Continuous Air Emissions Monitoring Using Ultraviolet Differential Optical Absorption Spectroscopy and Auto-Gas Chromatography

Ignacio Gallardo, Mark Modrak
AECOM
Austin, Texas

CONFERENCE
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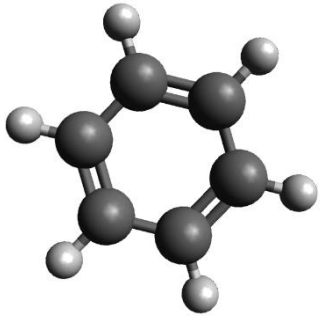
Background

Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards

- Final rule published by EPA on December 1, 2015
- As part of the rule, refineries must implement benzene emissions monitoring program along facility fenceline using diffusive passive samplers
- Facilities were required to have a fenceline monitoring program in place by January 2018.



Background

Benzene Fenceline Monitoring with Diffusive Passive Samplers (EPA Method 325 A/B)

- Deploy multiple diffusive passive samplers around perimeter of facility along fenceline
- Samplers deployed for a period of two-weeks, then sent to lab to be analyzed for two week-integrated benzene concentration
- Difference between the highest and lowest benzene concentration observed along fenceline is calculated for each period
- Yearly average must be below 9 µg/m^3 or 2.8 ppbv

Alternative Fenceline Monitoring Approaches

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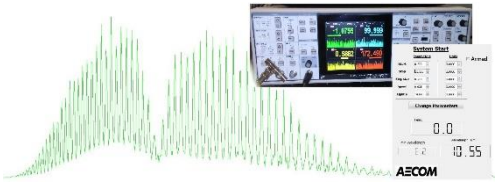
Alternative Fenceline Monitoring Approaches

- EPA rule allows operators to implement alternative fenceline monitoring approaches to account for offsite upwind sources, or identification of sources from within facility that are excluded from the rule
- Alternative methods must meet the following criteria:

- *Sufficient benzene detection limits (well below action levels)*
- *Sufficient data resolution-* ***Time-Resolved Data is Key!***
- *Coupled with wind speed and wind direction data*
- ***Cost-Effective (from site operator's perspective)***



2 Potential Alternative Monitoring Approaches

- The challenge is to identify monitoring approaches that meet as many of the necessary criteria as possible (e.g. low benzene detection limits, temporal and spatial data resolution, proven track record, cost-effective)

- **Open-Path UV-DOAS**

- **Auto-Gas Chromatography**

Open-Path Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS)

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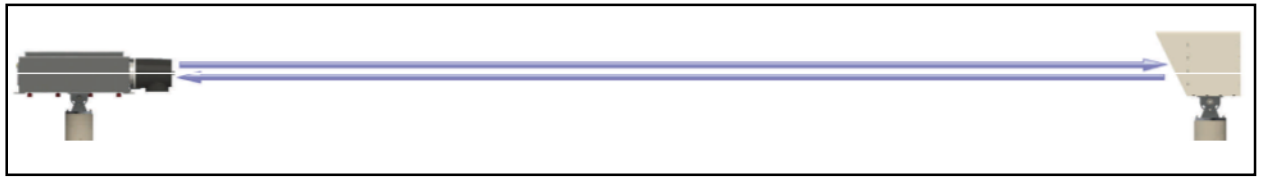
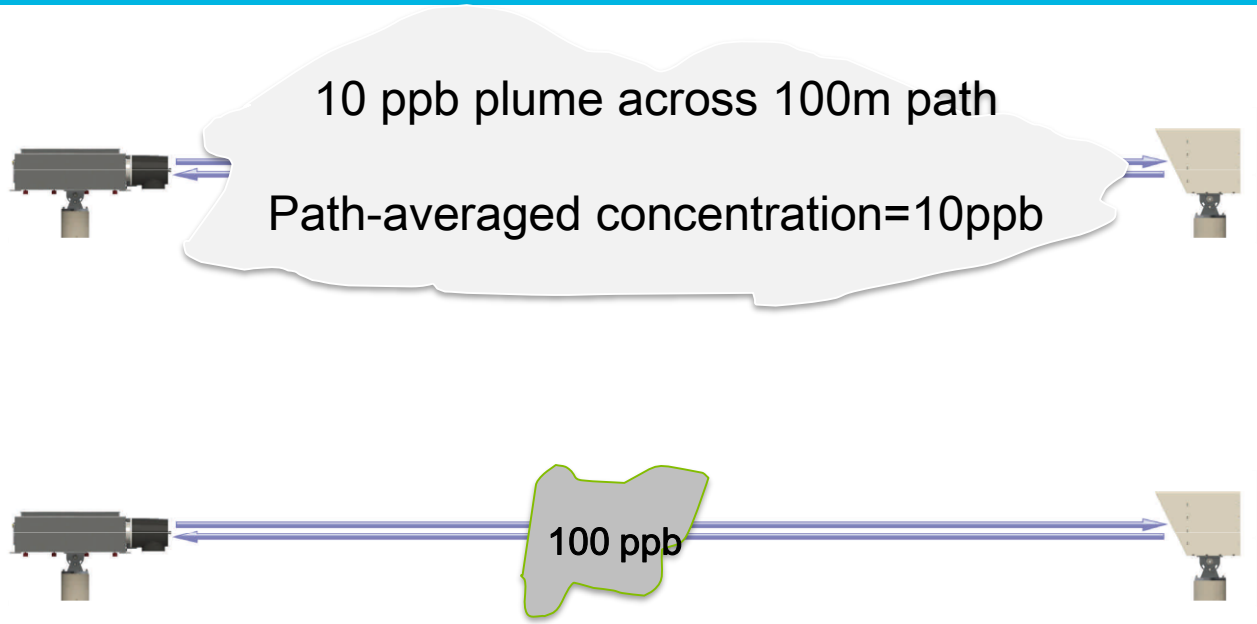
Open-Path UV-DOAS

- Source/Detector deployed at one end of configuration with retro-reflecting mirror deployed at opposite end of configuration
- One-way path length of 100 m to 1 km
- Signal is aligned and optimized on mirror, better stability and data capture with investment in site infrastructure (especially if plan on permanent installation)
- Collects path-integrated benzene concentration, averaged over 30s to several min

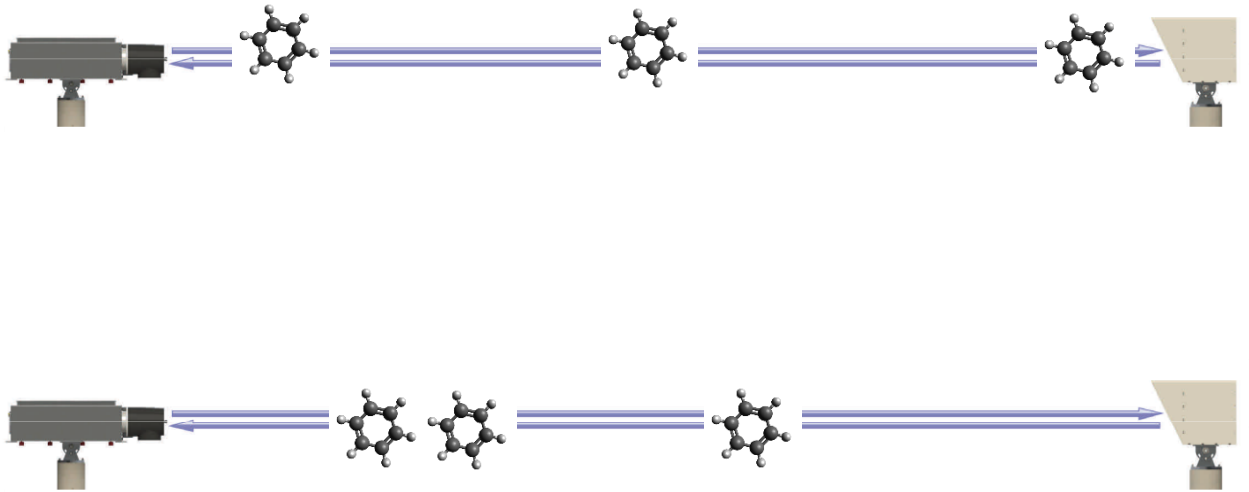


Open-Path Measurements



100 ppb over 10m of the 100m path will also result in a path-averaged concentration of 10 ppb

Open-Path Measurements



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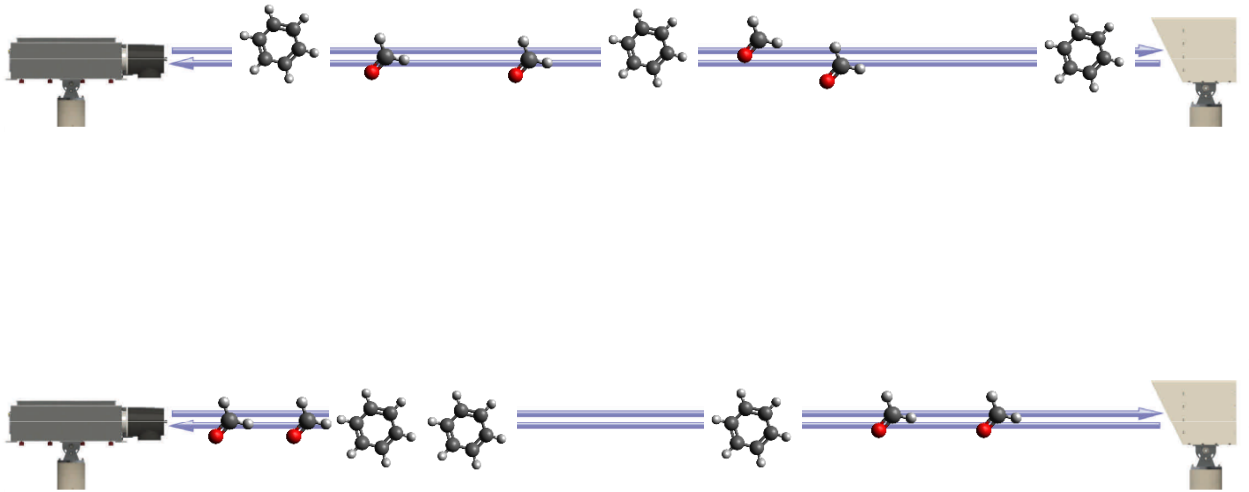

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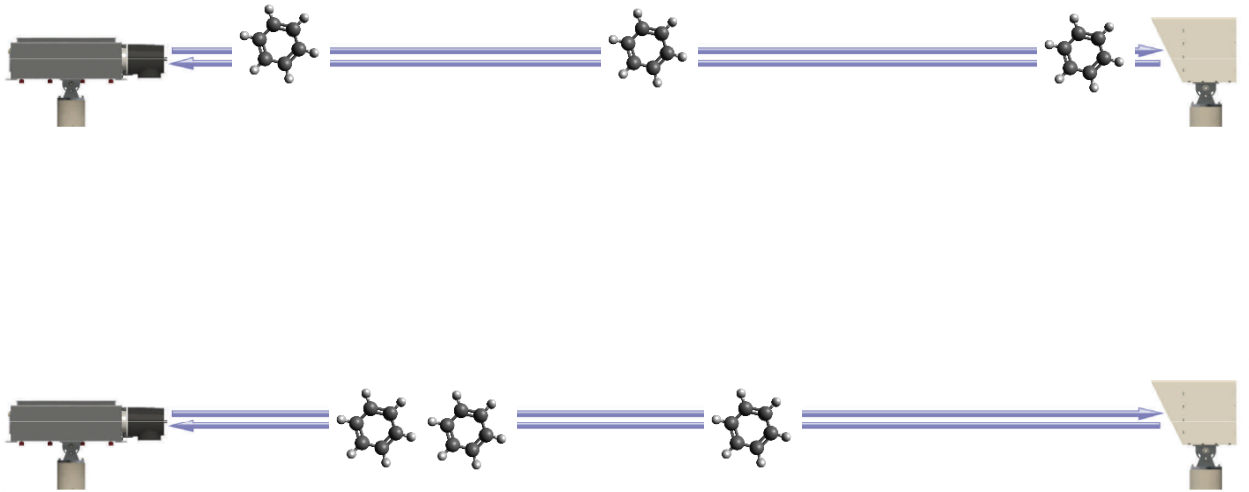

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Open-Path UV-DOAS

Advantages

- Superior spatial coverage (plume capture)
- Sufficient temporal resolution (updates as rapidly as every 30 seconds)
- Established approach with approved measurement methods
- Sufficient benzene sensitivity (as low as 300 pptv)

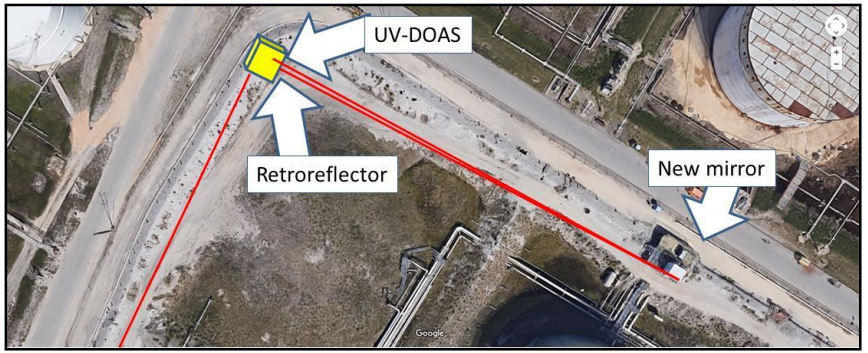
Limitations

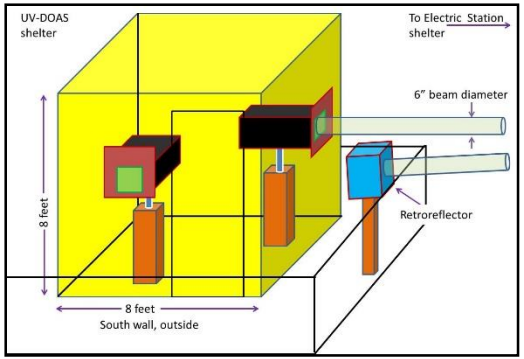
- Can be costlier than other methods due to site infrastructure requirements
- Although data analysis is largely automated, best to have a Spectroscopist to verify results and optimize analysis methods

Example UV-DOAS Instrument Shelter

Example Active Fenceline Monitoring Project

- Data is being used to identify near-field benzene sources, and potential leaks within the facility
- Facility is planning to submit a Site-Specific Monitoring Plan to US EPA that includes the data generated by UV-DOAS
- Instruments have been collecting data continuously for almost 2 years, with very little downtime
- Maintenance trips conducted every 3 to 6 months





Auto-Gas Chromatography

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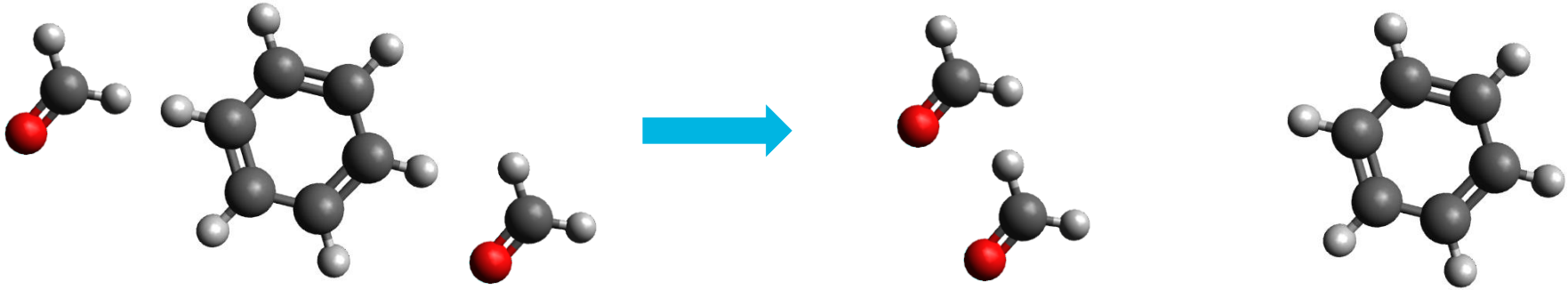
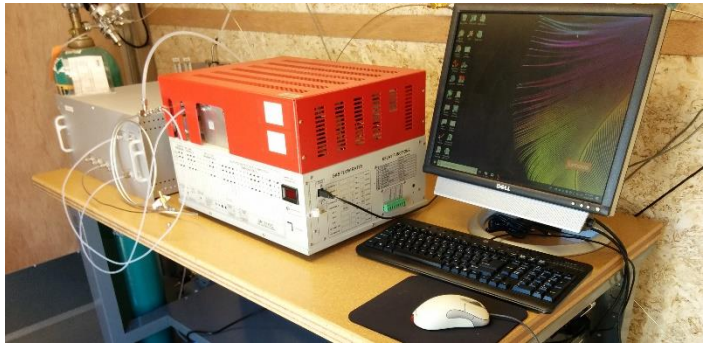
Auto-Gas Chromatography

- Air sample pulled through a pump into instrument
- Fixed sample location, housed in climate-controlled instrument shelter
- Capable of analyzing for multiple compounds simultaneously
- Proven technology with good track record (instrument currently deployed as part of regional air monitoring networks in Texas)



Auto-Gas Chromatography

- Fixed and mobile stations



Auto-Gas Chromatography

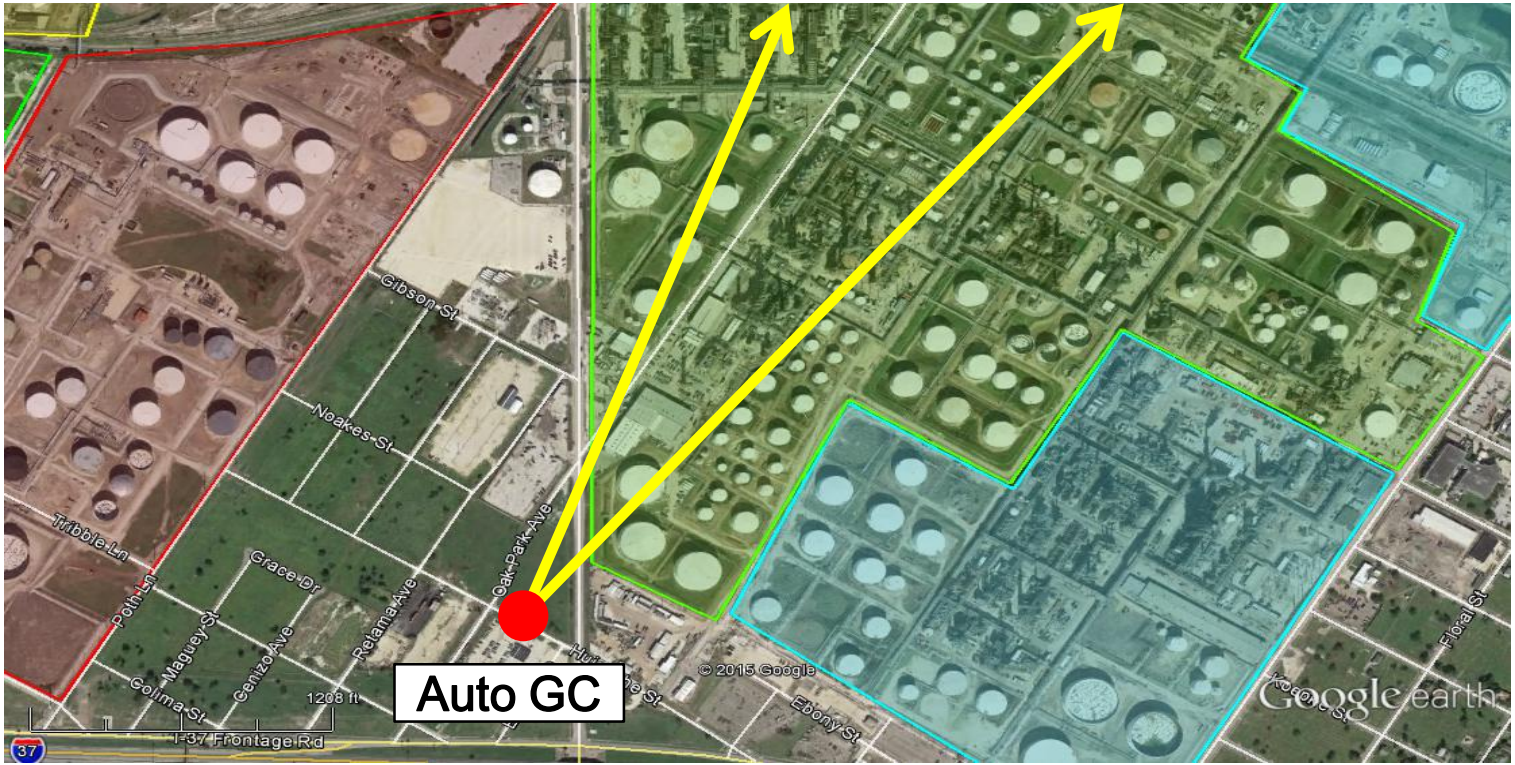
Advantages

- Very low measurement sensitivity for most compounds, including benzene
- Robust
- Relatively easy to operate, with minimal regular maintenance needed

Limitations

- Measurement from a single point, so relying on favorable winds for plume capture
- Deployment of a sufficient number of instruments to document offsite sources potentially costly

Example Auto GC Configuration



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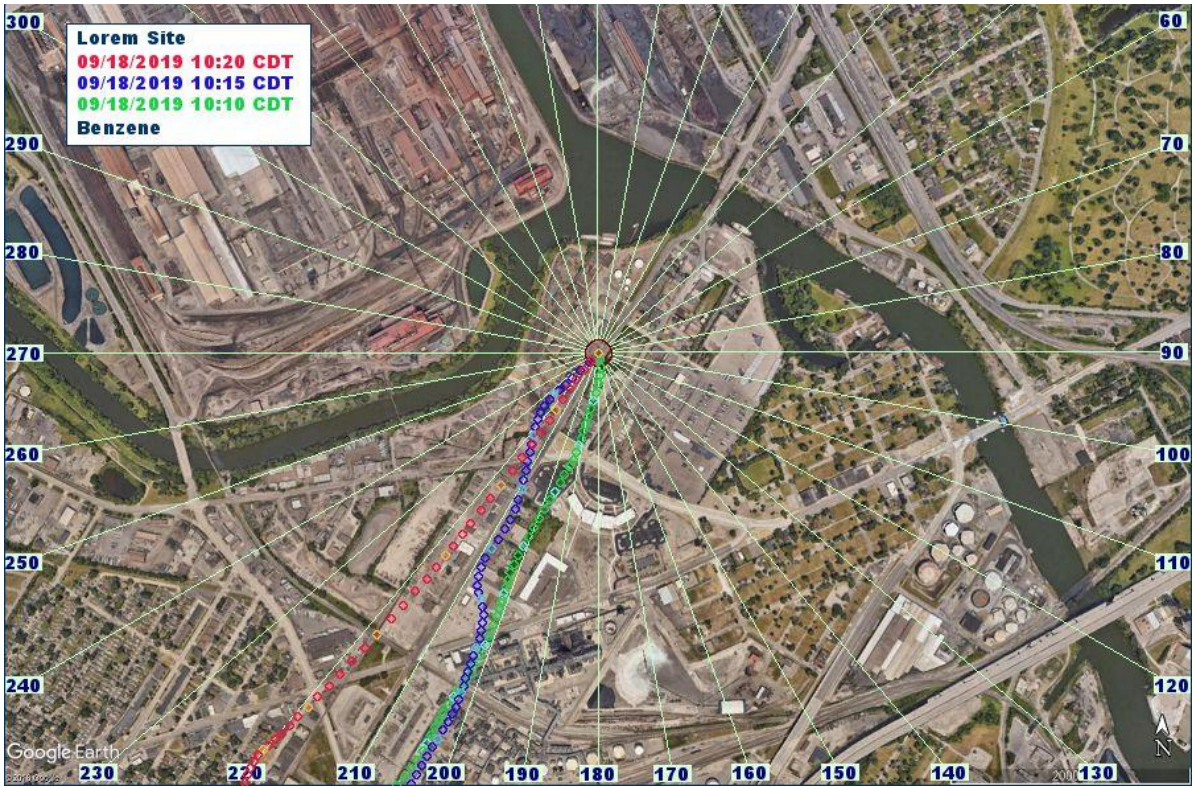
Identifying Source Location and Strength Using Auto GC Results

Lorem Ipsum-Center, 09/18/2019 10:20 CDT, Benzene: 167.6 ppbv, WS: 9.5 mph, WD: 202°



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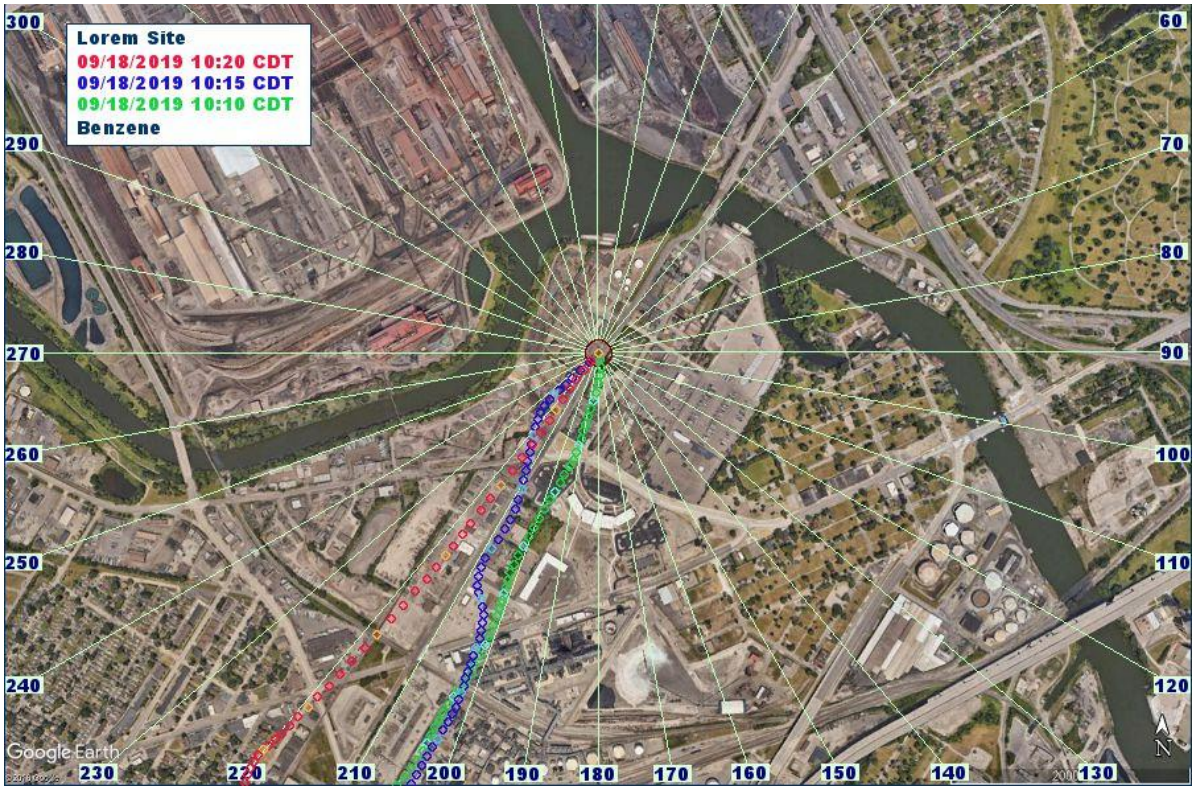

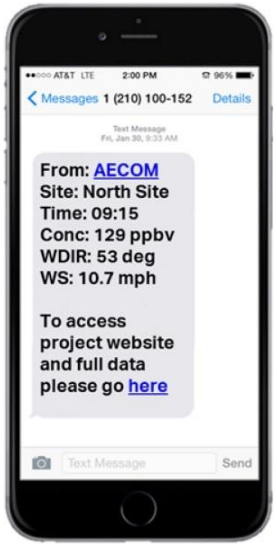

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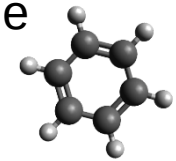
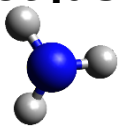
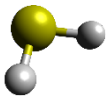
Summary

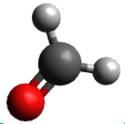
- Final Refinery Sector RTR/NSPS Rule published by EPA on December 1, 2015
- Rule allows operators to implement alternative fenceline monitoring approaches to account for offsite upwind sources, or sources excluded from the rule
- Alternative methods must meet several criteria, including sufficient measurement sensitivity and temporal resolution, be an established approach with a good track record, and cost-effective to implement
- Open-Path UV-DOAS and Auto-Gas Chromatography are two viable methods for documenting emissions from offsite sources or emission locations within the facility



- **These measurement methods can be applied at a variety of different facilities-not just refineries, to measure a wind range of pollutants-not just benzene**








Thank You!
Ignacio.Gallardo@aecom.com
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