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Field and Mobile Measurements of Air Toxics Using Thermal Desorption, Broadband Cavity Ring-Down Spectroscopy

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Jake Margolis, Anthony Miller, Ph.D.

Prepared for the Environmental Measurement Symposium
in Garden Grove, CA on Monday, August 5th

Entanglement Technologies, Inc.
1192 Cherry Avenue
San Bruno, CA 94066

Agenda

- Introduction to thermal desorption, cavity ring-down spectroscopy
- AROMA for ambient air monitoring of hazardous air pollutants
- Mobile monitoring applications
- Stationary monitoring applications
- Summary and future projects

Entanglement Technologies is advancing quantum machines by building precision chemical monitoring equipment that push the limits of laser, cavity, electronic, and signal processing performance. AROMA, the best-in-class trace gas and vapor sensor, is our flagship product and was deployed for the first time in 2017.

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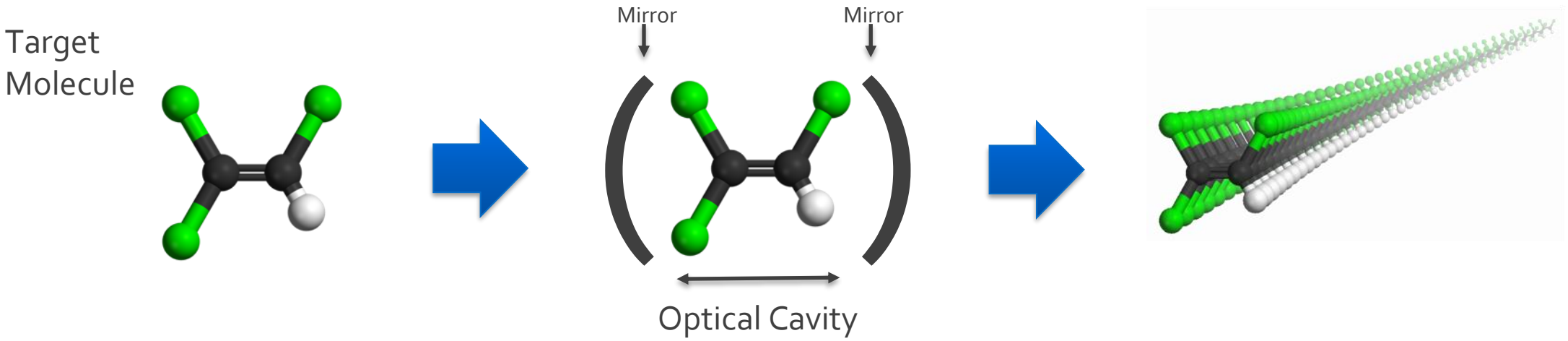
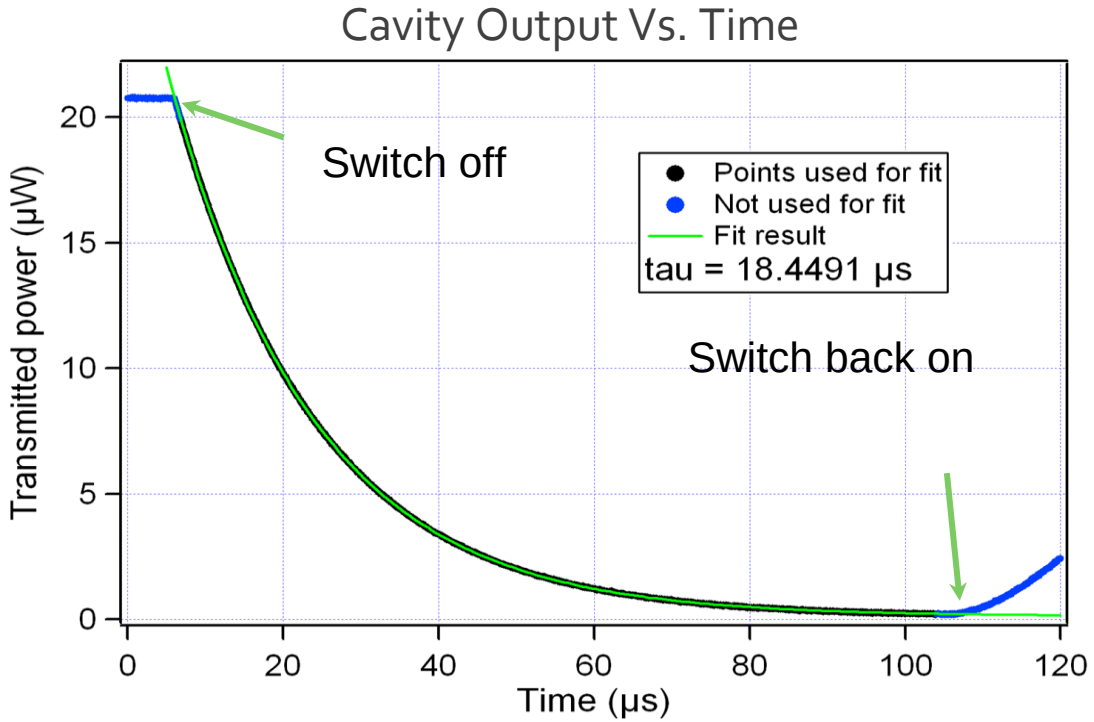
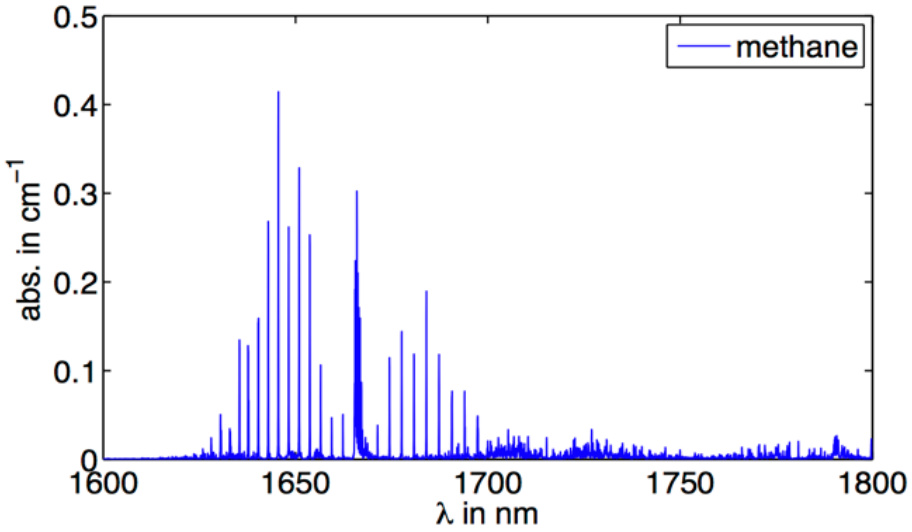
Cavity Ring-Down Spectroscopy





- Absorbance Enhancement by cavity finesse
- Minimum detectable absorbance length:
  - **10x distance to the moon.**
- Absorbance determined by measuring "Ring-down" time
- 1.6e10^{-12} $\mathrm{cm}^{-1}/\sqrt{\mathrm{Hz}}$

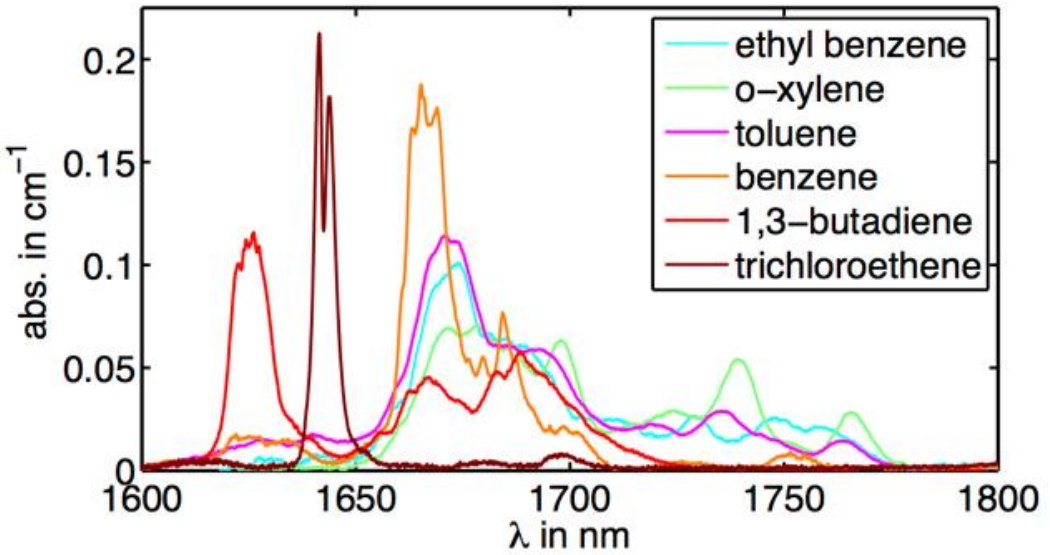
30 Seconds of Spectroscopy



Small molecules have sharp absorption peaks easily distinguished from sharp peaks of other small molecules.

Identify via wavelength scan

High density of states collapses discrete structure into broad bands



Simulated Data Generated by HITRAN; experimental data from PNNL Infrared Database

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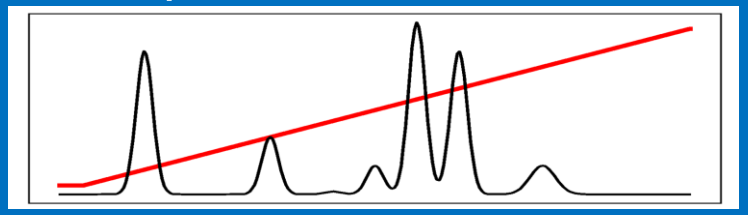
Thermal Desorption - CRDS

Separation Front End



Ramped thermal desorption chemical concentration and separation: Robust, fast, stable.

- > 10k cycles
- Insensitive to O_2, H_2O

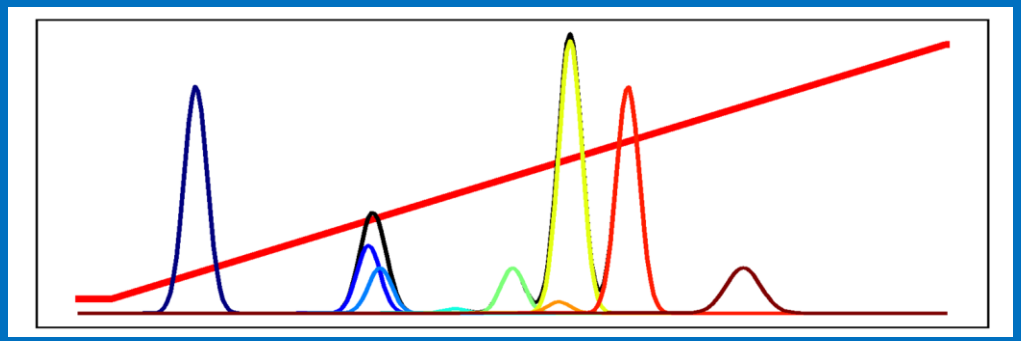
Inlet

- Direct/Air manifold
- Purge and Trap system

Embedded Instrument Management

- Proprietary FPGA based laser management
- Real-time data acquisition and management
- High precision analog and digital servo systems
- Internal library and automatic result processing

Tunable laser + CRDS Core



Rapid broadband spectroscopy eliminates need for complete separation and allows speciation.

- > 500 nm/sec tuning over ~100 nm.
- 50% duty cycle cavity locked CRDS
- Proprietary electro-optical servos and laser design provide robust performance in harsh vibrational environments
- MDAL as low as 1.2 x 10^{-12} $cm^{-1}/\sqrt{Hz}$

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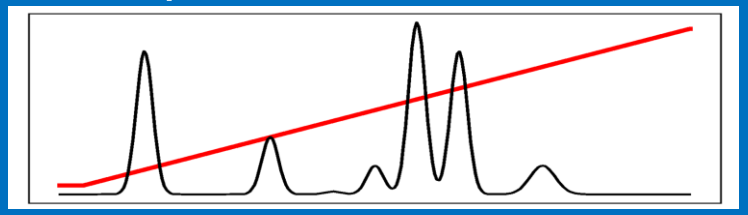
Thermal Desorption - CRDS

Separation Front End



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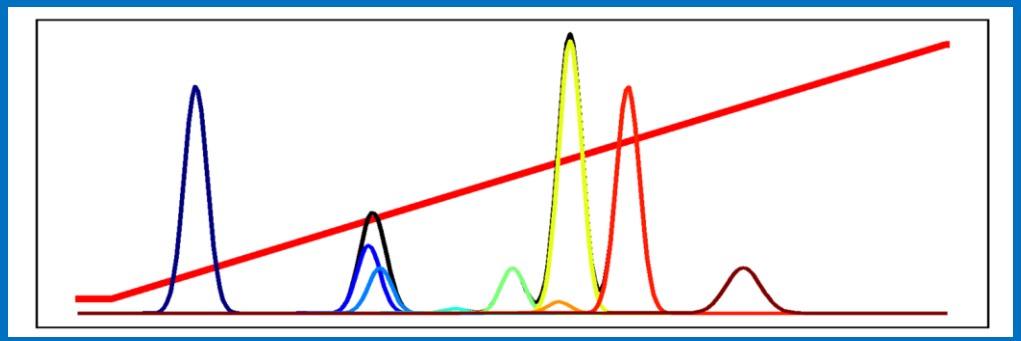

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RapidScan Mode – Direct CRDS

- Perform direct, whole atmosphere analysis for rapid source location
- Core operated at 300 torr, 100 sccm flow
- Results are classifications, not positive identifications
- Small molecules can be positively identified

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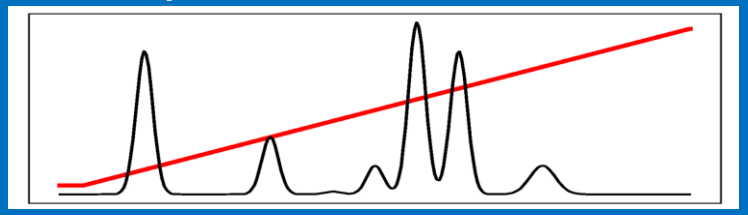
Thermal Desorption - CRDS

Separation Front End



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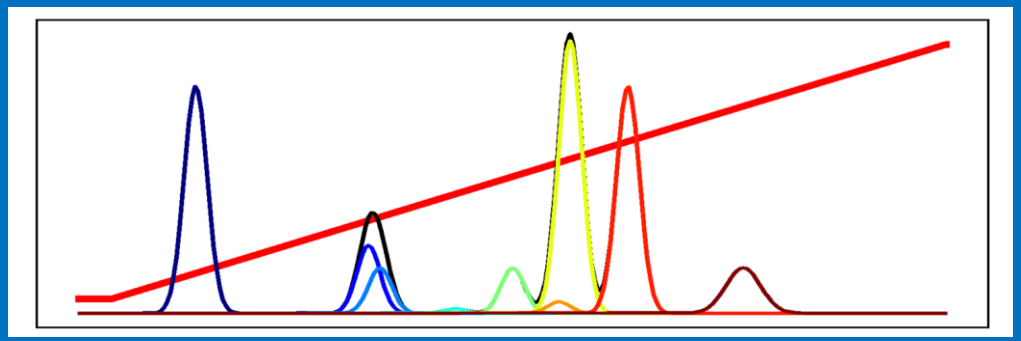

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LabScan Mode – TD-CRDS

- Collect a controlled volume atmospheric sample (up to 10L permissible)
- Concentrated sample for low detection limits
- Remove light molecules (particularly water)
- Provide GC-like chemical separation for speciated analysis

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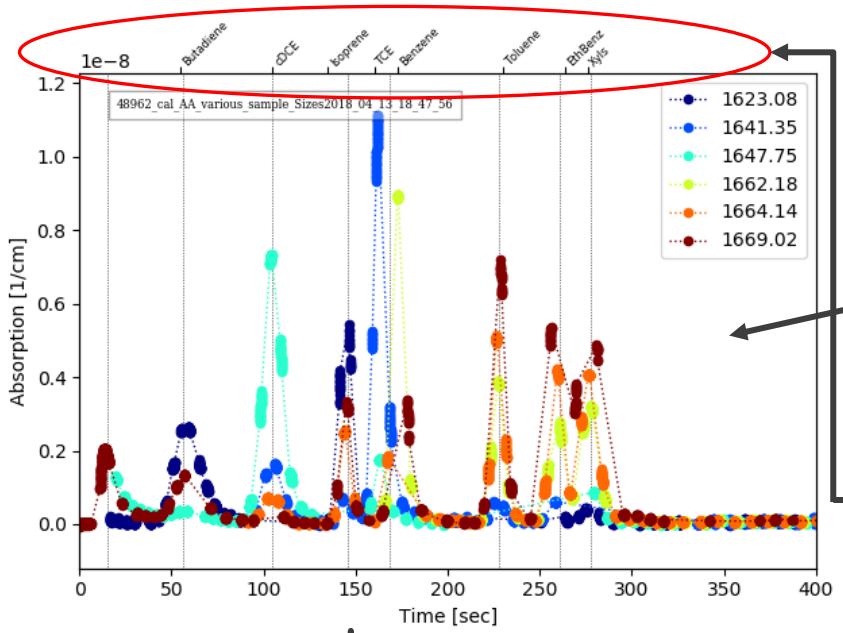
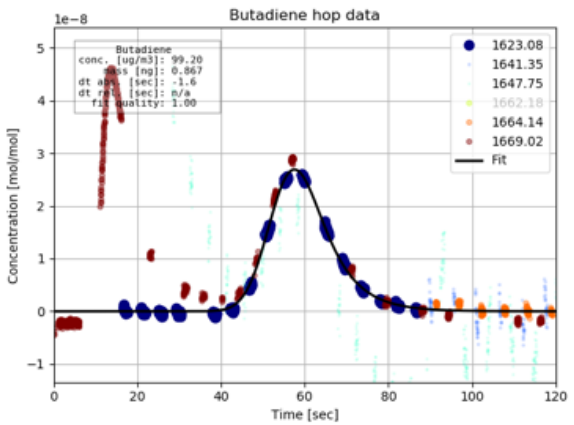
Multispecies Hopping: Real Data

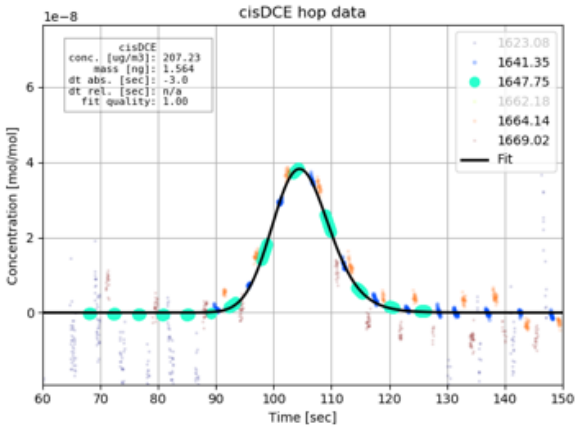


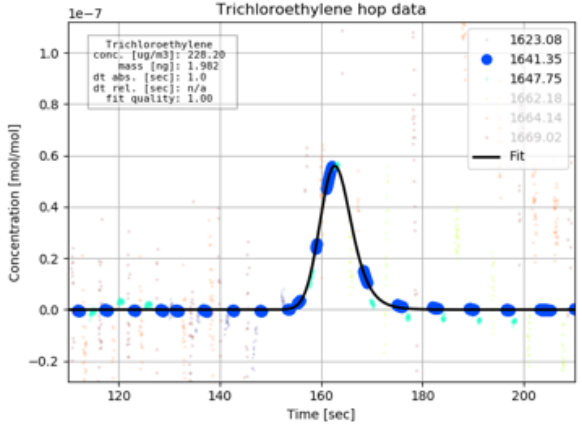
Spectroscopic Analysis

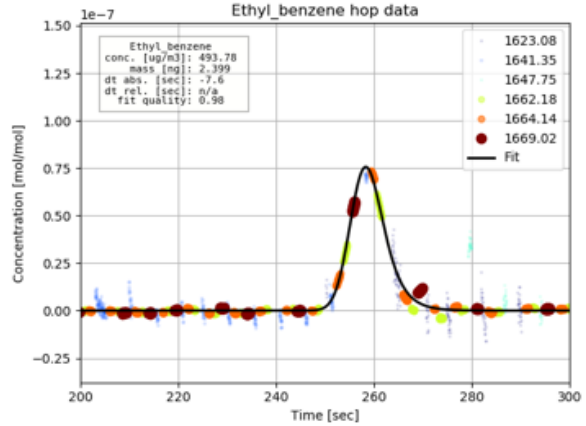
Fast hopping CRDS and analyte dispersion

- Raw data shows multiple species measured at multiple wavelengths
- Processing re-scales raw data by known absorption spectrum and performs automatic fitting, cleanly identifying individual analytes. Arrival time and spectroscopy provide independent metrics for positive compound identification.
- Data shown contains automated compound identification for 1,3-butadiene, 1,2-cDCE, isoprene, TCE, benzene, toluene, ethylbenzene, and all xylenes.









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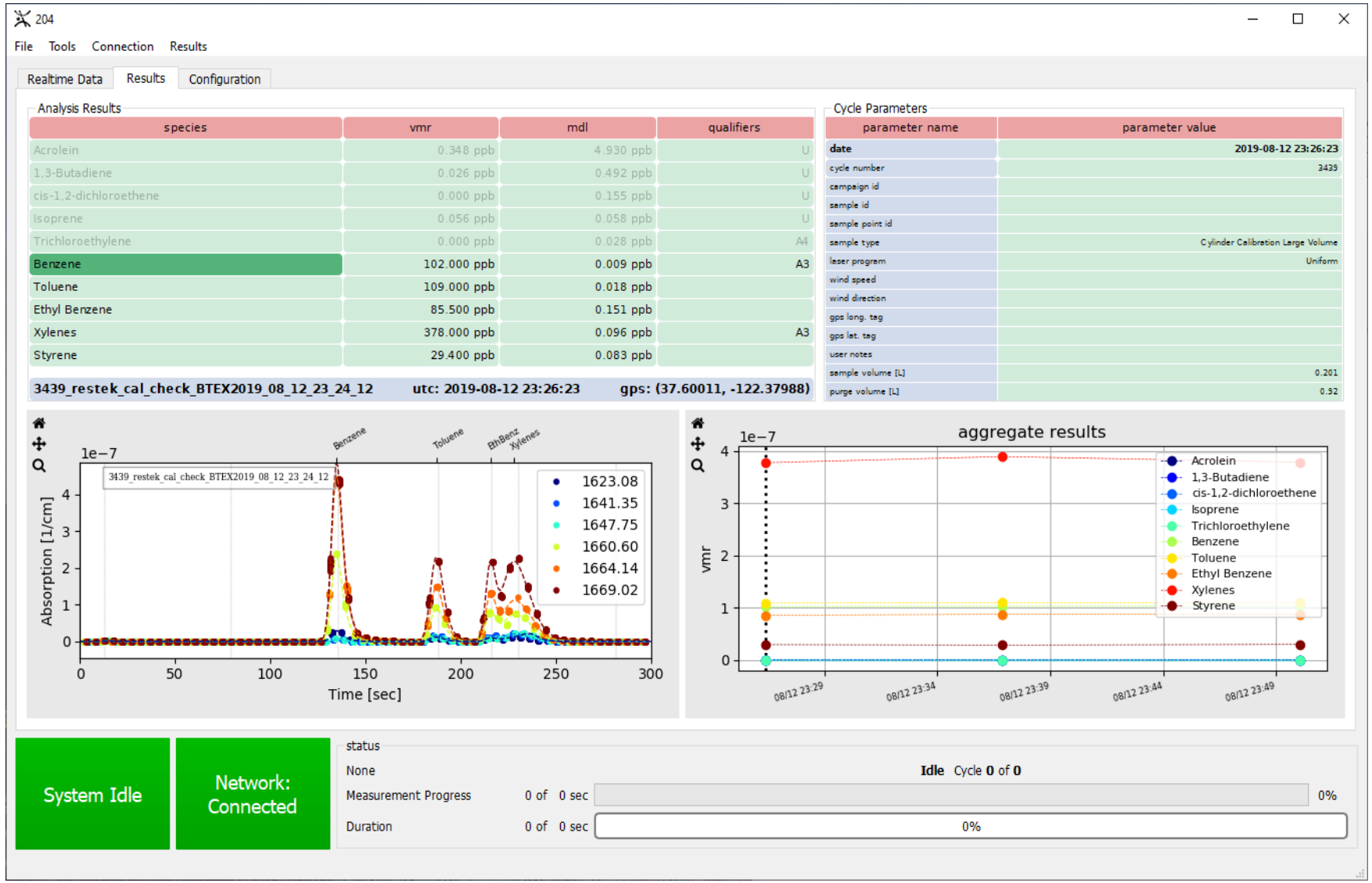
Data Display



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Typical Analyte List with Performance

Speciated Analysis Mode Analytical Performance		
Species†	**MDL (1500 mL sample)***	**MDL (100 mL sample)***
Benzene	< 10 pptv (0.03 µg/m3)	< 150 pptv (0.45 µg/m3)
Toluene	< 50 pptv (0.15 µg/m3)	< 750 pptv (2.25 µg/m3)
Ethylbenzene	<100 pptv (0.45 µg/m3)	<1500 pptv (6.75 µg/m3)
Xylenes	<100 pptv (0.45 µg/m3)	<1500 pptv (6.75 µg/m3)
Trichloroethylene	< 50 pptv (0.10 µg/m3)	< 750 pptv (1.50 µg/m3)
1,2-cisDichloroethylene	< 100 pptv (0.40 µg/m3)	< 1500 pptv (6 µg/m3)
Isoprene	< 100 pptv (0.30 µg/m3)	<1500 pptv (5 µg/m3)
1,3-butadiene	< 200 pptv (0.55 µg/m3)	< 4 ppbv (9 µg/m3)
Acroleine	< 200 pptv (0.55 µg/m3)	< 4 ppbv (9 µg/m3)
Styrene	< 500 pptv (2.1 µg/m3)	< 10 ppbv (42 µg/m3)
Ethylene Oxide**	< 10 pptv (0.02 µg/m3)	< 1 ppbv (1.80 µg/m3)
<Zero level drift (per analyte)	< MDL	
Analytical Precision (per analyte)††	greater of 25% of measured value or MDL	
Analytical Accuracy (per analyte)††	greater of 30% or MDL	

Measurement	
Analysis Time	< 10 Minutes
Sampling Duration	1-45 Minutes
Calibration	As required by testing protocol
Data Reporting	Attached PC, WAN gateway compatible
Data Format options	json, csv, kml
Global Positioning System	Built-In
Sample Volume Range	5-5000 scc
Sampling Flow Range	2-500 sccm

† Additional species available upon request and via software updates
†† Equivalent Performance to EPA TO-15 laboratory requirements
*MDL sample volume dependent
** Requires Analyte-specific instrument configuration

Other compounds of interest that can be measured:

Hydrogen Sulfide
Hydrogen Cyanide
Carbon Monoxide
Methane
Water
Carbon Dioxide
Butane
Propane
Acetone
Isopropanol
Methanol
Etc…

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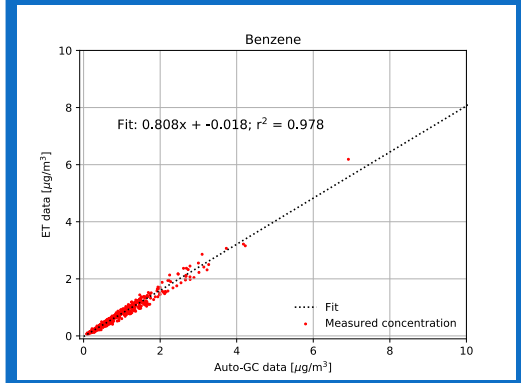
Performance Validation

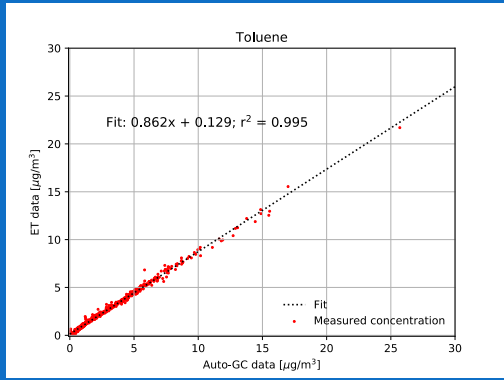
BAAQMD

- Month-long, 24/7, unattended, side-by-side with dual column auto-GC

r^2 benzene > 0.97

r^2 toluene > 0.99



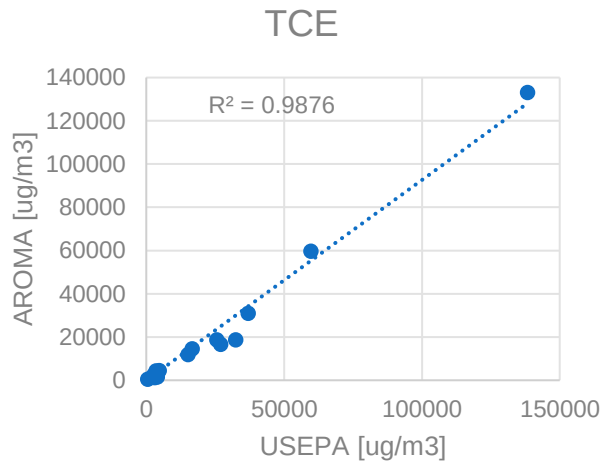


Species	Mean Conc [µg/m3]	MDL [µg/m3]	MDL [pptv]
Benzene	0.05	0.0045	1.4
Toluene	0.08	0.01	2.6
Ethylbenzene	0.07	0.10	4.4
Xylenes	0.20	0.044	10

EPA Region 9

- Side-by-side measurements with gold standard (SUMMA canister + GC/MS by TO-15) measurements performed by EPA lab (region 9).

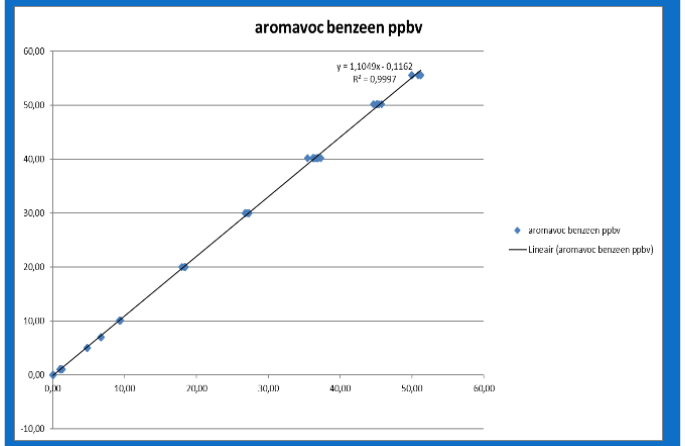
r^2 TCE > 0.98



Netherlands DCMR

- Benzene measurements made over 23 days compared to ENVEA GC-PID
- Long-term drift showed a 7.5% relative standard deviation
- The demonstrated detection limit for benzene was 10ppt

r^2 benzene > 0.99



Mobile Deployments

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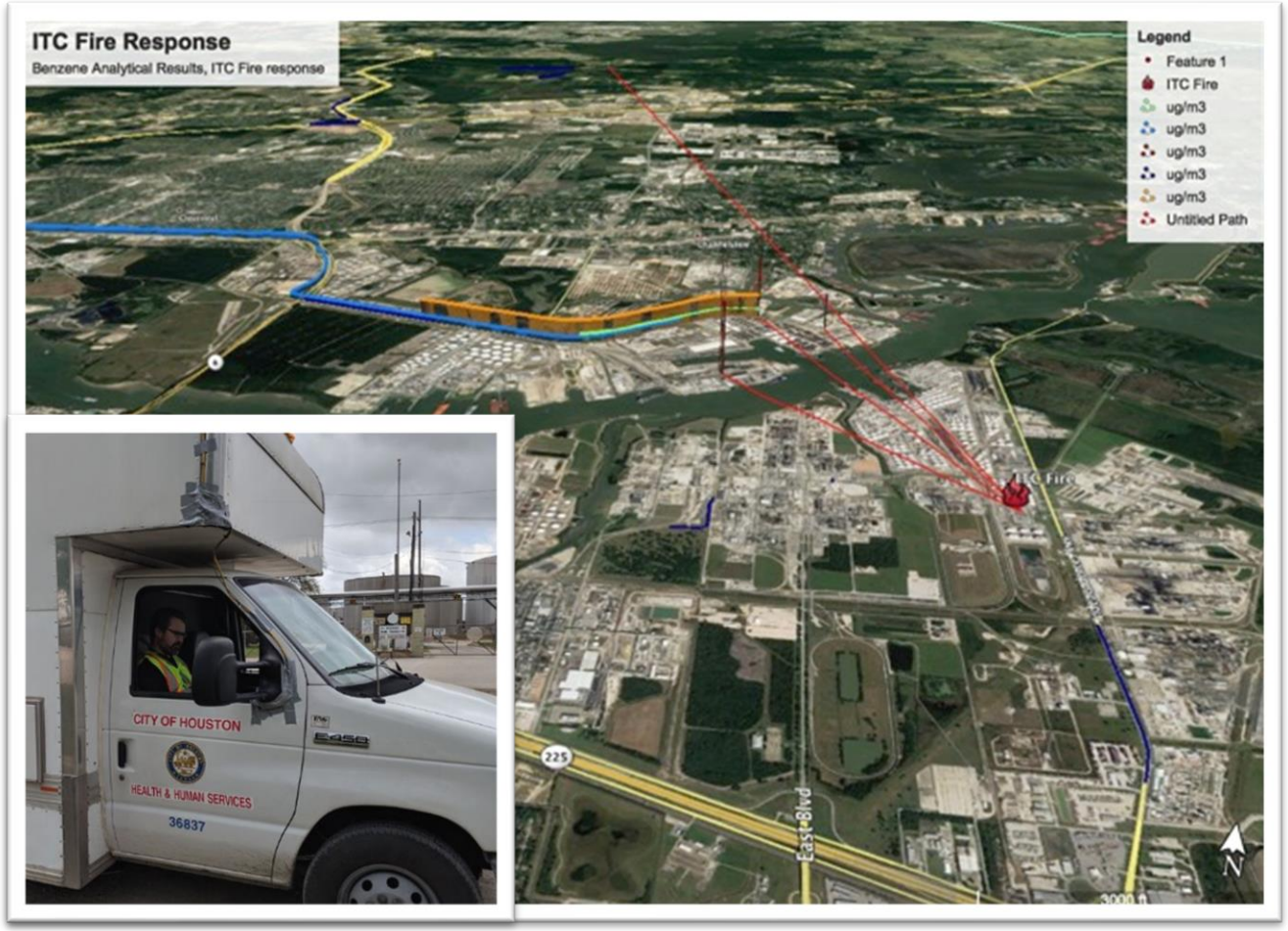
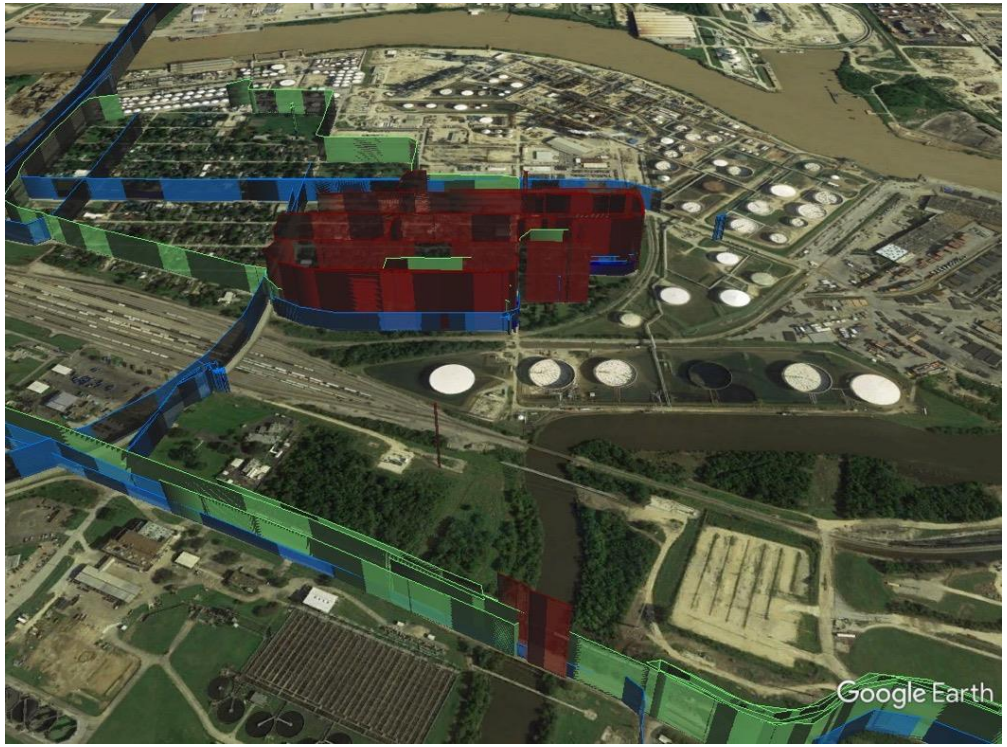
Emergency Response - ITC Fire, Houston TX

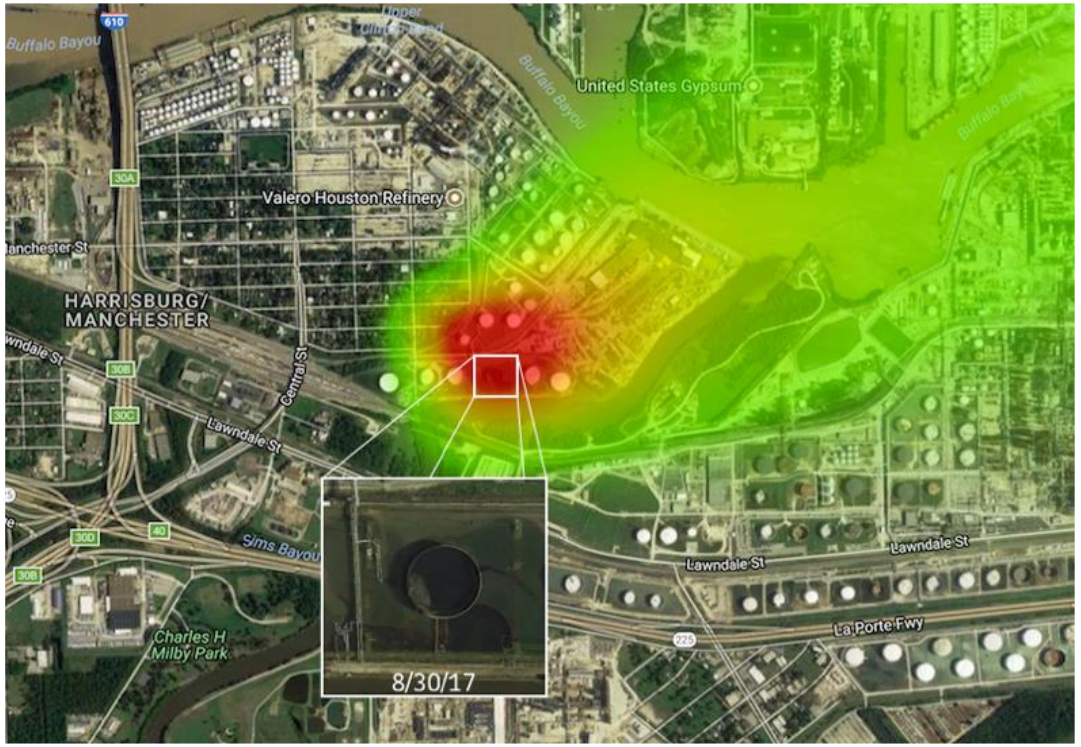


Concentrations of benzene across the Houston Ship Channel from the ITC facility were in the hundreds of parts-per-billions, even days after the fire.

Elevated benzene concentrations were measured as far as 12 miles downwind with AROMA-VOC

Leak Source Identification – Hurricane Harvey





Likelihood of source origin using concentration, locations, and met data

Good agreement with subsequent satellite data

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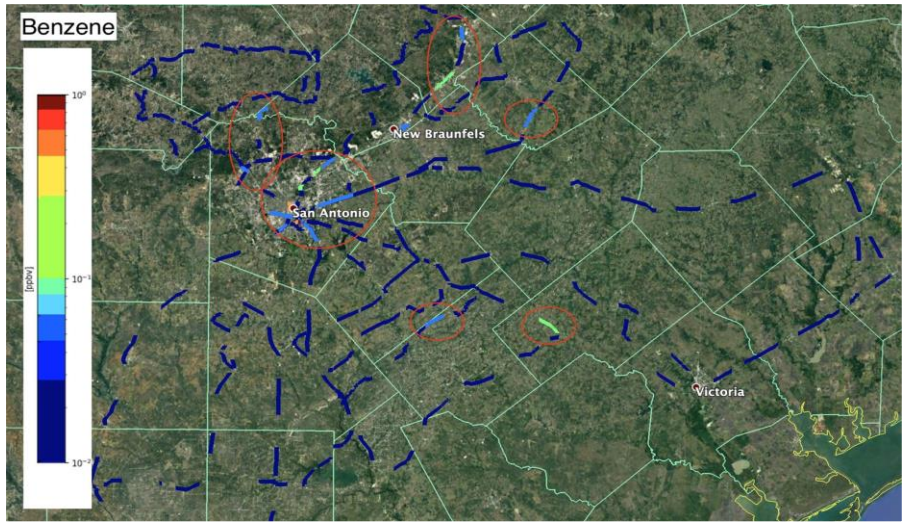
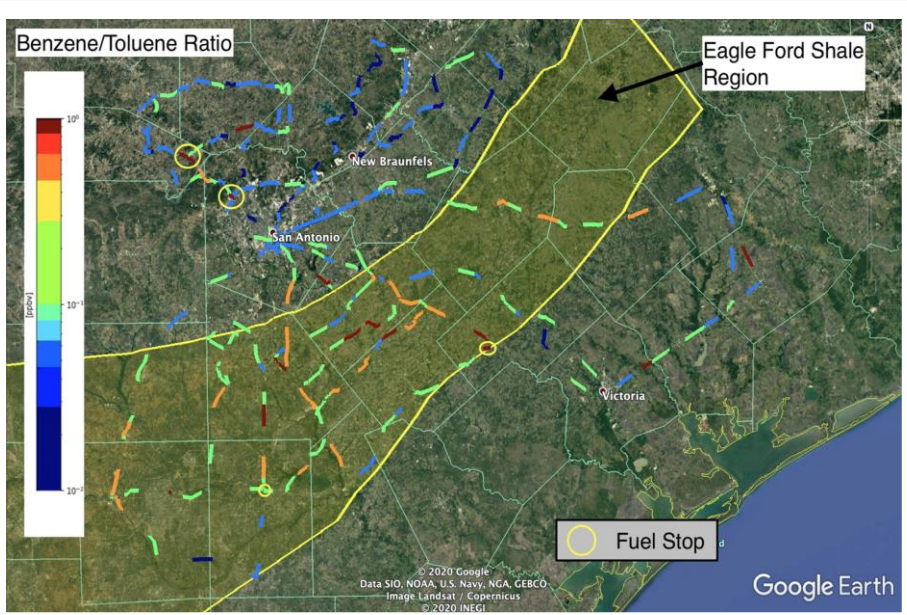
Large Area Survey – San Antonio, TX





- ~300 miles covered per day for 10 days
- AROMA-VOC for VOC data (inc. BTEX, isoprene, styrene)
- Routes selected based on VOC point sources, historical wind data, and back trajectory analysis on high ozone days
- Benzene / Toluene ratio provides the highest sensitivity of all compound ratios measured
  - B/T ratio of ~1 is consistent with a variety of oilfield emissions [Schade 2018]
- Analysis showed significant shift in source type from:
  - MSATs and vehicle emissions surrounding San Antonio
  - Oil and Gas operational fingerprints within petroleum-producing regions

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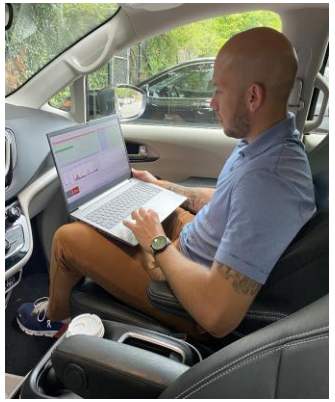
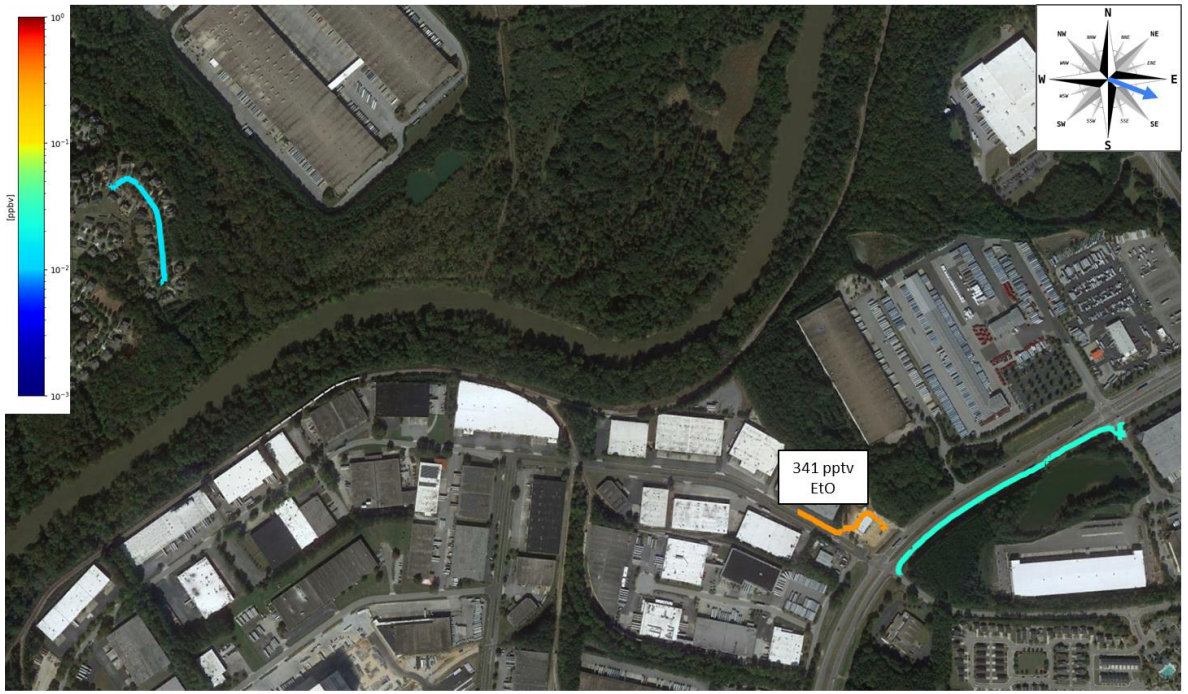
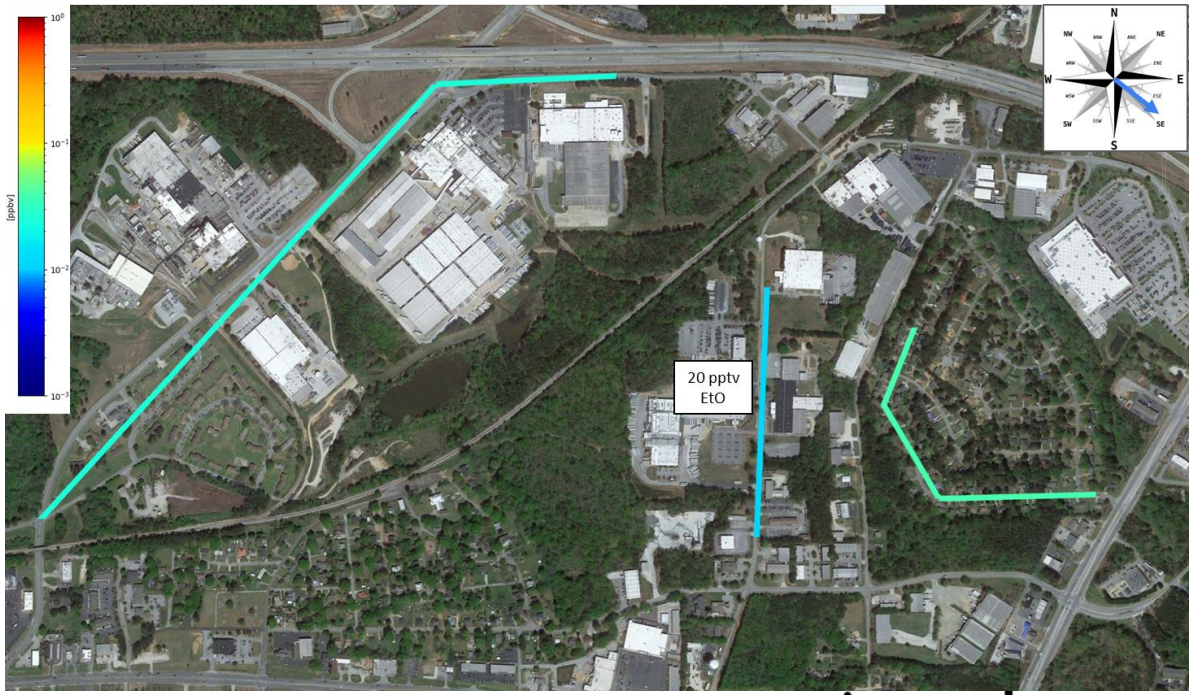
Ethylene Oxide Around Sterilization Facilities

- Mobile measurements of ethylene oxide around two sterilization facilities in Georgia.
  - A rental minivan was used as the mobile platform for this work.
  - Ambient concentrations around 20 pptv



AROMA-ETO installed in rental minivan for mobile monitoring in Georgia





Ethylene oxide measurements at two sterilization facilities in GA. Upwind and downwind measurements were made as well as at site, which is labeled by the boxes with ethylene oxide concentrations.

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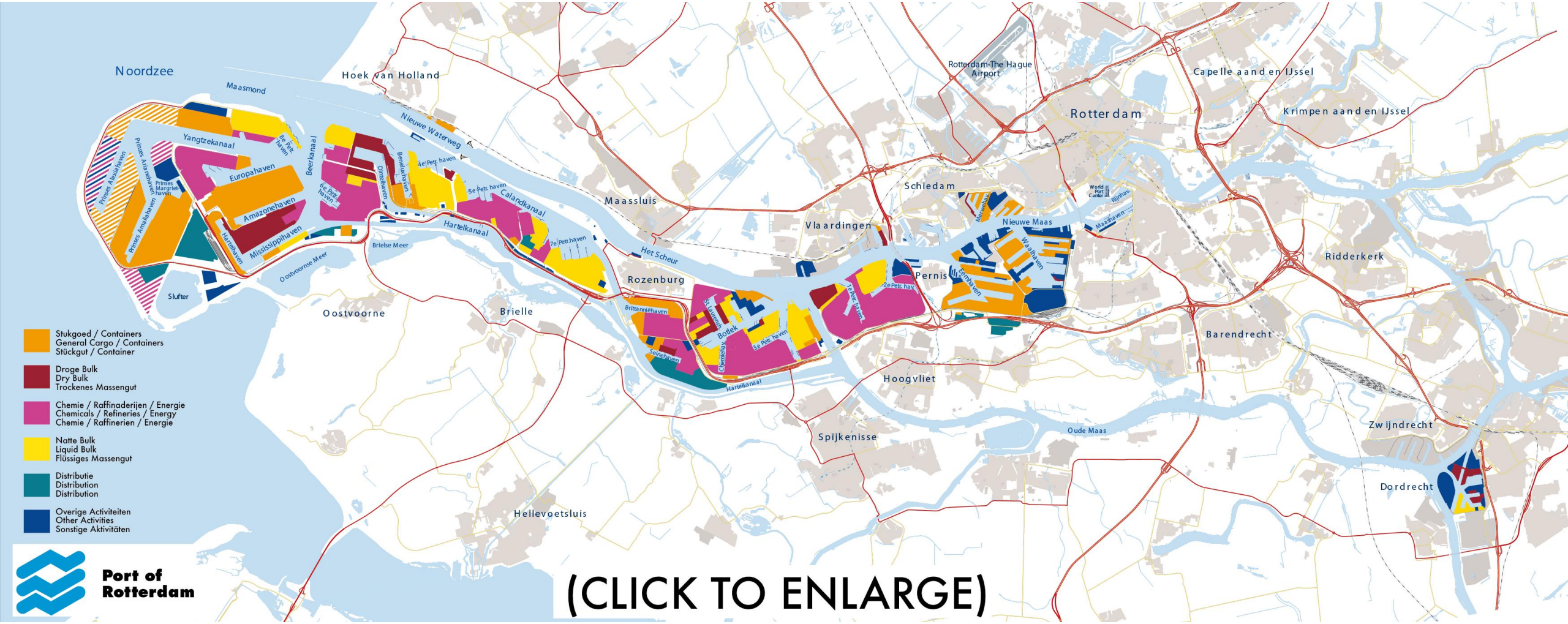
Port of Rotterdam – RapidScan Survey



Port of Rotterdam – RapidScan Survey

Port of Rotterdam – RapidScan Survey

Stationary Deployments

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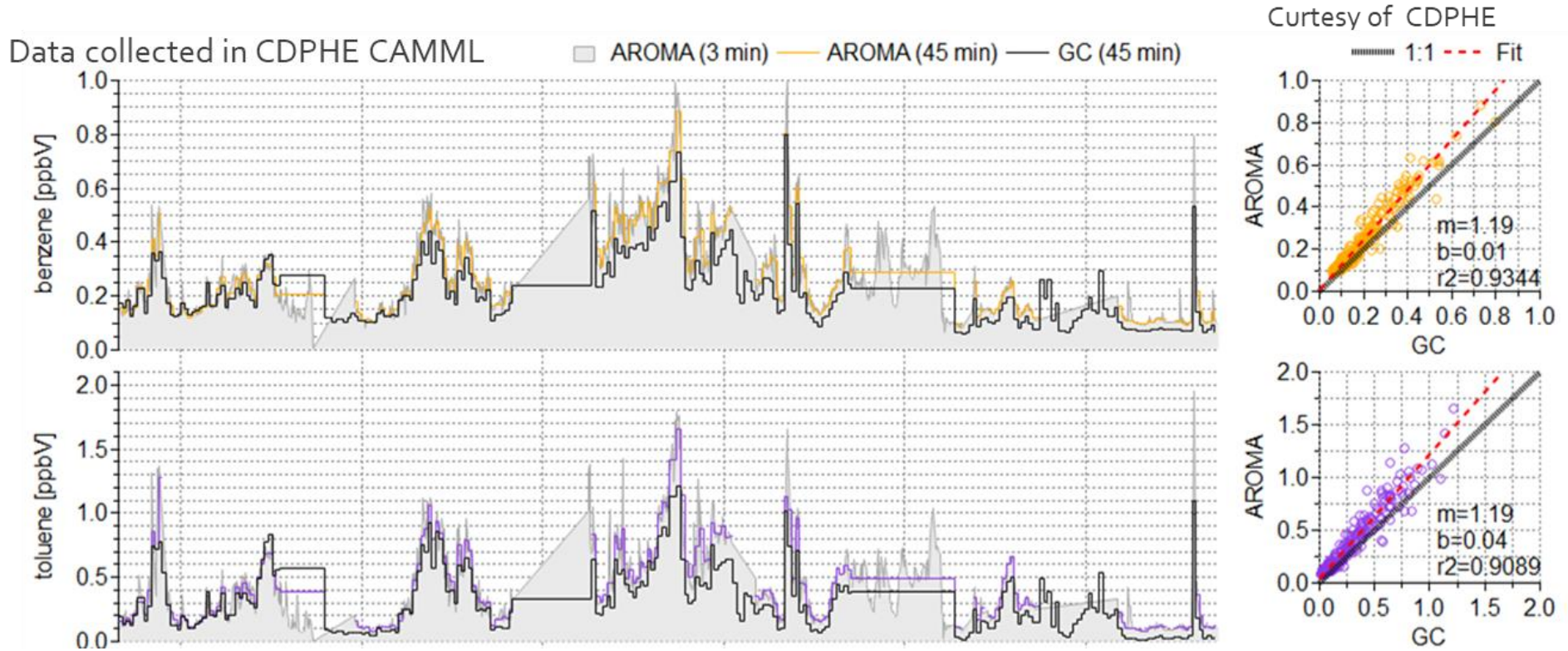
Measurements at Oil and Gas Wells



Stationary measurements made in Longmont, CO. AROMA BTEX measurements were made next to an oil well pad and co-located dual auto-GC.

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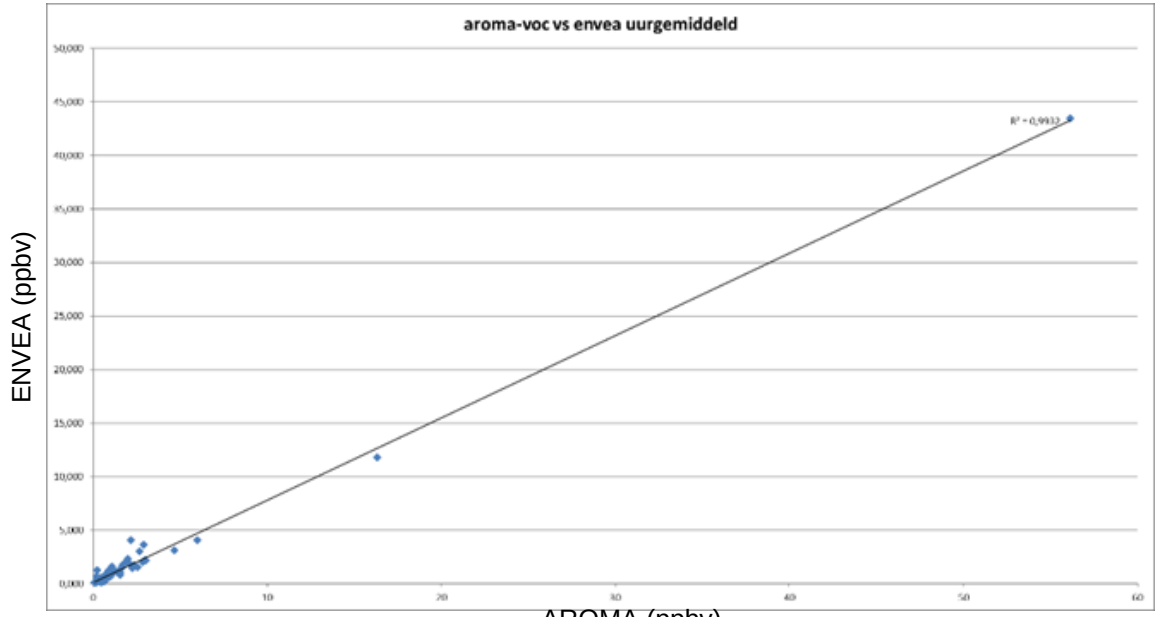
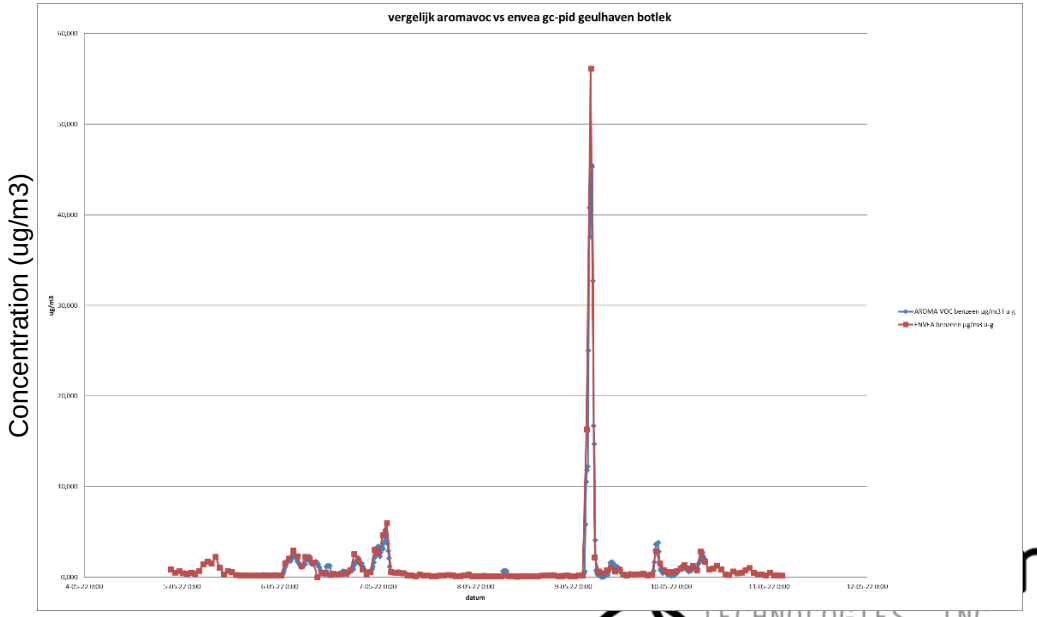
Stationary Monitoring in the Port of Rotterdam

- From 5 May to 10 May 2022, the AROMA-VOC was placed at a measuring point of the DCMR air monitoring network (BOT geulhaven)
  - 12-minute total sample collection and run time (sample frequency)
- Comparison of measurements made with AROMA-VOC compared to the GC-PID analyzer from the monitoring network stationed there showed excellent correlation for benzene (R2>0.99)
- Hourly averaged data and shorter sample periods were compared





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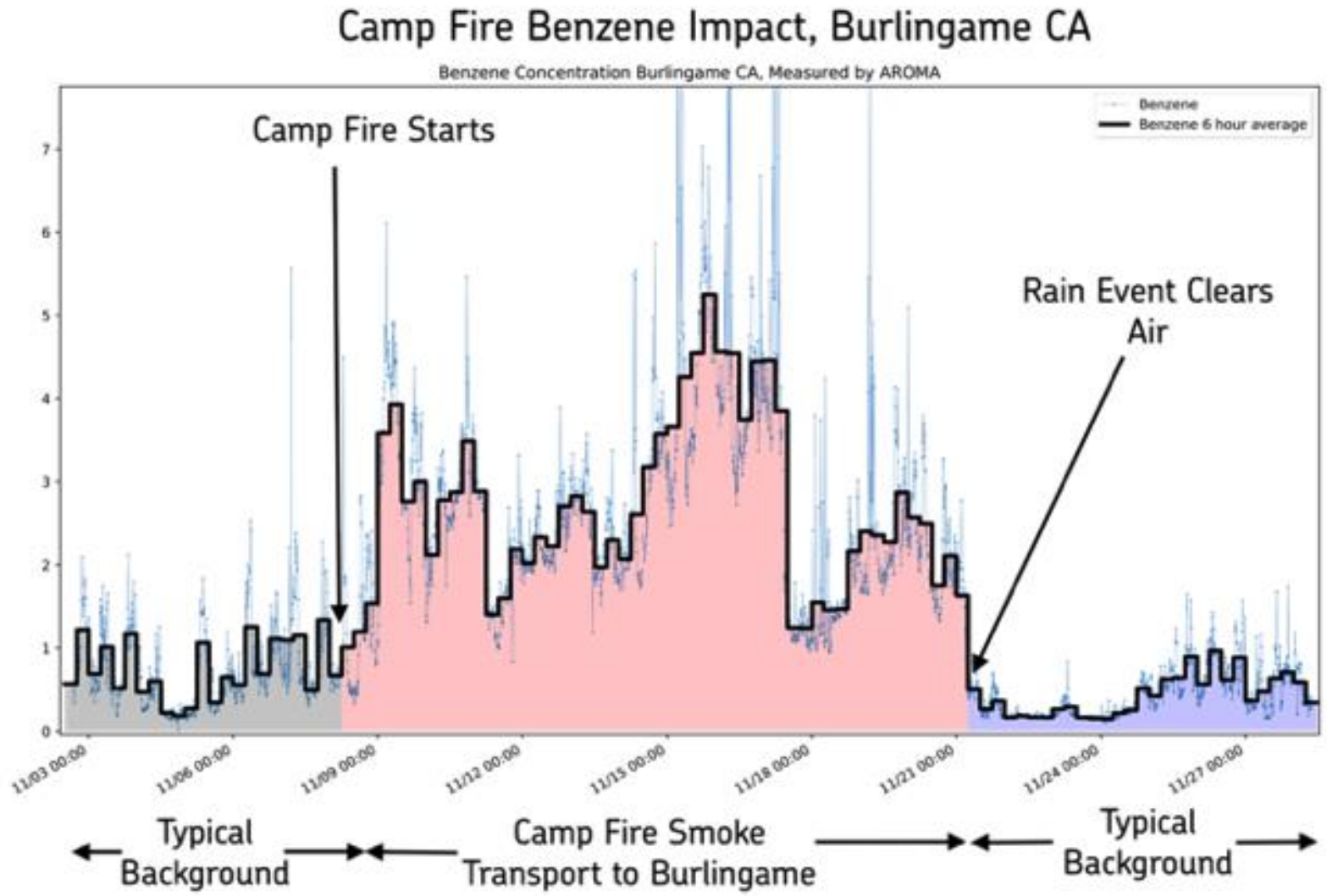
Ambient Air Quality Impacts of Camp Fire



AROMA also monitors VOCs in water!

After the Carr Fire in 2017, AROMA was used to test multiple wells in multiple water districts most heavily impacted by the fire using a simple sparge interface. Detection limits for benzene and other VOCs were below 50 ng/L.

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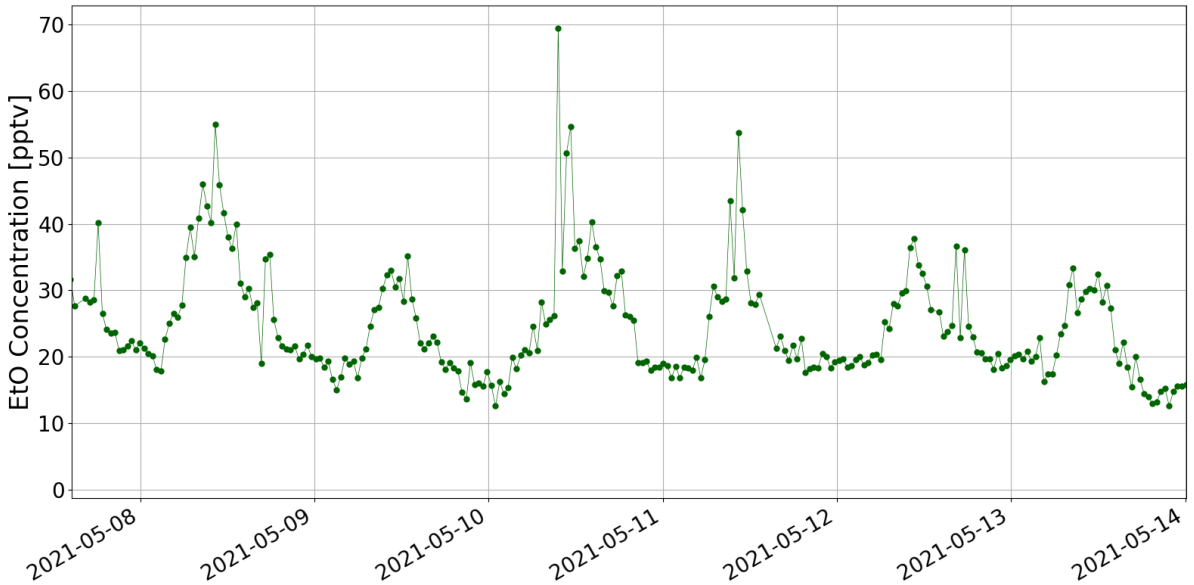
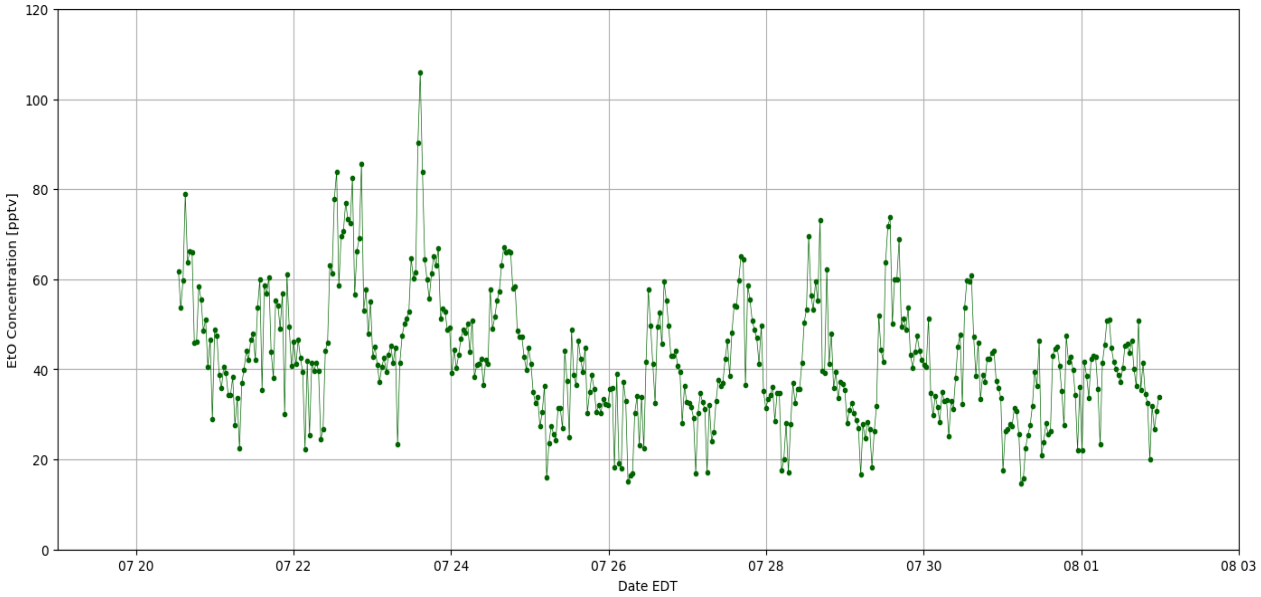
Continuous Ambient Measurements of Ethylene Oxide



EtO concentrations measured at ground-level in San Bruno, CA from May 8 - 14, 2021. Each line on the x-axis is at midnight (PST).



EtO concentrations measured at ground-level in DeKalb County, GA from July 20 – August 3, 2022.

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Summary and Conclusions

- AROMA is exceptionally robust and very easily deployable for stationary and mobile studies
- TD-CRDS can address air toxics monitoring needs
- AROMA-ETO can measure below 10 pptv ethylene oxide in ambient air
- AROMA has been proven in the field by numerous groups including:
- Various options for collaboration with Entanglement Technologies

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Questions?

For more information, please contact:
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