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Real-Time VOC Measurements in Ambient Air Using Thermal Desorption, Broadband Cavity Ring-Down Spectroscopy

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Prepared for the 38th Annual National Environmental Monitoring Conference in Minneapolis, MN on Monday, July 31st

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

Agenda

- Introduction to thermal desorption, cavity ring-down spectroscopy
- AROMA modes of operation
- AROMA for ambient air monitoring of hazardous air pollutants
- Field data
- Exploring contaminants of emerging concern in air
- Summary

About Entanglement Technologies

Entanglement Technologies is advancing quantum machines by building practical, commercially viable precision sensors that push the limits of laser, cavity, electronic, and signal processing performance.

AROMA, the best-in-class trace gas & vapor sensor, is our first product in market and was deployed in 2017.

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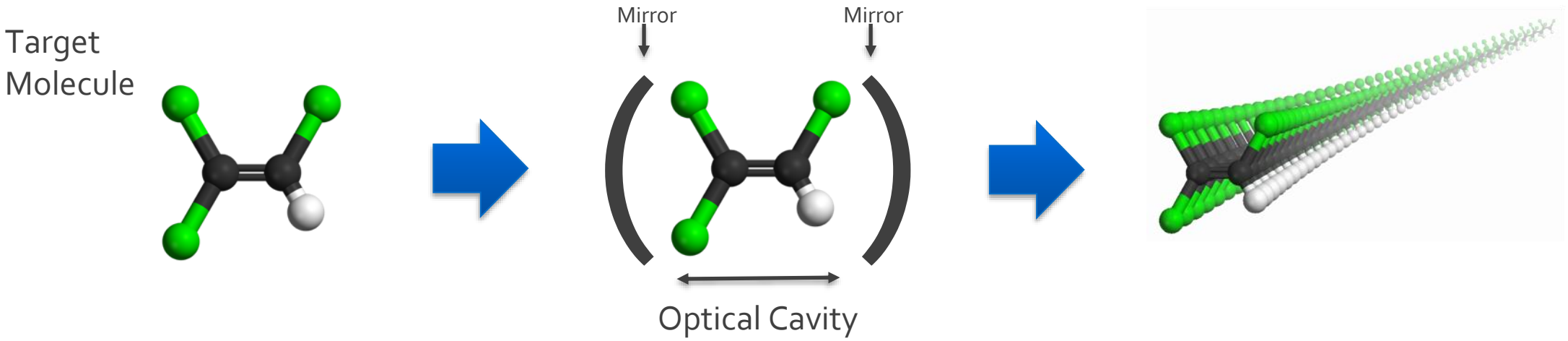
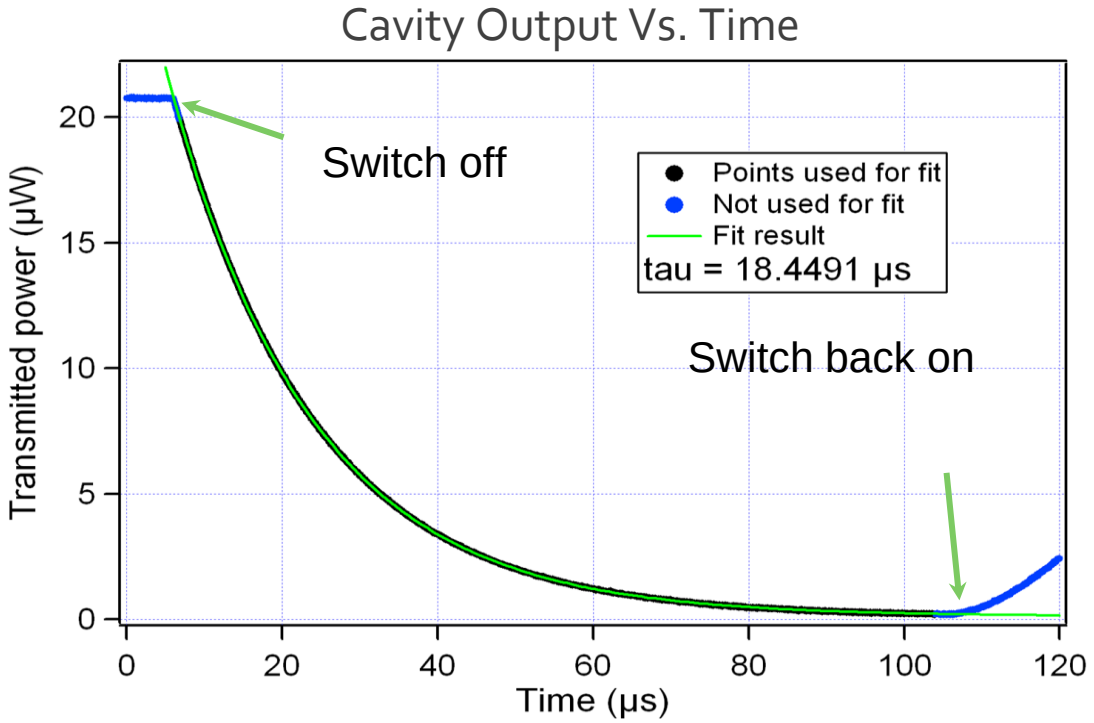
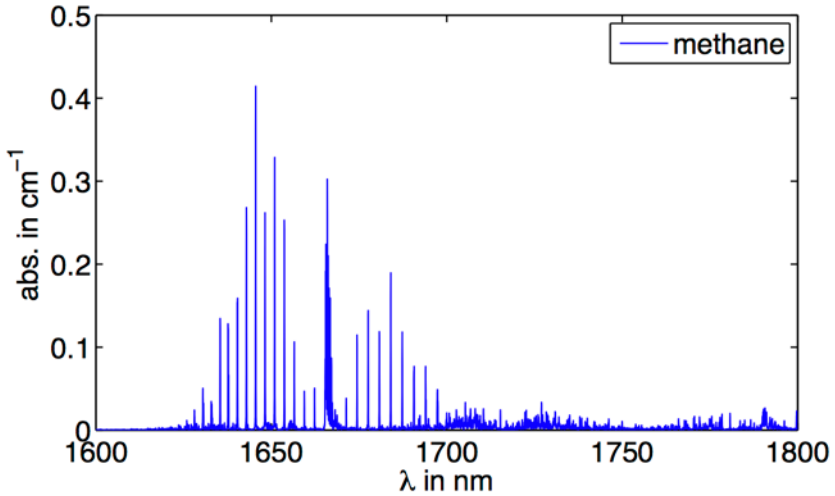
Cavity Ring-Down Spectroscopy





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

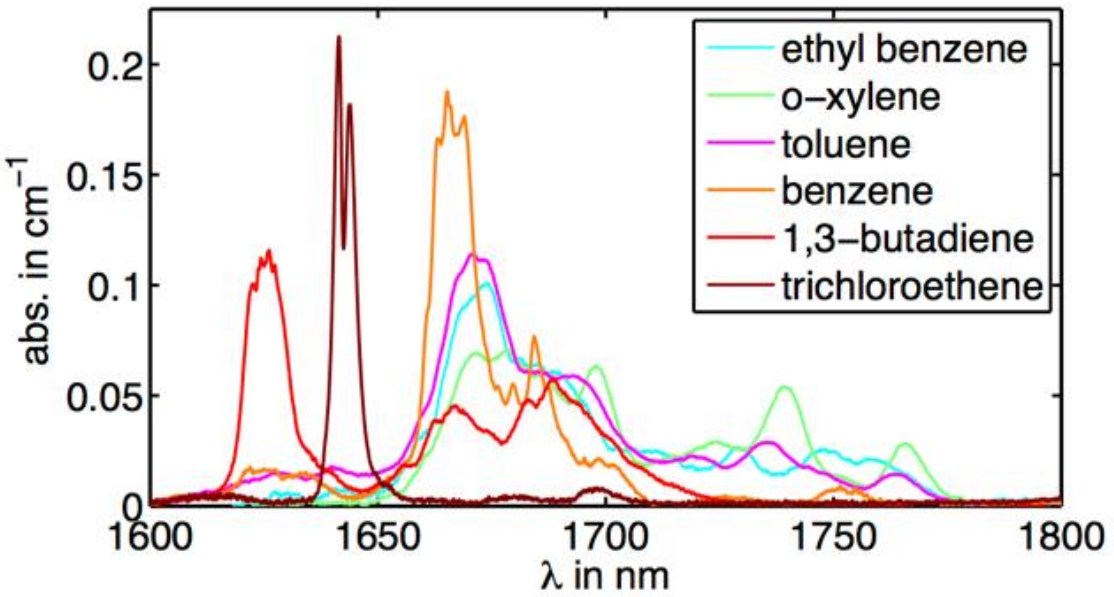
30 Seconds of Spectroscopy



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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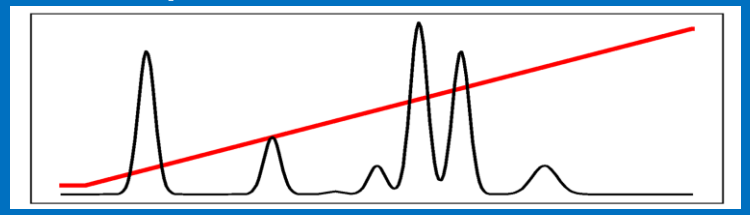
Thermal Desorption - CRDS

Separation Front End



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

- > 10k cycles
- Insensitive to O_2, H_2O

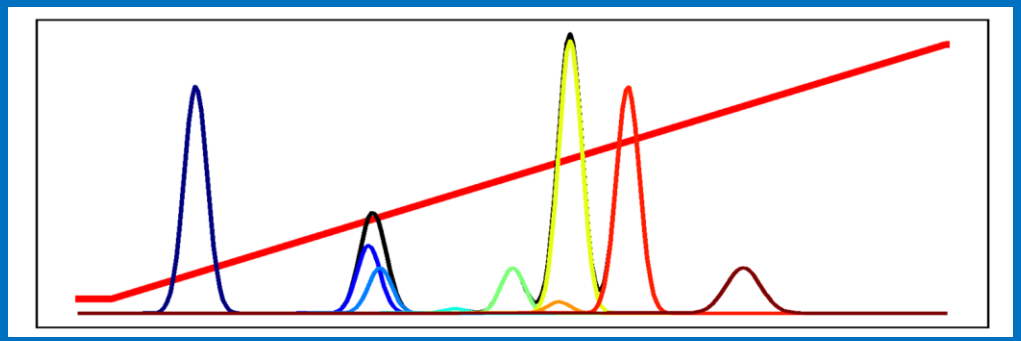
Inlet

- 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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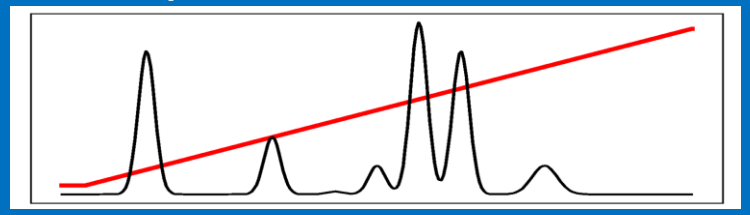
Thermal Desorption - CRDS

Separation Front End



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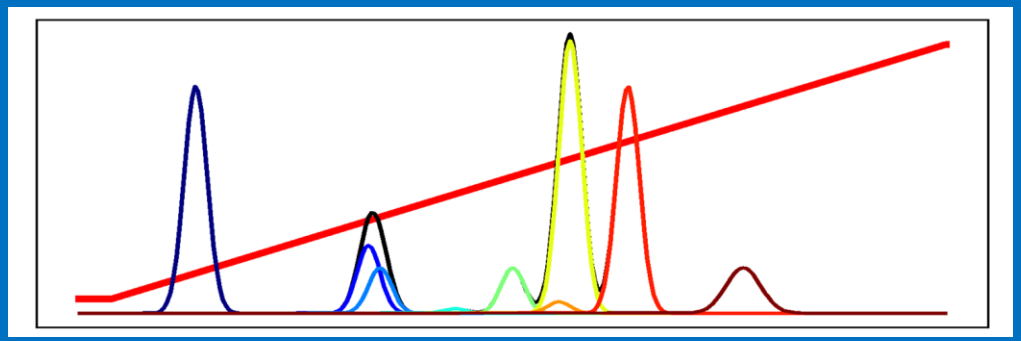

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RapidScan Mode – Direct CRDS

- 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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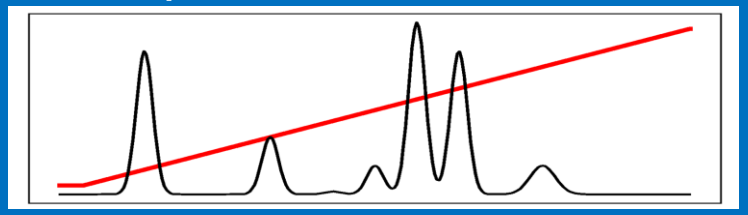
Thermal Desorption - CRDS

Separation Front End



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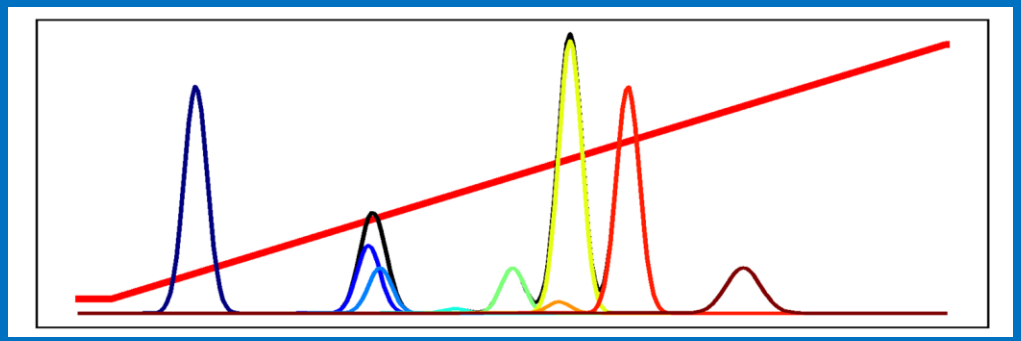

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LabScan Mode – TD-CRDS

- 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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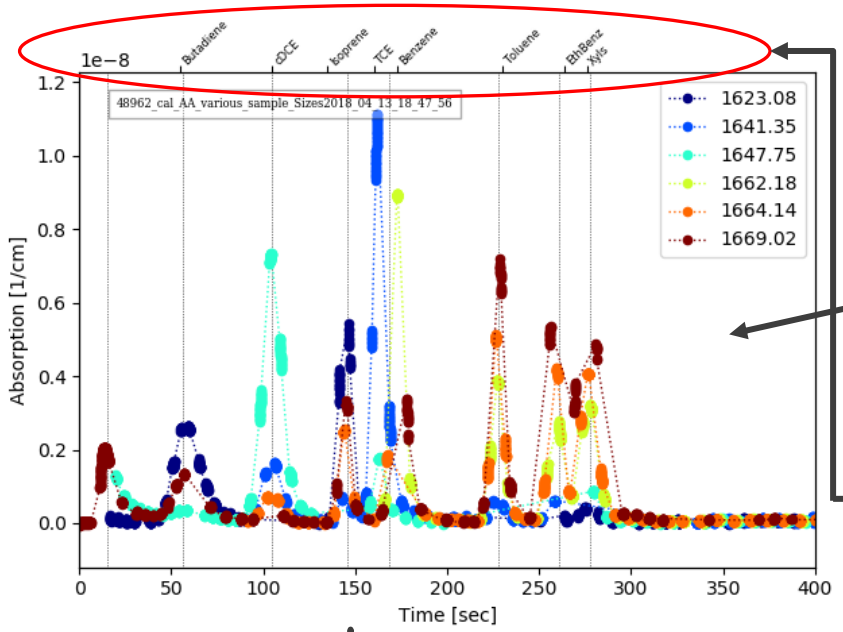
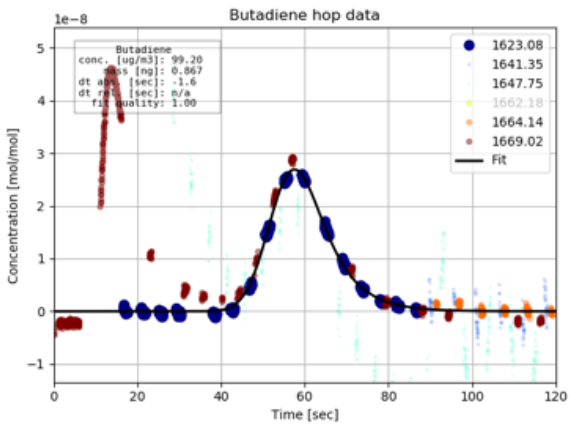
Multispecies Hopping: Real Data

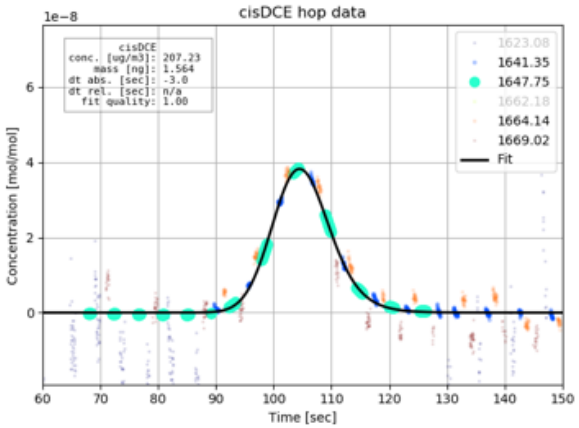


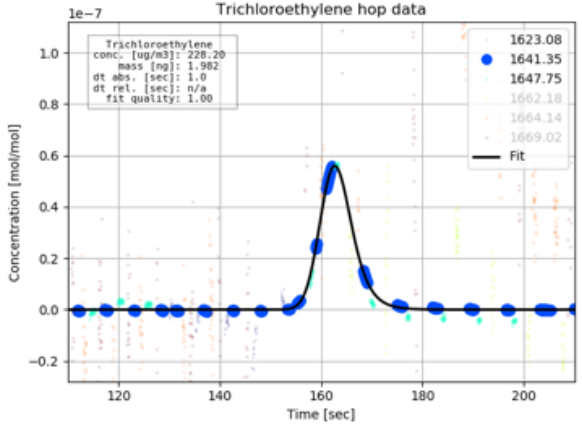
Spectroscopic Analysis

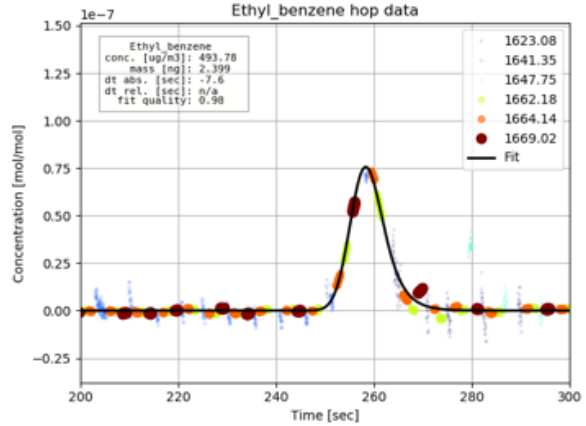
Fast hopping CRDS and analyte dispersion

- 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

204

File Tools Connection Results

Realtime Data | Results | Configuration

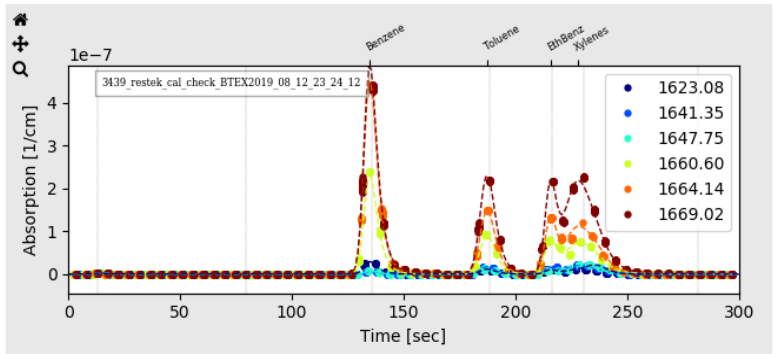
Analysis Results

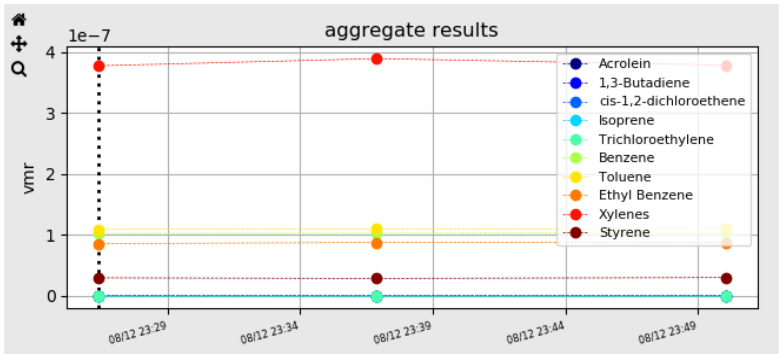
species	vmr	mdl	qualifiers
Acrolein	0.348 ppb	4.930 ppb	U
1,3-Butadiene	0.026 ppb	0.492 ppb	U
cis-1,2-dichloroethene	0.000 ppb	0.155 ppb	U
Isoprene	0.056 ppb	0.058 ppb	U
Trichloroethylene	0.000 ppb	0.028 ppb	A4
Benzene	102.000 ppb	0.009 ppb	A3
Toluene	109.000 ppb	0.018 ppb	
Ethyl Benzene	85.500 ppb	0.151 ppb	
Xylenes	378.000 ppb	0.096 ppb	A3
Styrene	29.400 ppb	0.083 ppb	

Cycle Parameters

parameter name	parameter value
date	2019-08-12 23:26:23
cycle number	3439
campaign id	
sample id	
sample point id	
sample type	Cylinder Calibration Large Volume
laser program	Uniform
wind speed	
wind direction	
gps long. tag	
gps lat. tag	
user notes	
sample volume [L]	0.201
purge volume [L]	0.92

3439_restek_cal_check_BTEX2019_08_12_23_24_12 utc: 2019-08-12 23:26:23 gps: (37.60011, -122.37988)





System Idle

Network: Connected

status

None **Idle** Cycle **0** of **0**

Measurement Progress 0 of 0 sec 0%

Duration 0 of 0 sec 0%

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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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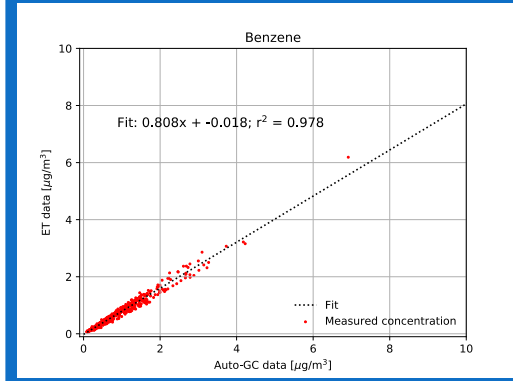
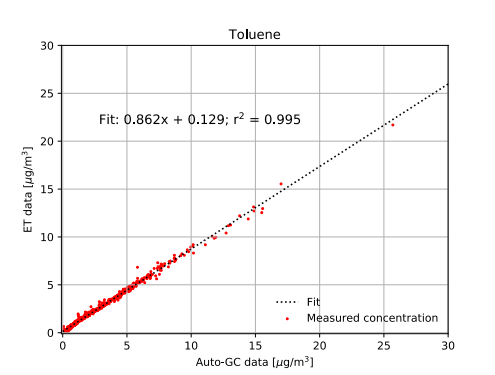
Performance Validation

BAAQMD

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

r^2 benzene > 0.97
r^2 toluene > 0.99





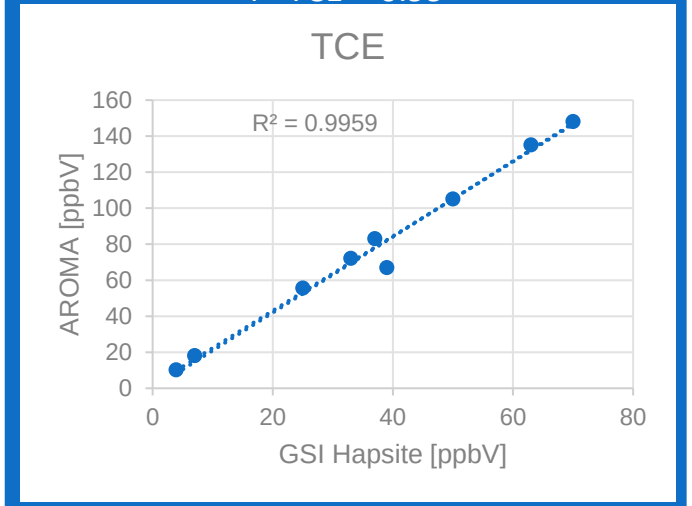
Species	Mean Conc [µg/m3]	MDL [µg/m3]	MDL [pptv]
Benzene	0.05	0.0045	1.4
Toluene	0.08	0.01	2.6
Ethylbenzene	0.07	0.10	4.4
Xylenes	0.20	0.044	10

BAY AREA AIR QUALITY MANAGEMENT DISTRICT

GSI & ESTCP

- Tedlar-based co-sampling of sanitary sewer headspace vs GC/MS
- Included in ESTCP sanitary sewer methodology study.

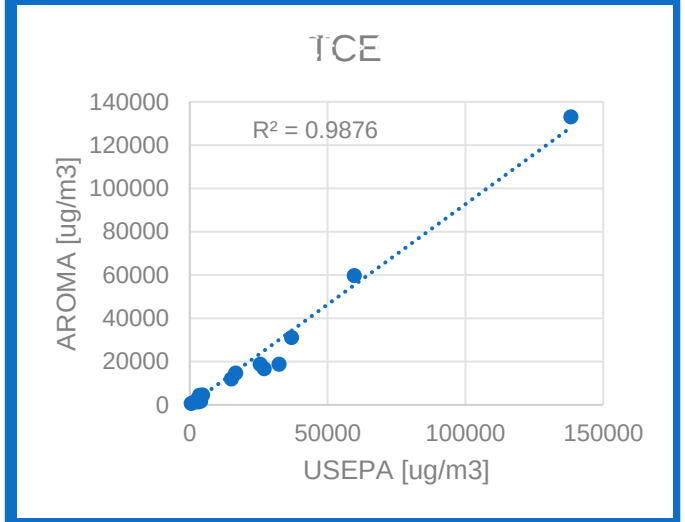
r^2 TCE > 0.99



GSI ENVIRONMENTAL

EPA Region 9

- Side-by-side measurements with gold standard (SUMMA canister + GC/MS by TO-15) measurements performed by EPA lab (region 9).
- The dynamic range was so large that EPA used ET results to select dilution for analysis to prevent contamination of their instrument.



Example Deployments

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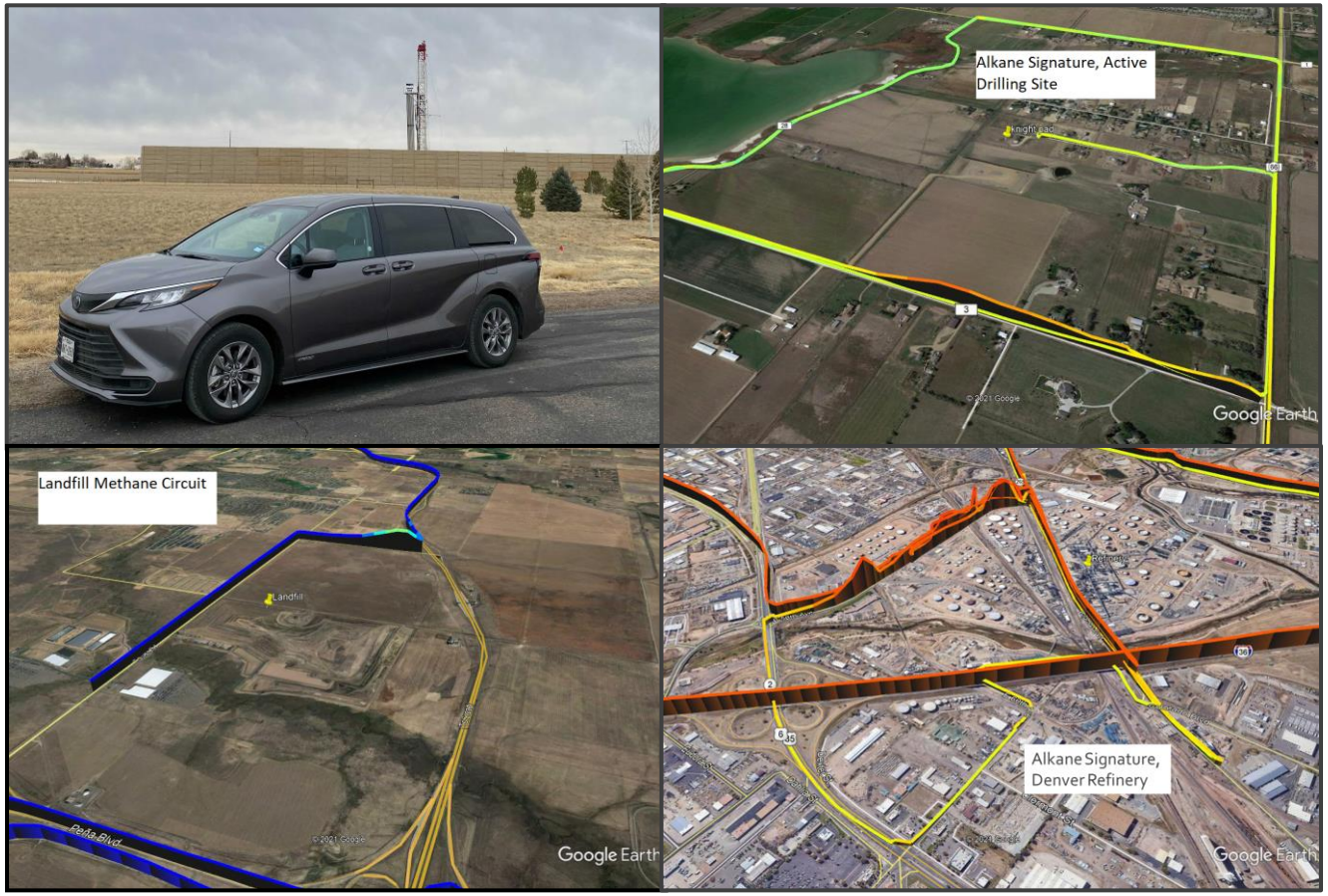
Mobile Emissions Mapping - Colorado

- Data collected from a rental mini-van during transit from Longmont to Denver
- AROMA Running in RapidScan mode
- Battery Supply
- Installation time: 30 minutes
  - Includes de-installation from fixed site and re-installation in rental mini-van



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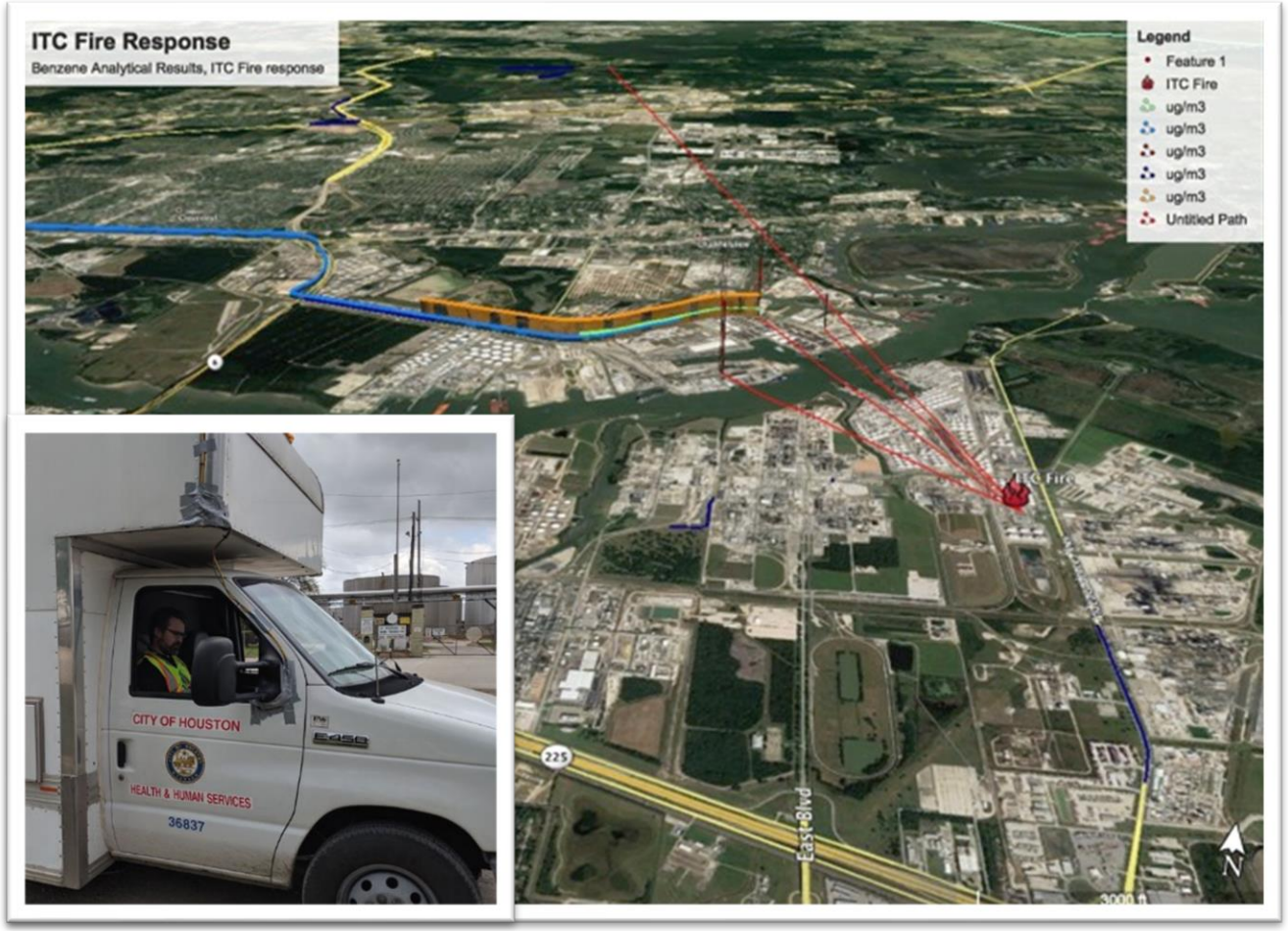
Emergency Response - ITC Fire, Houston TX

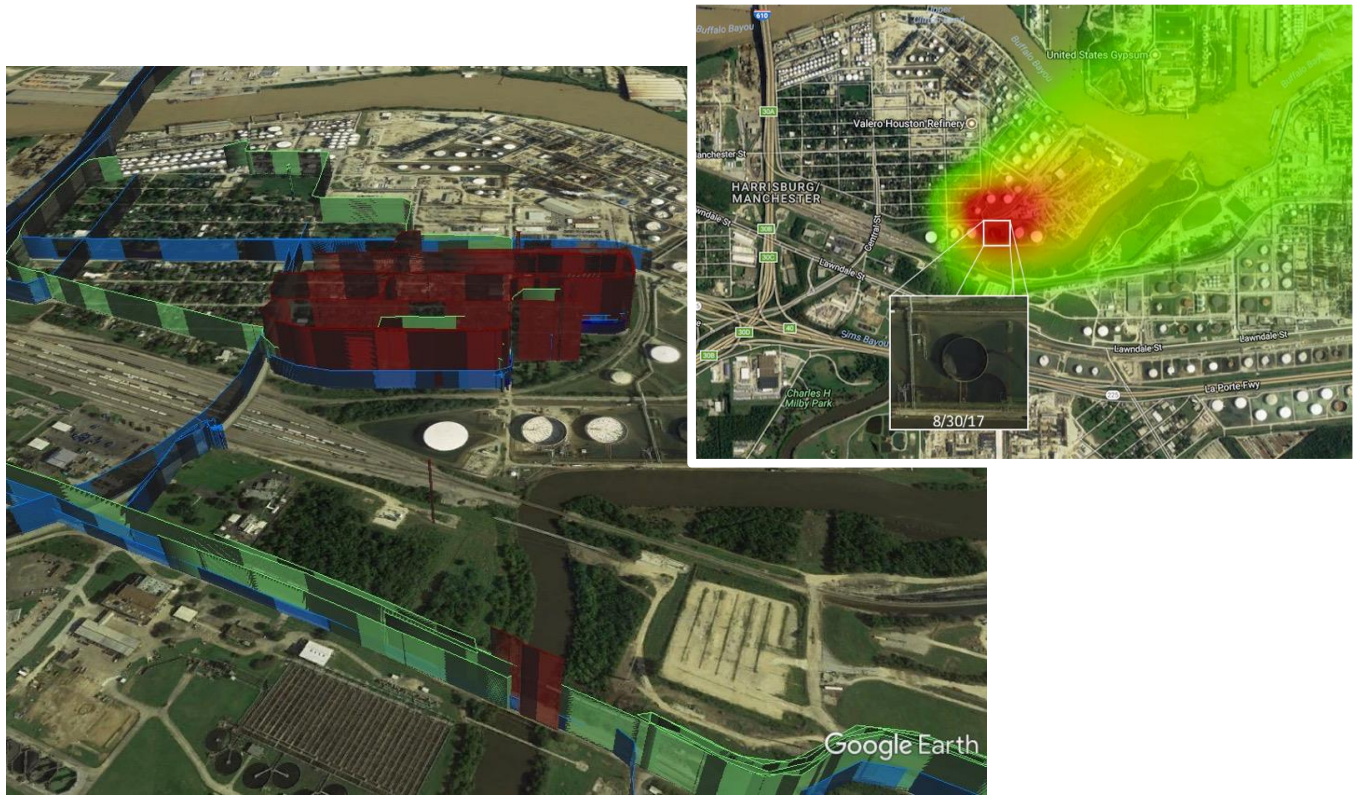


Concentrations of benzene across the Houston Ship Channel from the ITC facility were in the hundreds of parts-per-billions, even days after the fire.

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

Leak Source ID and Plume Fingerprinting – Hurricane Harvey

Leak Source Identification



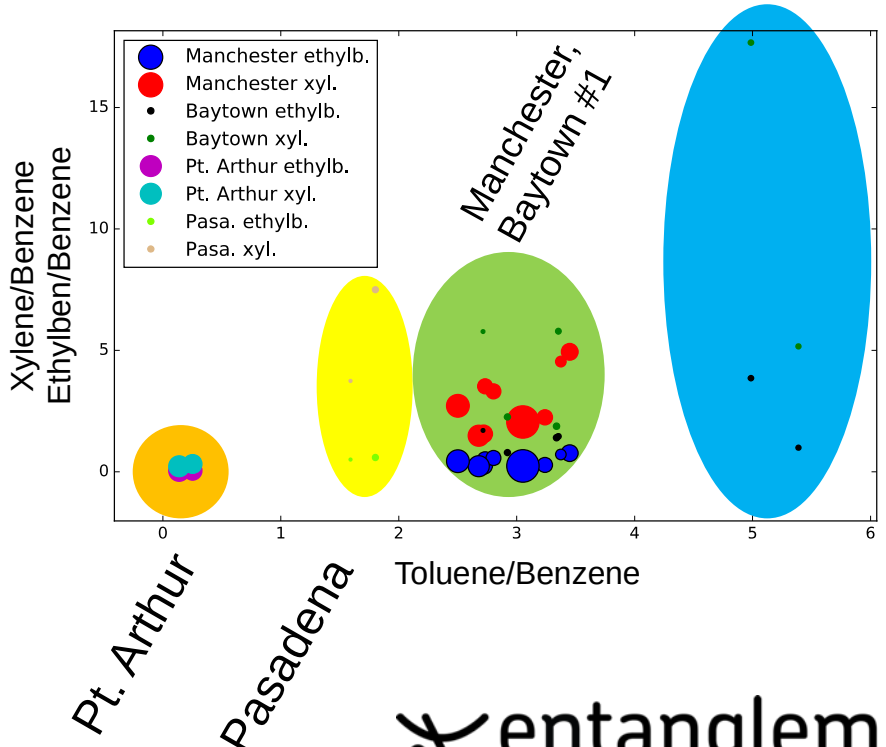
Likelihood of source origin using concentration, locations, and met data

Good agreement with subsequent satellite data

Plume Fingerprinting

5 of 6 plumes show distinct BTEX ratios

Allowed for differentiation of two overlapping plumes at Exxon Baytown



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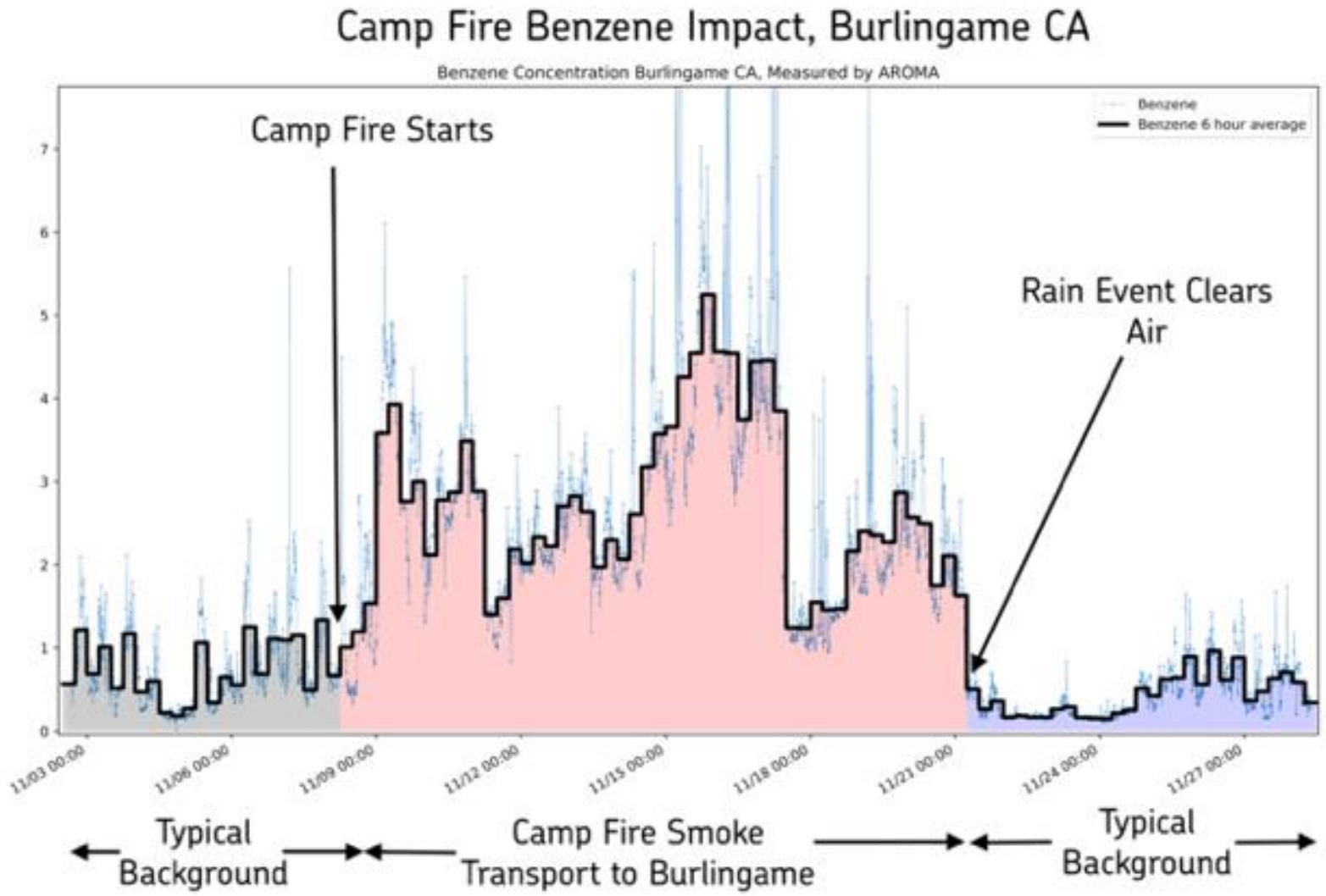
Ambient Air Quality Impacts of Camp Fire



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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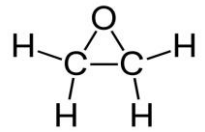
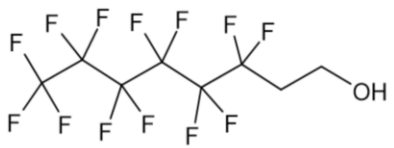
Compounds of Emerging Concern in Air

- Ethylene Oxide (EtO)
  - Many challenges with measuring ethylene oxide including low analytical detection limits needed (based on the EPA's risk assessment) and background levels are not well-understood



EtO

- PFAS
  - PFAS in the environment is a major challenge as there are many compounds, variable toxicity, and low analytical detection limits needed
  - Some OTM methods for PFAS in air
  - Ambient air analysis includes in-field use of Tof-CIMS, PTR-MS, and FTIR
  - Fluorotelomer alcohols (FTOH) have been detected in indoor and outdoor environments and could act as a proxy for other PFCAs such as PFOA.
    - Martin, et al., 2002 measured 29 pg/m3 6:2 FTOH in a rural environment to 87 pg/m3 6:2 FTOH in an urban environment.
    - Implications for vapor intrusion (Abusallout et al., 2022)



6:2 FTOH

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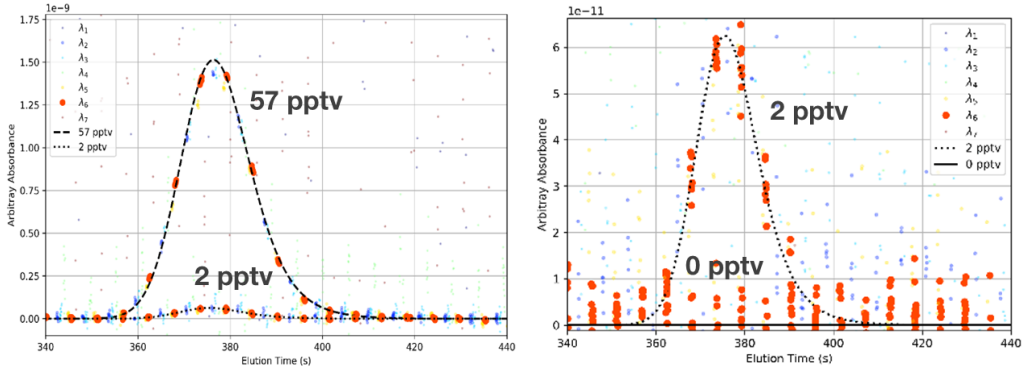
Ambient Air Monitoring of EtO

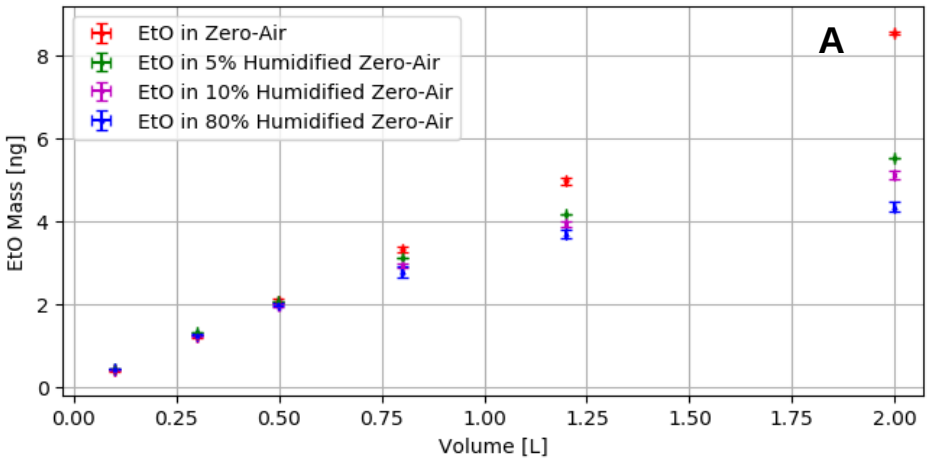
AROMA-ETO is a GC-CRDS system capable of measuring ethylene oxide and other VOCs in ambient air below 10 pptv in a 20-minute analysis time.

Analysis Mode	Analysis Time	Sensitivity
RapidScan	5 seconds	1 ppbv
LabScan	20 minutes	< 10 pptv

- Considerations to reach pptv MDLs
  - Sample is collected on a sorbent prior to analysis
    - Humidity
    - Sample Volume
  - Increased Relative Humidity has a detrimental effect on EtO retention on the sorbent above 600 mL
  - 600 mL (e.g. collection of 200 mL/min for 3 minutes) is the upper recommended limit for the AROMA-ETO sampling volume

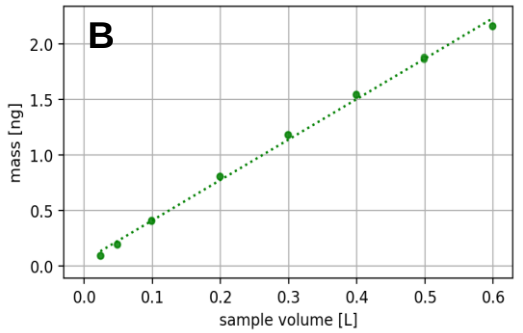


Above figures show LabScan measurements of ethylene oxide in zero air. The calculated detection limit for ethylene oxide is 0.65 pptv.



(A) EtO mass as a function of sample volume at different RHs.

(B) Linear response of mass on column vs sample volume.



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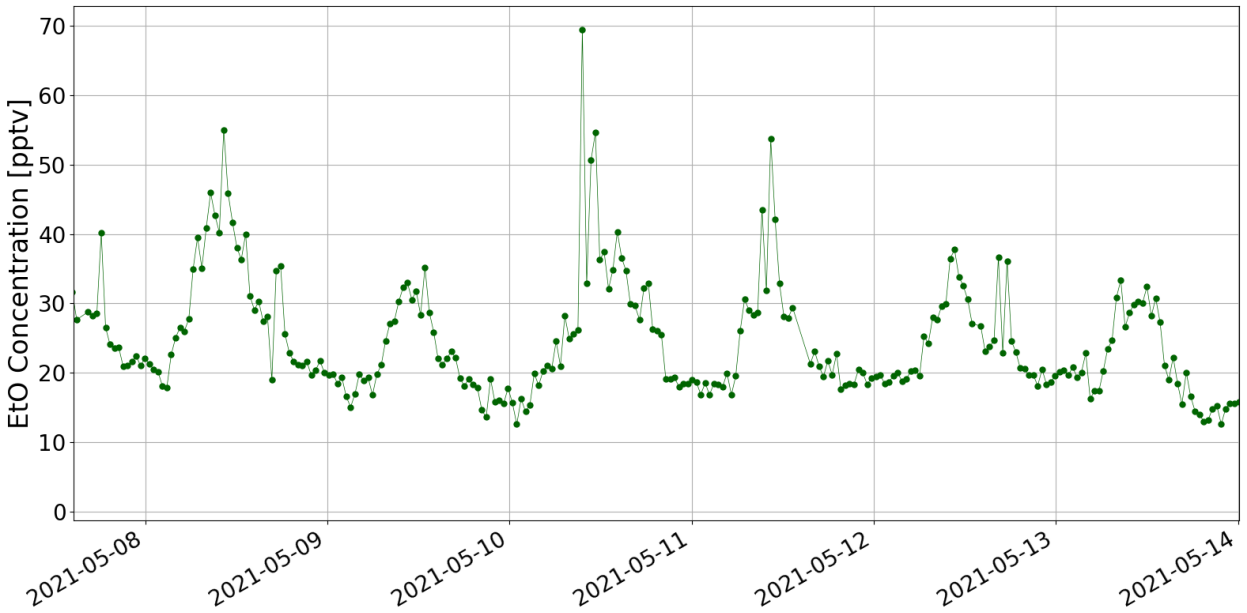
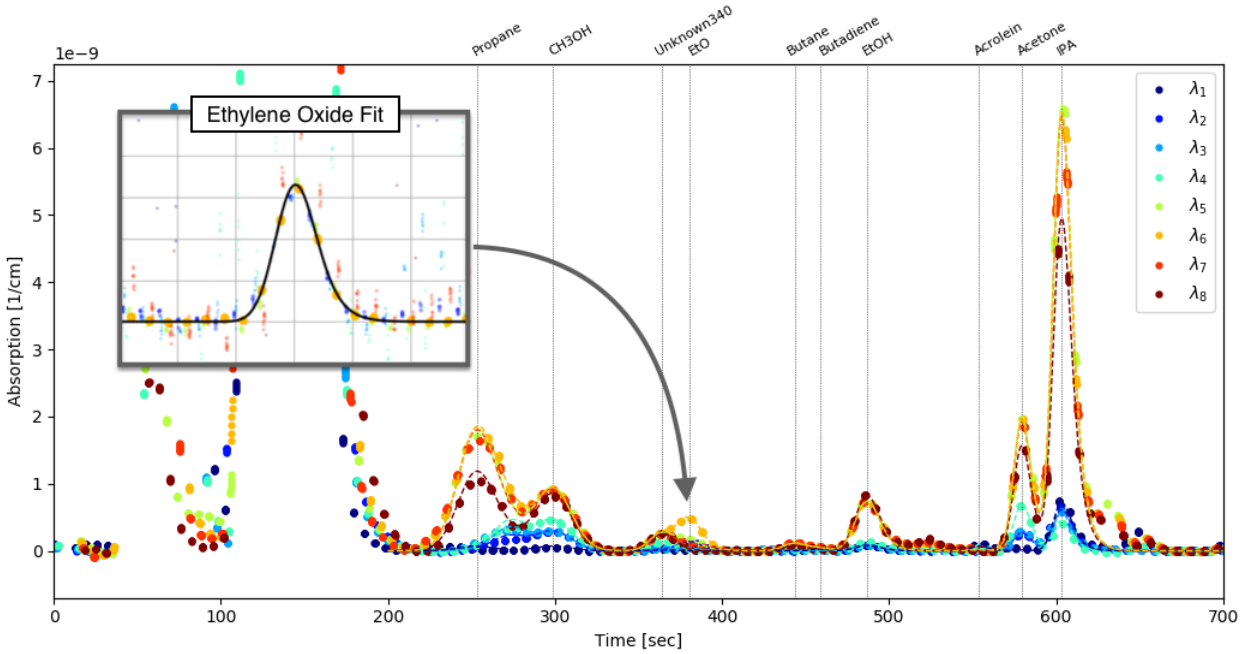
Continuous Ambient Measurements of Ethylene Oxide



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).



Typical analysis trace measured at ground-level in San Bruno, CA. Ethylene Oxide fit result shown in inset plot.

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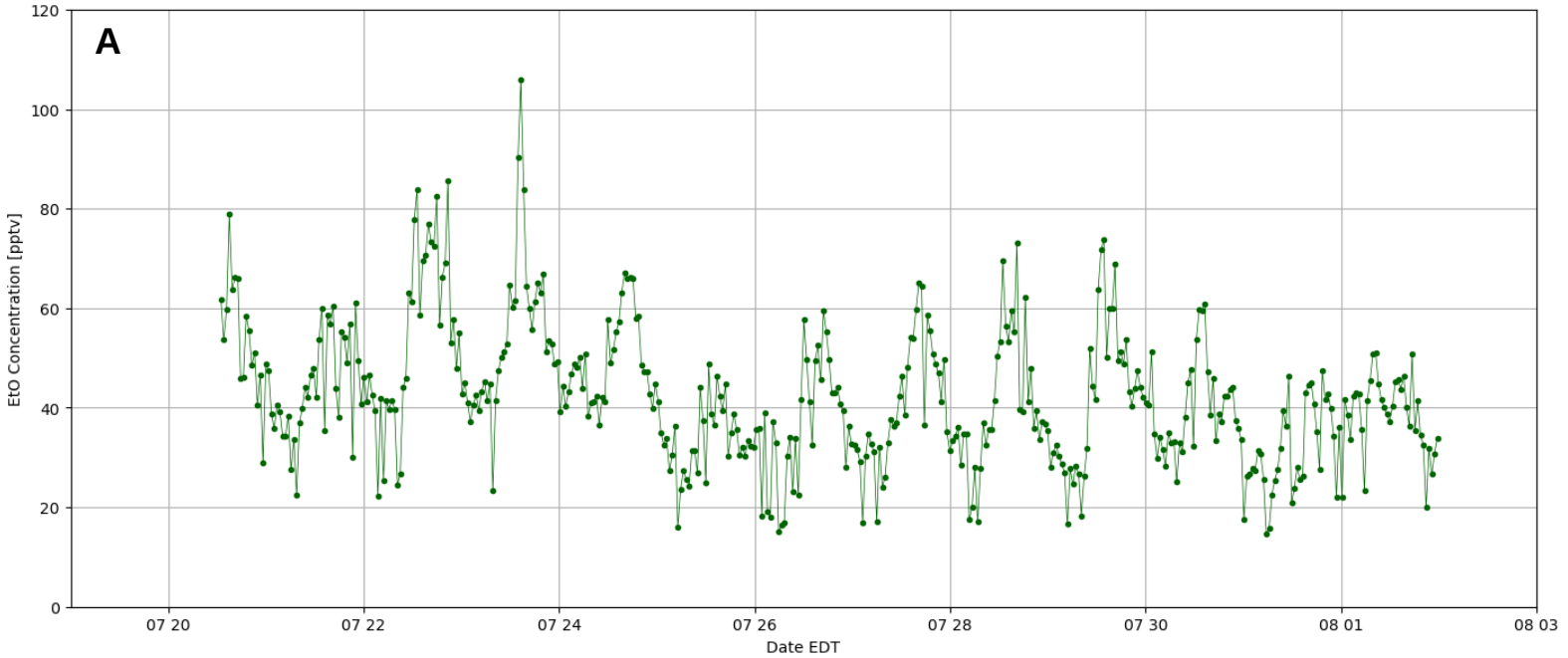
Ambient Measurements of Ethylene Oxide



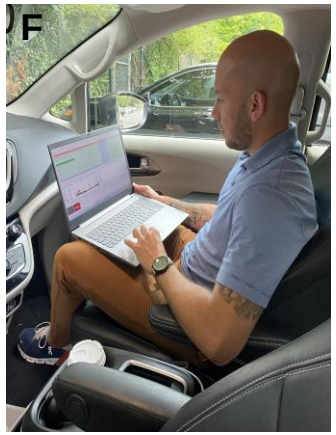
Pictures courtesy of Georgia Environmental Protection Division

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

(B) South DeKalb NATTS site managed by Georgia EPD. This is considered an urban background site.

(C) AROMA-ETO installed in the South DeKalb NATTS site and remotely operated by Entanglement Technologies.

(D) EtO measurements at a sterilization facility in GA. Upwind and downwind measurements were made as well as at site, which is labeled by the boxes with EtO concentrations.



(E) AROMA-ETO installed in rental minivan for mobile monitoring in Georgia.

(F) Entanglement Technologies' Pedro Benavides viewing AROMA-ETO data in real-time.

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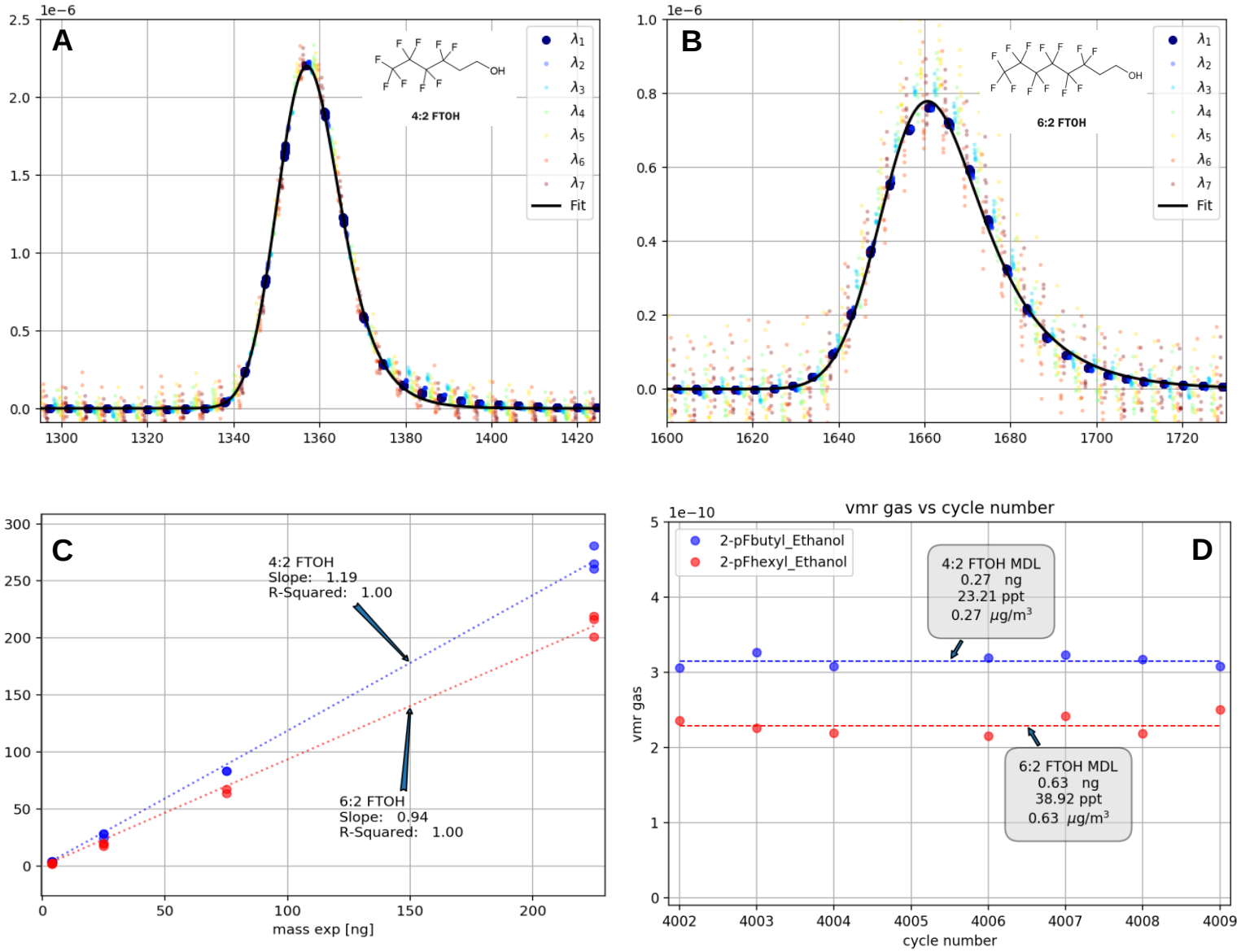
Measuring FTOHs in Air



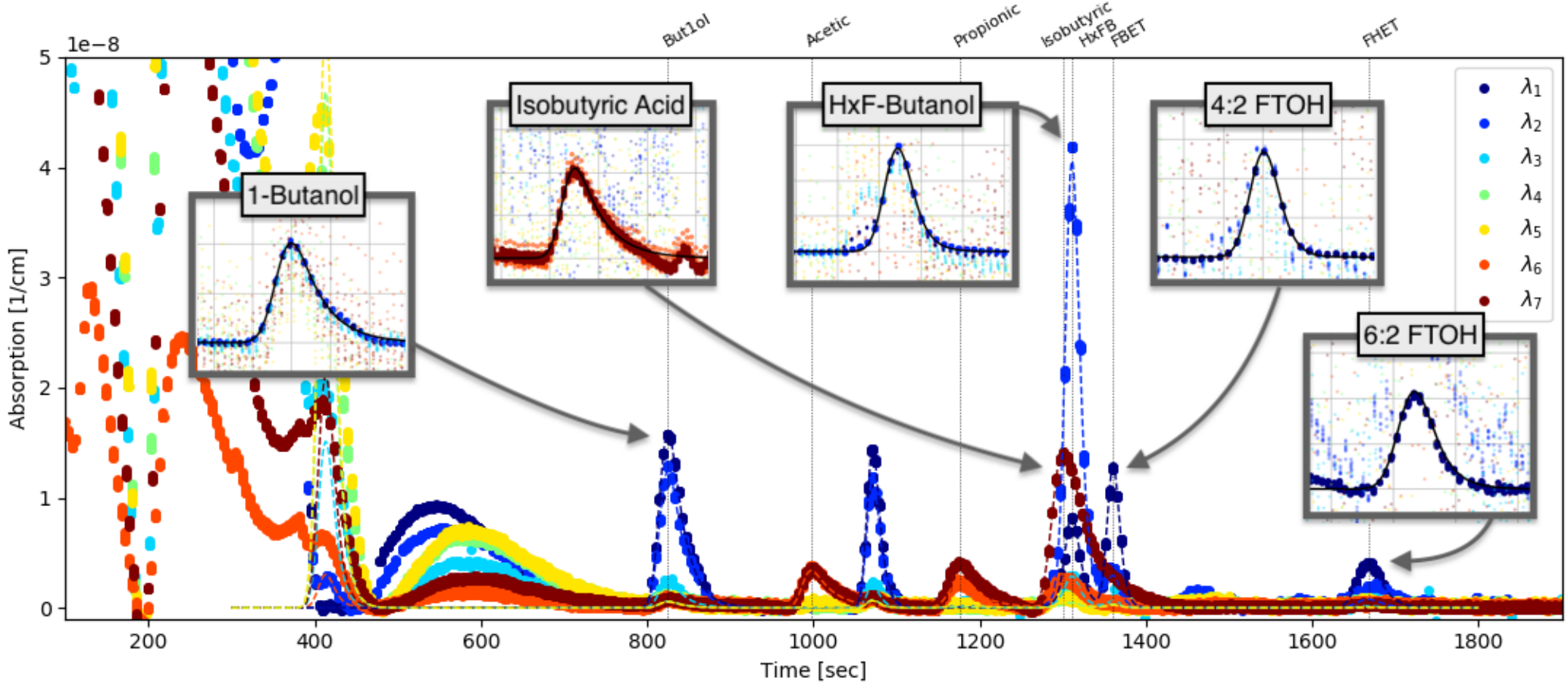
(A) Spectral fit of 1H,1H,2H,2H-Perfluoro-1-hexanol (4:2 FTOH)

(B) Spectral fit of 1H,1H,2H,2H-Perfluoro-1-octanol (6:2 FTOH)

(C) Mass calibration curve from injection of varying volumes of 25 ppm 4:2 and 6:2 FTOH

(D) Calculated method detection limits of 4:2 and 6:2 FTOH are 23 pptv and 39 pptv, respectively.

Multi-Compound Analysis



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Summary and Conclusions

- AROMA is exceptionally robust and very easily deployable for stationary and mobile studies
- TD-CRDS can address emerging contaminant 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:

EDF Environmental Defense Fund – Finding the ways that work; Stanford University; PCS Pollution Control Services; United States Environmental Protection Agency; Baylor University; City of Houston Texas; City of Redding California; Colorado State University; Chevron; Geosyntec consultants; California Air Resources Board; Phillips 66; GSI Environmental; Colorado Department of Public Health & Environment; University of Kentucky; Bay Area Air Quality Management District; FIU; eki environment & water; DCMR milieudienst Rijnmond; STI Sonoma Technology, Inc.

- Various options for collaboration with Entanglement Technologies

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Questions?

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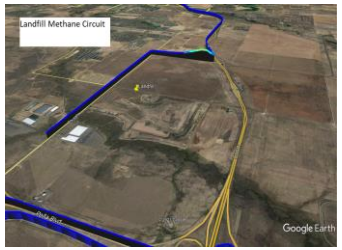
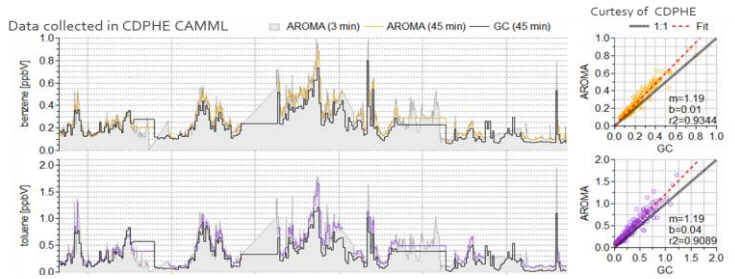
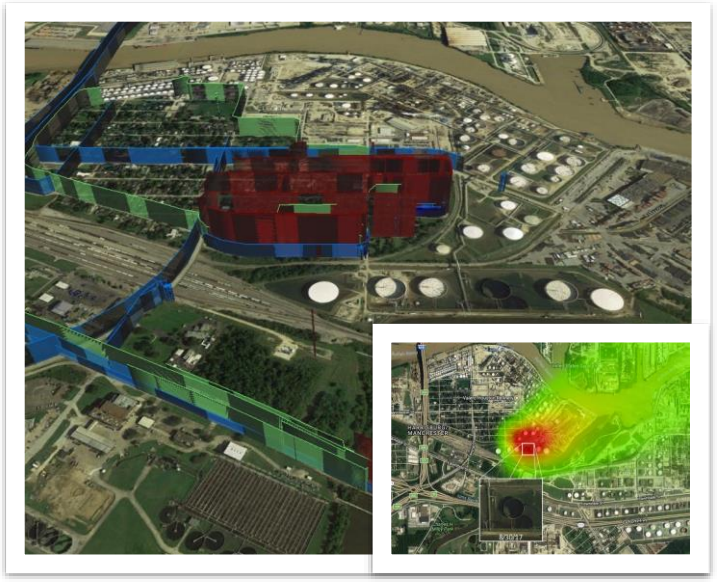
New Approach, New Capabilities

- *Rapid Emergency Response*
- *Automated hyper-local pollution mapping*
- *Broad area surveys with automatic source localization*
- *Process Control for online intervention at emission point*
- *Enables plume fingerprinting and flux determination for secondary analyses of data*

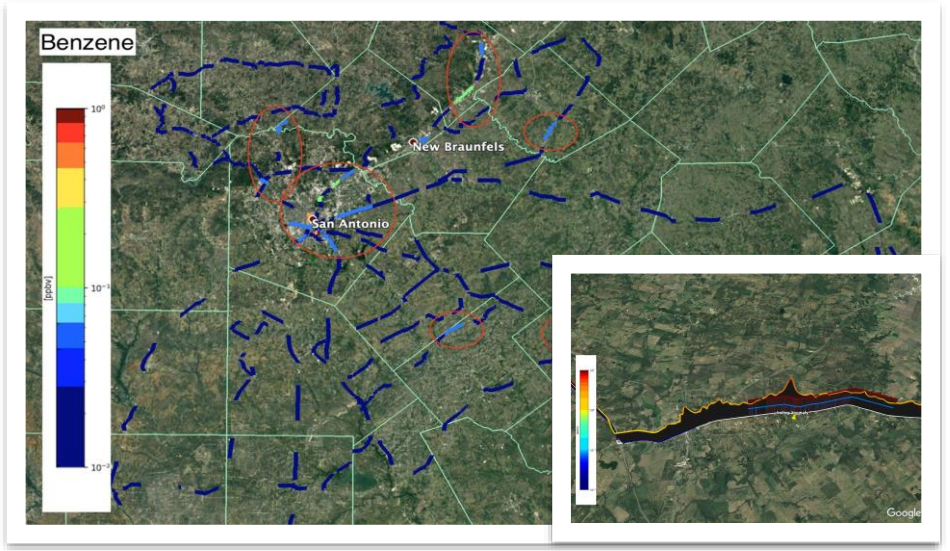




Mobile and stationary measurements made in Longmont and Denver, CO. AROMA BTEX measurements were made next to an oil well pad and co-located dual auto-GC. Mobile measurements were made from a rental minivan as well as a CDPHE vehicle.



Mobile monitoring after Hurricane Harvey in Houston, TX.
Likelihood of source origin using concentration, locations, and met data.
Good agreement with subsequent satellite data



Large area ozone precursor study in San Antonio, TX. Daily data example for benzene and combined LabScan and RapidScan data (inset).

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