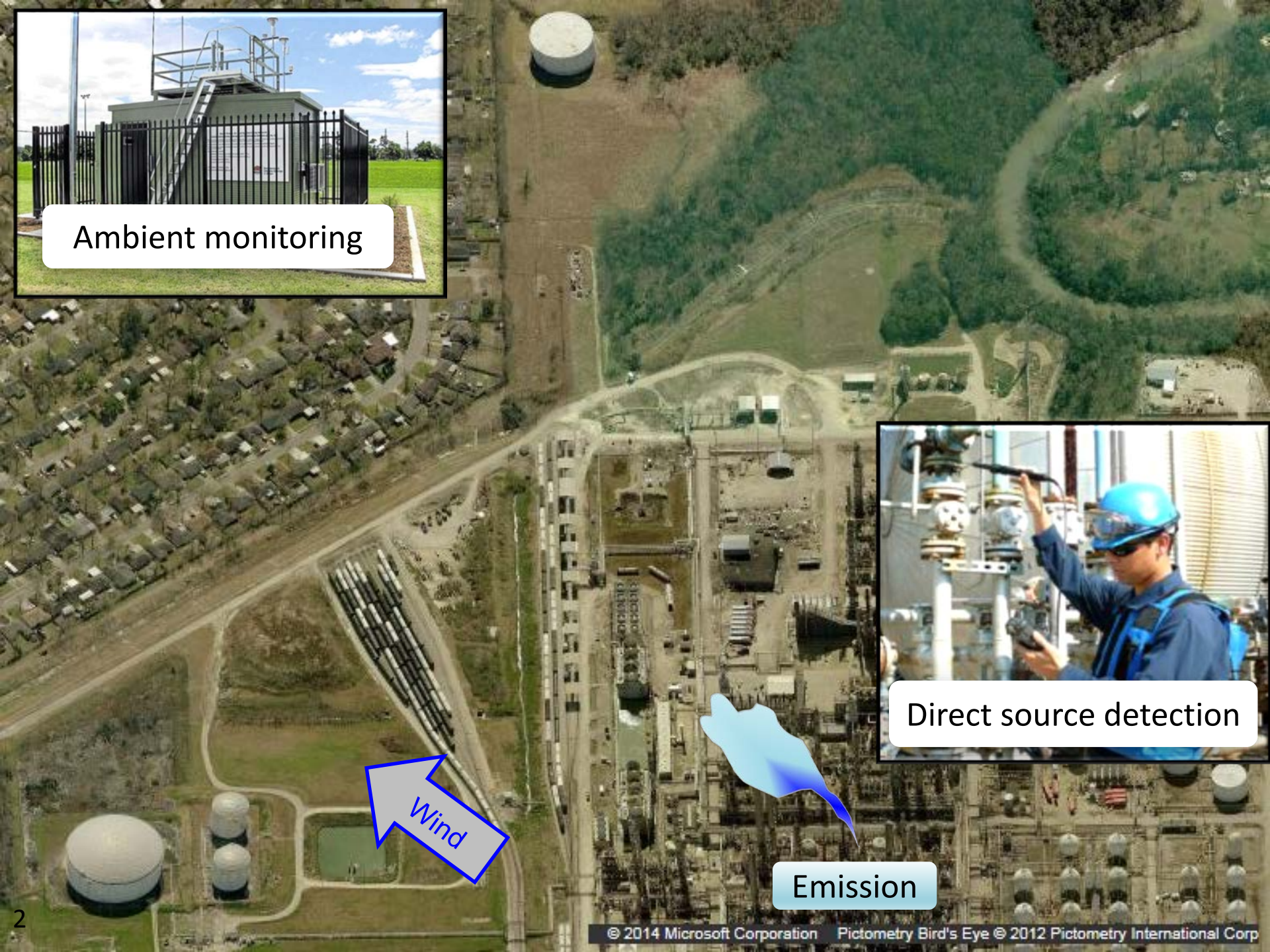


U.S. Environmental Protection Agency
Office of Research and Development

NRMRL Fugitive and Area Source Group
Source and Fenceline Measurements
Methods and Technology Development


Ambient monitoring
Direct source detection
Wind
Emission
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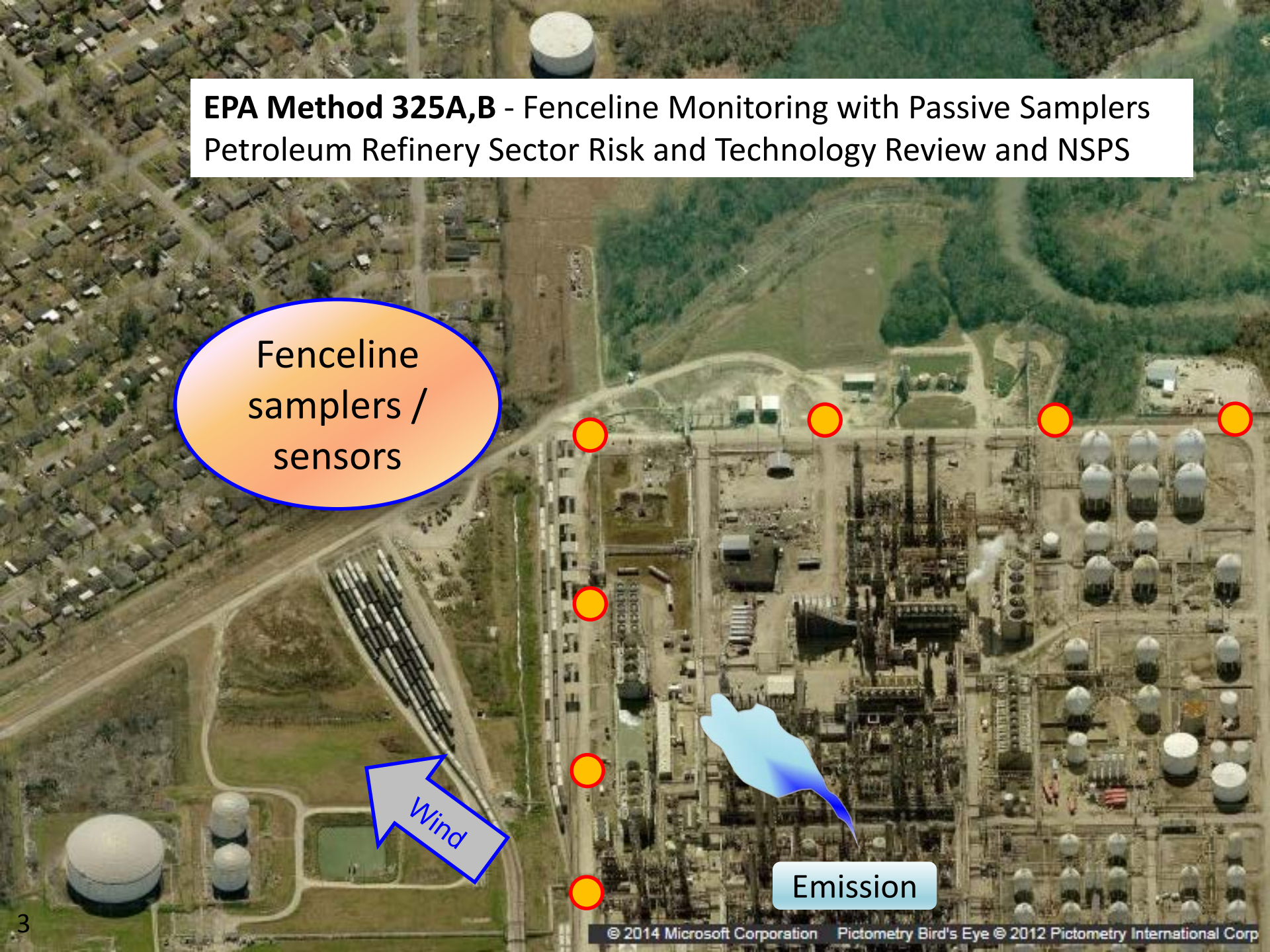
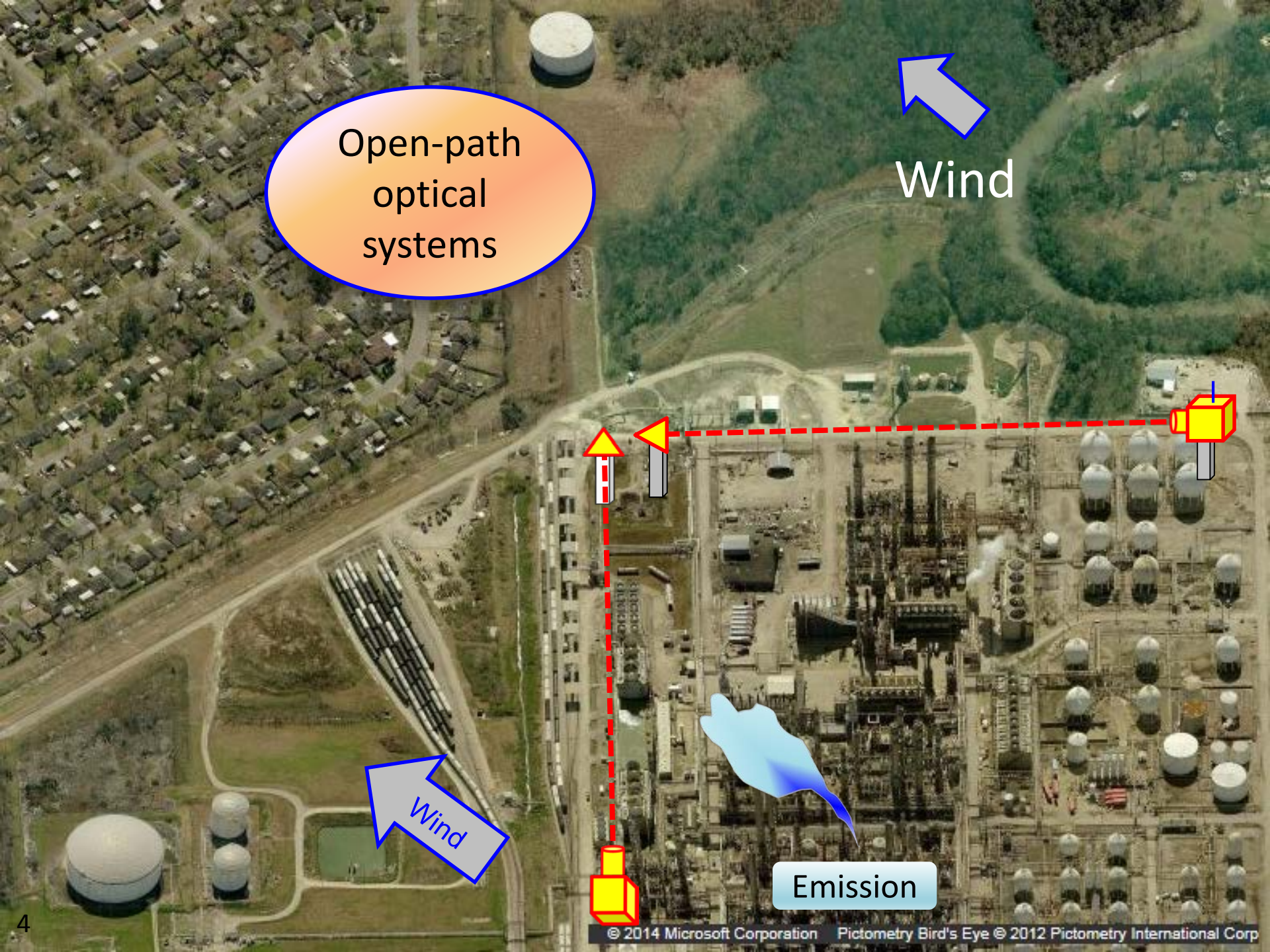
EPA Method 325A,B - Fenceline Monitoring with Passive Samplers
Petroleum Refinery Sector Risk and Technology Review and NSPS




Open-path optical systems
Wind
Wind
Emission
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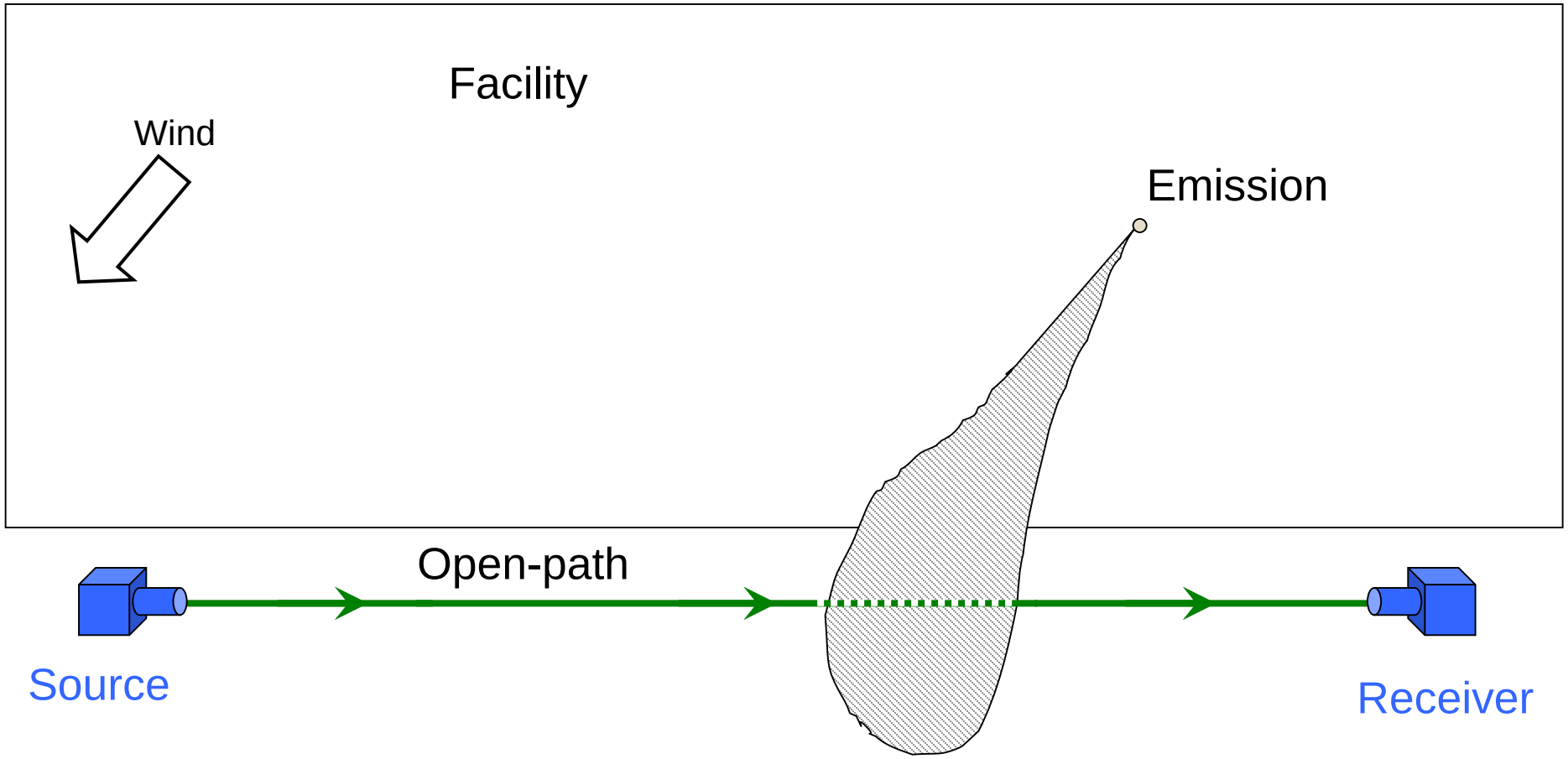
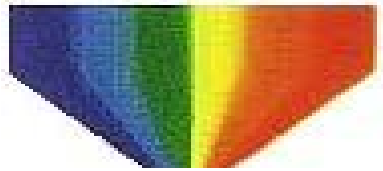
Project an optical beam light

Molecules absorb part of the optical spectrum



"fingerprint" spectral absorption

Open-path optical techniques



UV DOAS | TDL | FLIR | FTIR

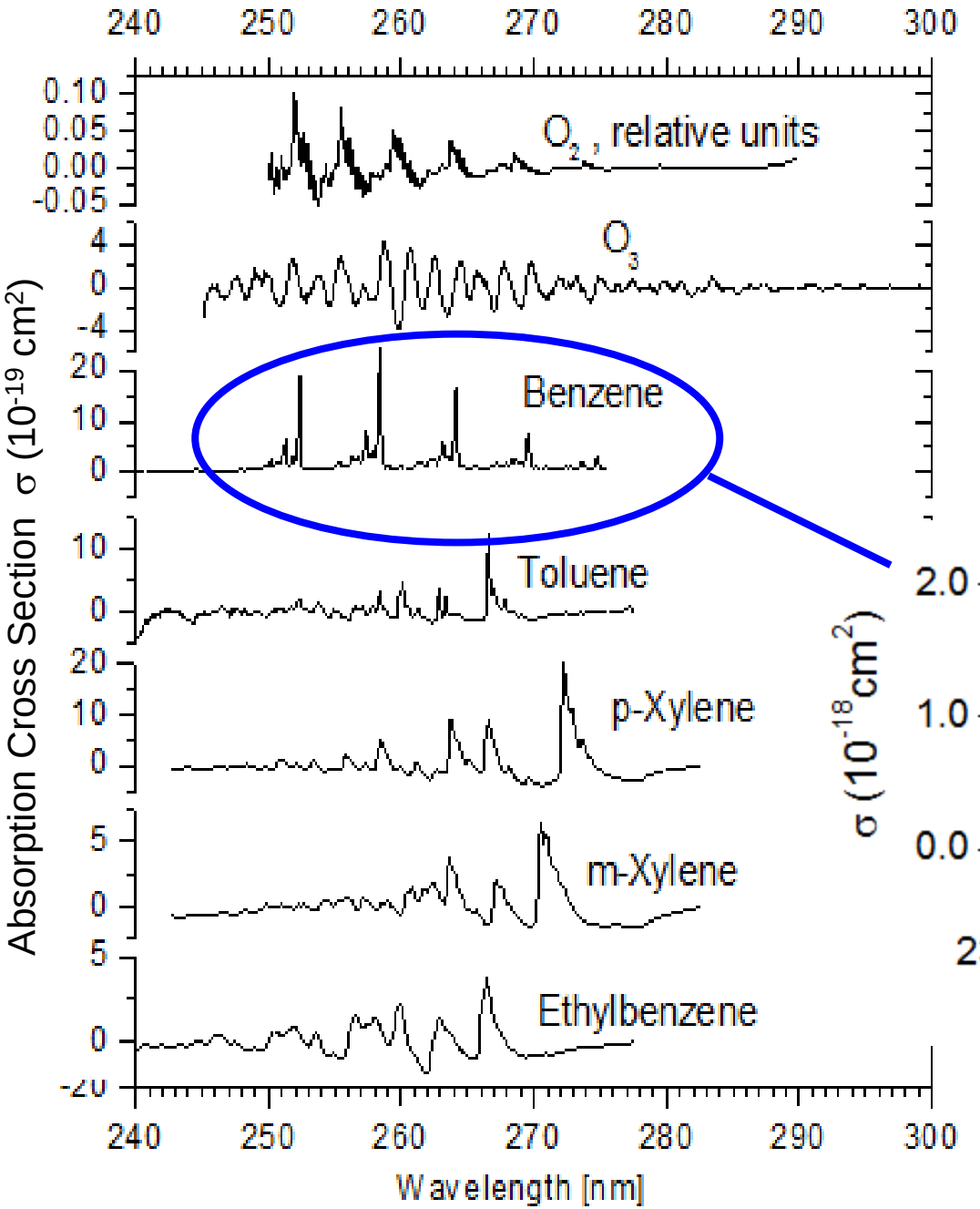
UV Differential Optical Absorption Spectroscopy (UV DOAS)

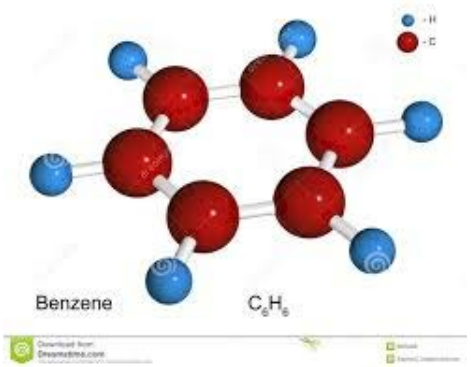
Tunable Diode Laser (scanning)

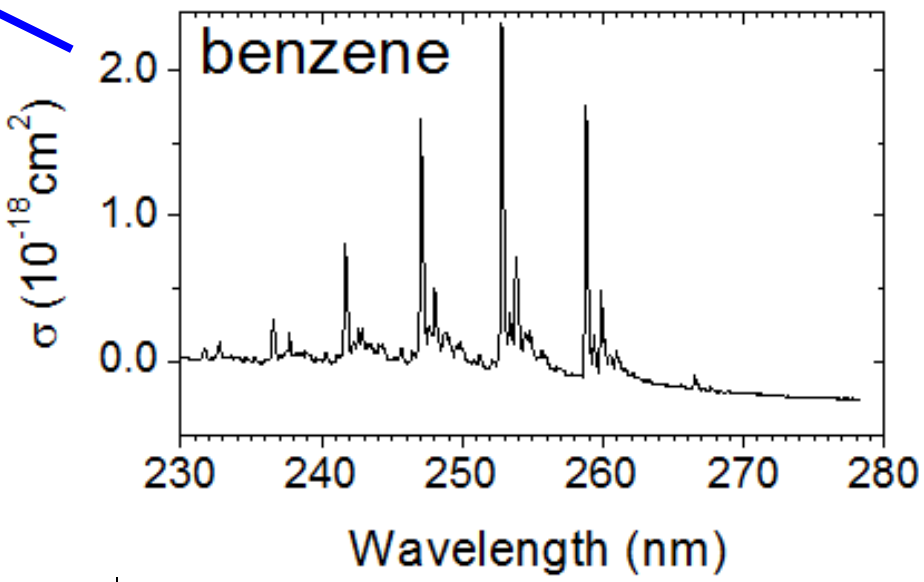
Forward-Looking InfraRed (leak imaging)

Fourier Transform InfraRed (scanning)

UV DOAS for benzene and BTEX*







*BTEX = benzene, toluene, ethylbenzene, m,o,p-xylenes

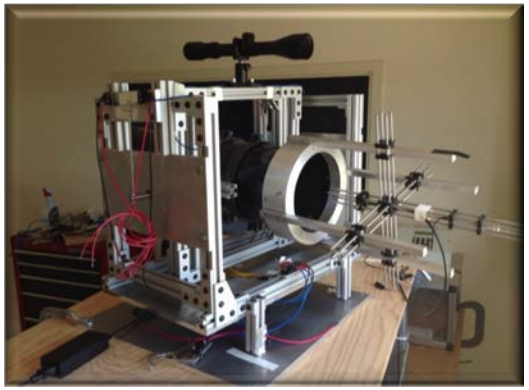
"Differential Optical Absorption Spectroscopy, Principles and Applications" U. Platt and J. Stutz, 2008 Springer-Verlag, Berlin, ISBN:978-3-540-21193-8

UV DOAS types

my perspective

Implementation cost

Research Grade
(e.g. J. Stutz – UCLA)



Commercial I
(e.g. OPSIS)

Commercial II
(e.g. Cerex)

Lower

Measurement performance

Examples of two Cerex systems for benzene

GD12

General use, **d**euterium source, 20**12**

Current deployment by City of Philadelphia AMS

- General use (multi-component)
  - Acetaldehyde, ammonia, 1,3-butadiene, formaldehyde, nitrogen oxide, sulfur dioxide, styrene, trimethylbenzene, BTEX, others
- Deuterium lamp
  - Lower power (lower S/N)
  - Deeper UV (access more compounds)
- 2012 technology
  - Older sensors (lower S/N)
  - Less advanced analysis
- Deployment near a refinery in Philly
- Optical cell calibration measurements in in Summer 2016

FX15

Fenceline use, **x**enon source, 20**15**

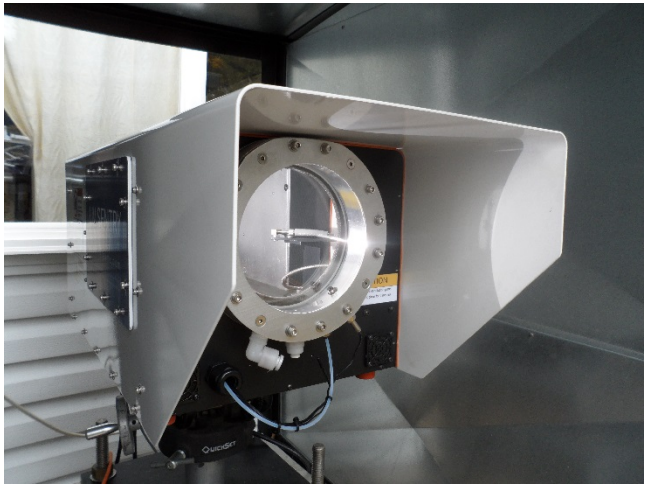
Prototype at EPA test range

- Fenceline optimized
  - Benzene (this study)
  - BTEX also possible with this setup
  - Other configurations are possible
- Xenon lamp (BTEX-optimized)
  - Higher power (higher S/N)
  - Power-optimized to 250 nm band (can't detect many compounds)
- 2015 / 2016 technology
  - Newer sensors (higher S/N)
  - New benzene-specific analysis
- Optical cell calibration at RTP test
- Hopeful for field deployment in 2016

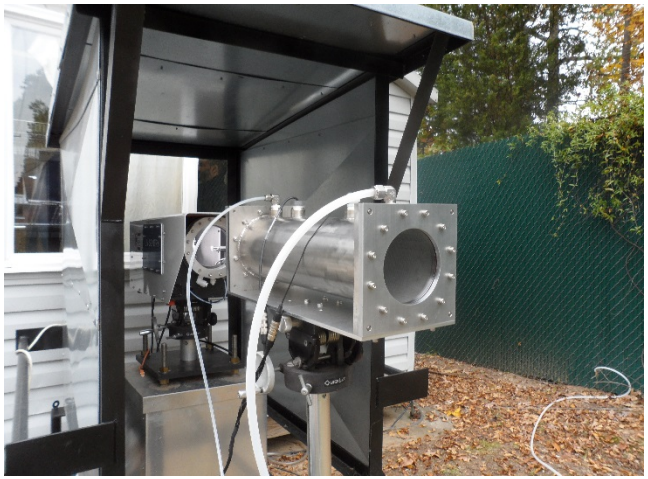
GD12 in South Philly

Deployed by City of Philadelphia Air Measurement Services (AMS)

FX15 at EPA Test Range



326 m to optical path



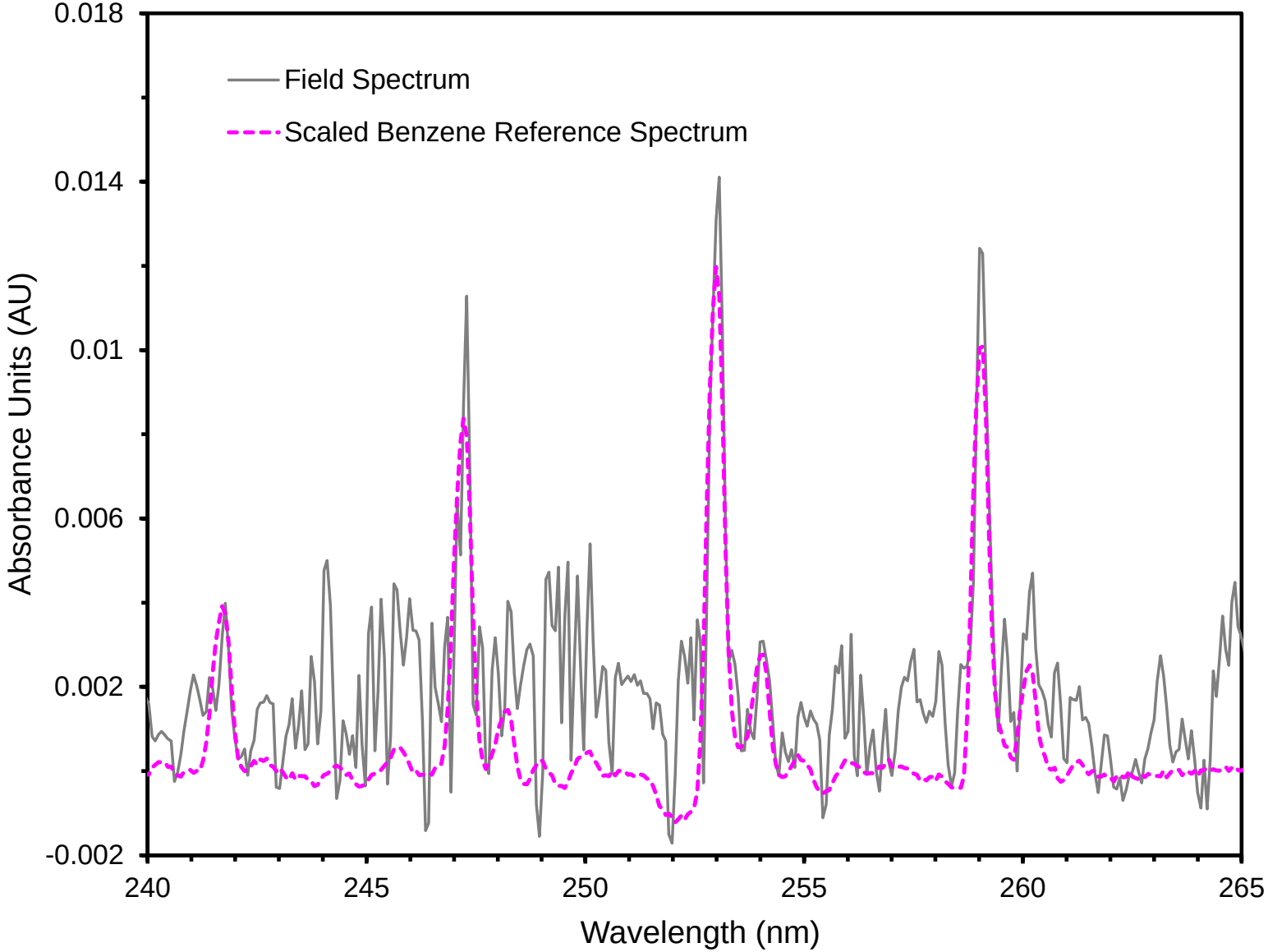
Method Detection limit (MDL)

What is the benzene MDL for the GD12 and FX15 systems?

- How to define MDL?
  - Depends in part on information provided by the system
  - Signal to noise ratio (SNR) limit
  - Interference limit (e.g. O_2 and ozone for benzene)
- Information provided by the system
  - Some variant of multicomponent classic least squares (CLS) analysis with synthetic (mathematically generated) or dynamically selected background reference
  - Dynamic background selected from "near in time" field spectra provides the best interference cancelation
- Effective system signal to noise ratio (SNR)
  - Determined benzene path averaged concentration (signal)
  - Standard deviation (σ) of residual in 275 nm to 276 nm window (noise)
  - **SNR > 3σ**
- Spectral fit quality (interference limit)
  - Software does not provide CLS residuals
  - Pearson correlation coefficent (R^2) of reference and determined spectra
  - **R^2 > 0.70**

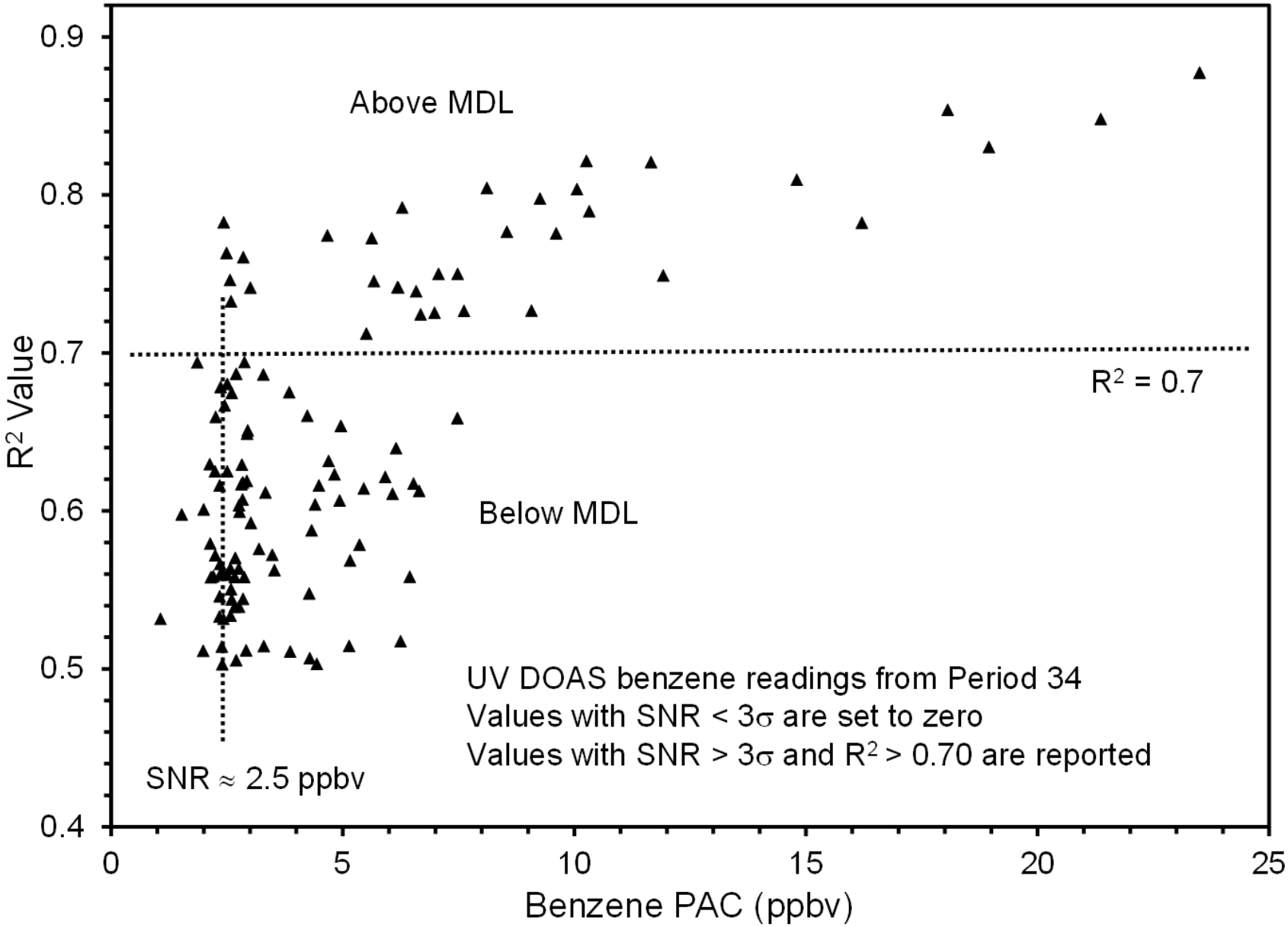
GD12 Benzene Field and Reference spectra (24 ppb)

acceptable SNR and R^2 values



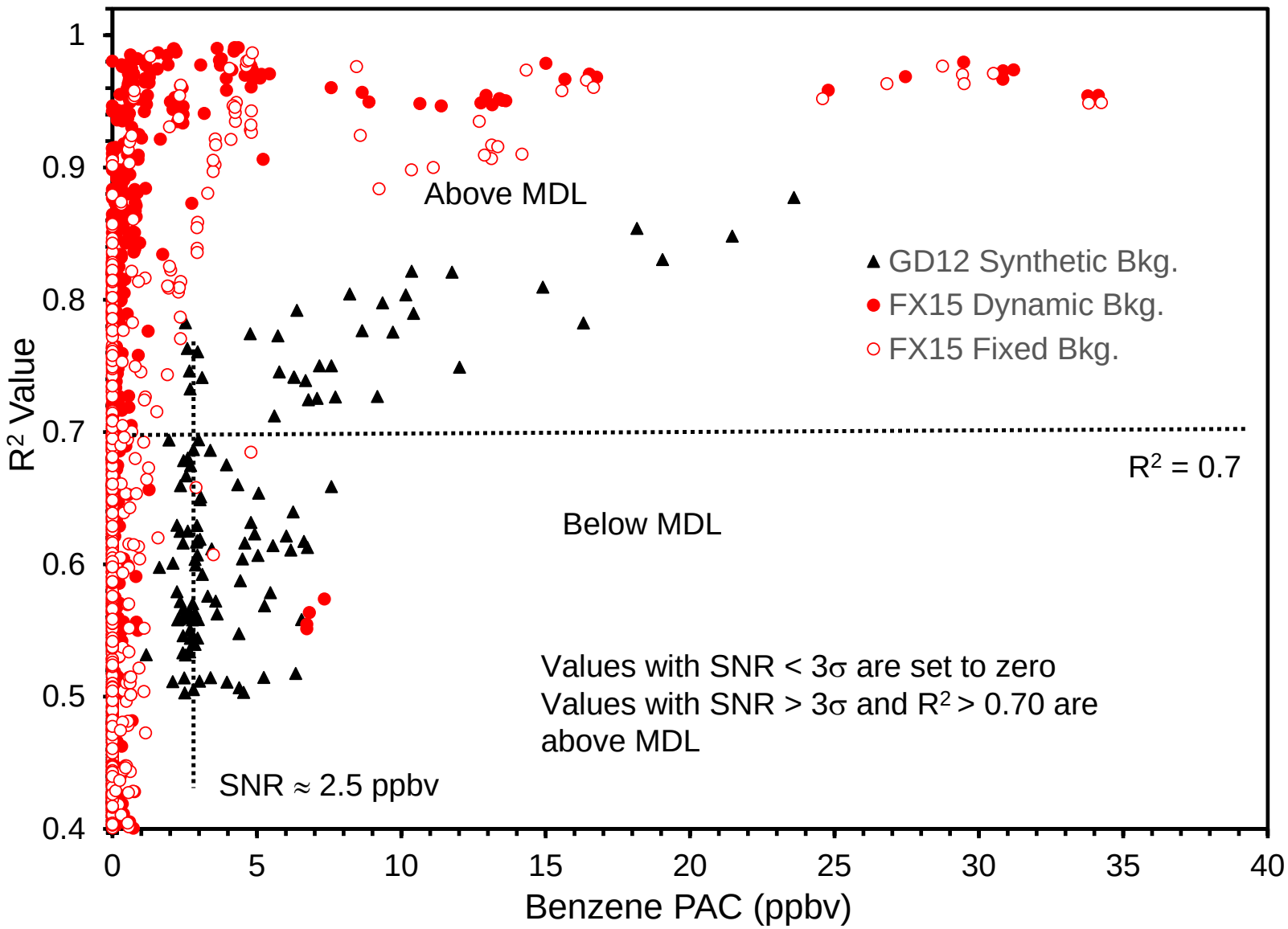
GD12 Benzene Data in Philadelphia

5 minute average over one day - not typical



GD12 and FX16 Benzene Test Range Data

similar optical paths ~ 325 m



What we have learned so far?

- Lower cost commercial UV DOAS units continue to improve
- Newer, optimized systems can achieve lower benzene detection levels
- Benzene MDLs < 1 ppbv are possible with optimized systems
- Dynamic background subtraction is important for low MDLs
- Progress is being made to automate analysis
- Work continues (other vendors welcome)

Thanks!

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