A comparison of a PTR-ToF-MS against four other VOC measurement methods using standardized techniques during fence-line monitoring in seven states

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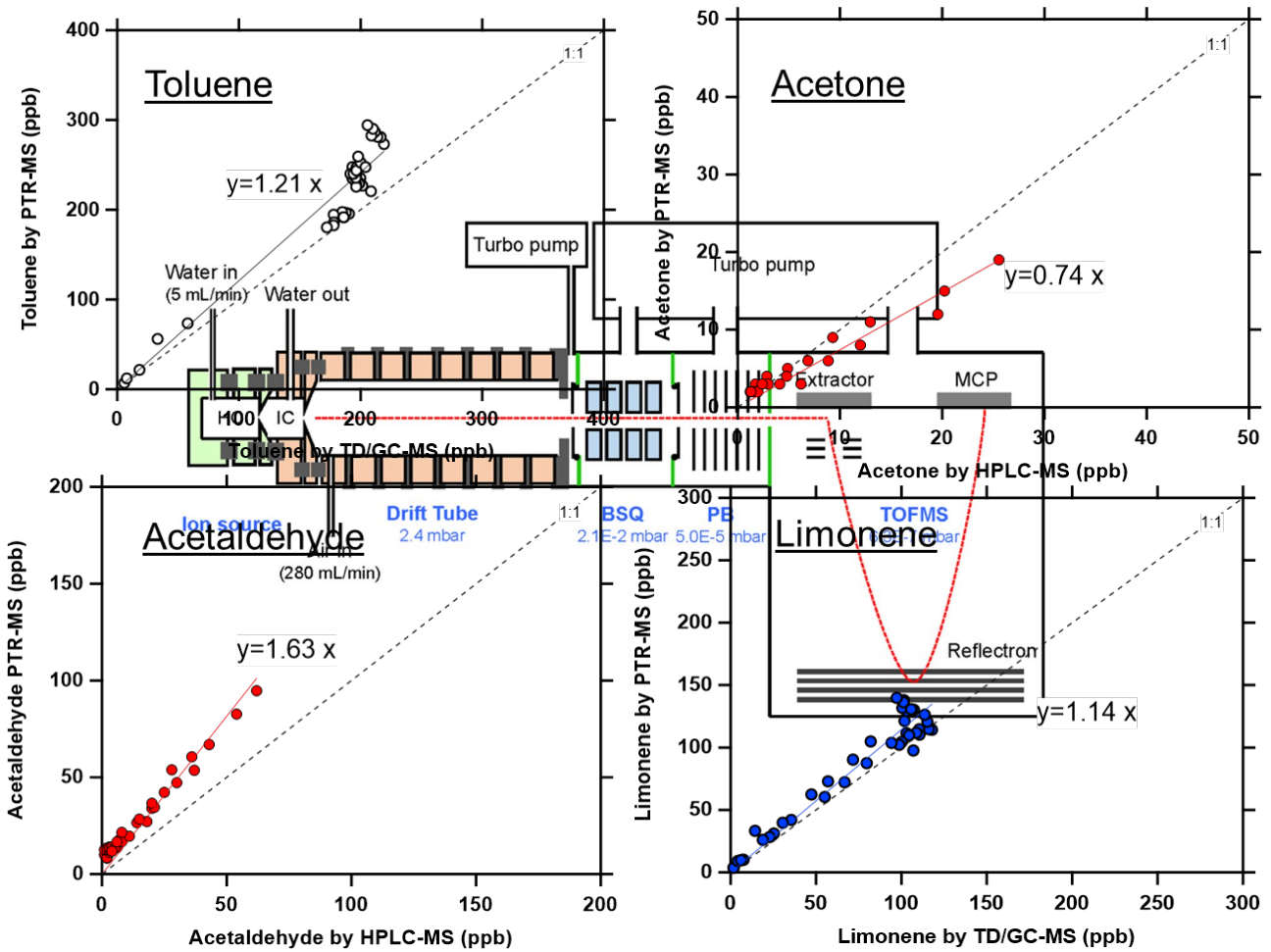
Study Objectives

- Conduct fenceline monitoring around VOC-emitting facilities across 7 states
- Comparisons of PTR-ToF-MS against:
  - Offline GC-MS
  - UV-DOAS
  - SIFT-MS
  - Auto-GC-FID
- Evaluate intercomparison methods for stationary and mobile measurements

Proton Transfer Time-of-Flight Mass Spectrometer (PTR-ToF-MS) and Laboratory Testing

- Previous studies have found that the PTR-ToF-MS compares well with traditional VOC-measuring techniques
- Yuan et al. (2016) concluded that the accuracy of the PTR-MS is ~20% across 58 studies
- Six controlled large chamber studies were collected across 9 periods
- Sorbent tubes were used to collect measurements over 10-15 minutes
- PTR-ToF-MS measurements were compared against:
  - HPLC-MS (ISO 16000-3)
  - TD/GC-MS (ISO 16000-6)



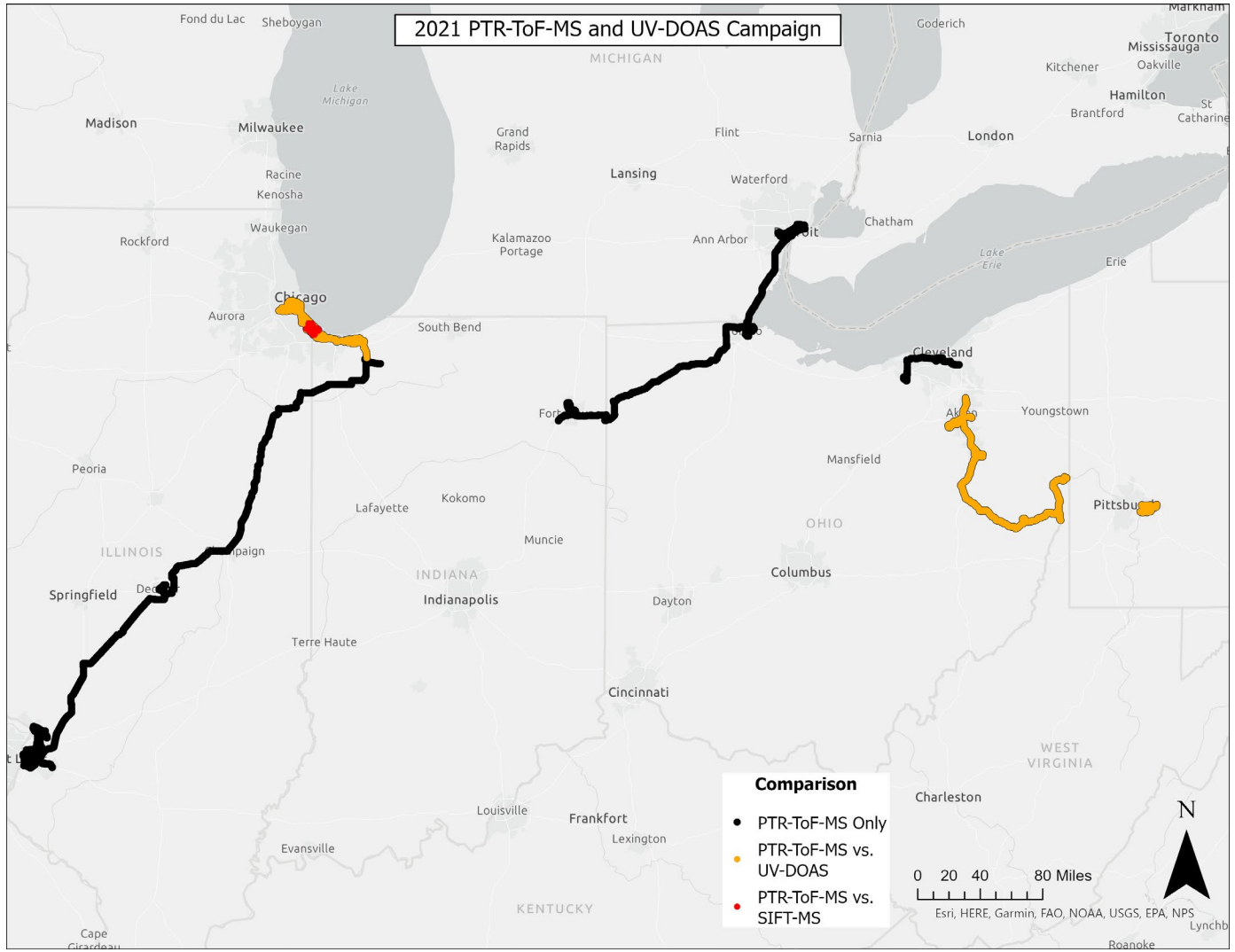
[Yuan et al. 2016]

Campaign Study Area

- 11 days of measurements in August 2021
- Measurements were taken across seven states
- Ambient air was evaluated around ~50 facilities
- Comparisons were conducted at different periods of the study

The study primarily focused on 18 different compounds:

Acetaldehyde	Toluene
Acrylonitrile	Styrene
1,3-Butadiene	Benzaldehyde
Acrolein	Xylene
Acetone	Trimethylpentane
2-Butanone (MEK)	Trimethylbenzene
Benzene	Naphthalene
Ethyl acetate	Trichloroethylene
MTBE	1,4-Dichlorobenzene



Instrumentation

Three mobile platforms were used during fenceline measurements:

A) US EPA Geospatial Measurement of Air Pollution (GMAP)

1. DUVAS Technologies Ultra-Violet Differential Optical Absorption Spectrometer (UV-DOAS)
2. GPS-Weather Station
3. Canisters (EPA TO-15 Method, ~15-30 seconds)

B) RJ Lee Group Mobile Laboratory

1. Ionicon PTR-TOF-MS 4000
2. GPS-Weather Station
3. Canisters

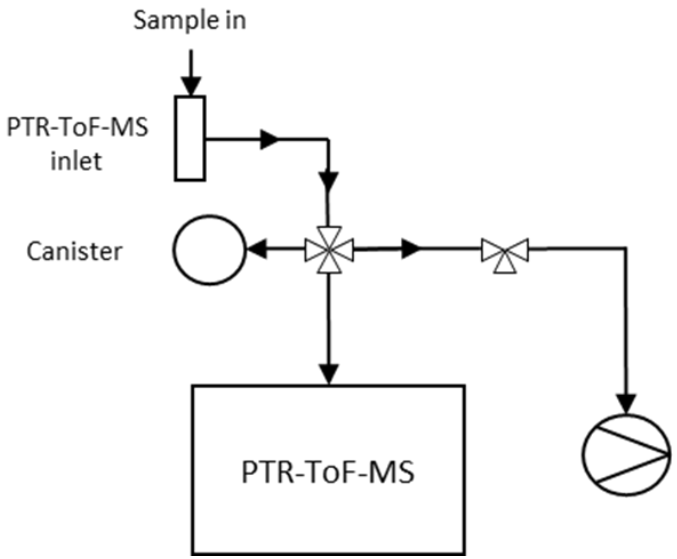
C) Syft Technologies Mobile Laboratory

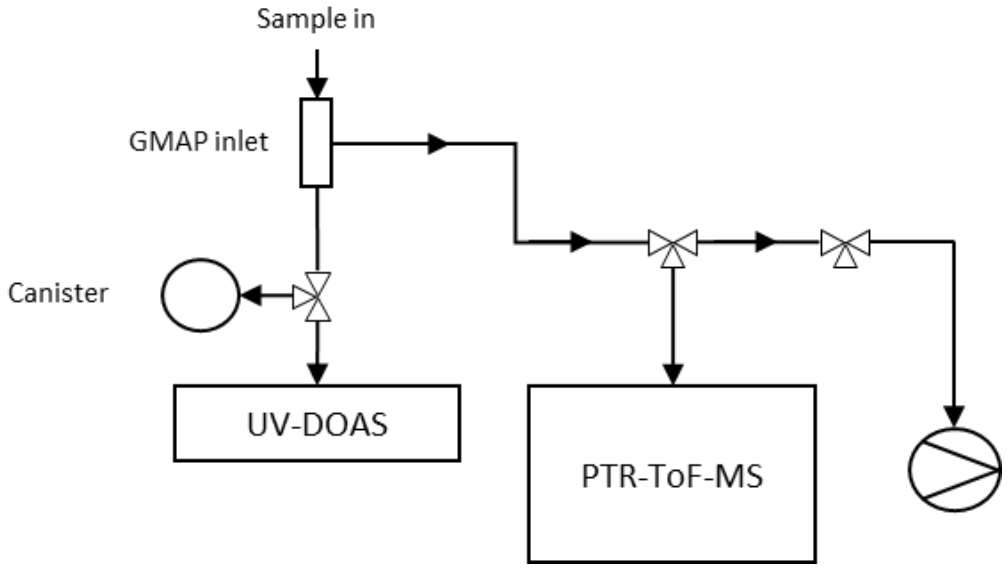
1. SIFT-MS (Voice200ultra)
2. GPS-Weather Station

D) PAMS Monitoring Site (MDNR)

1. Chromatec GC-FID

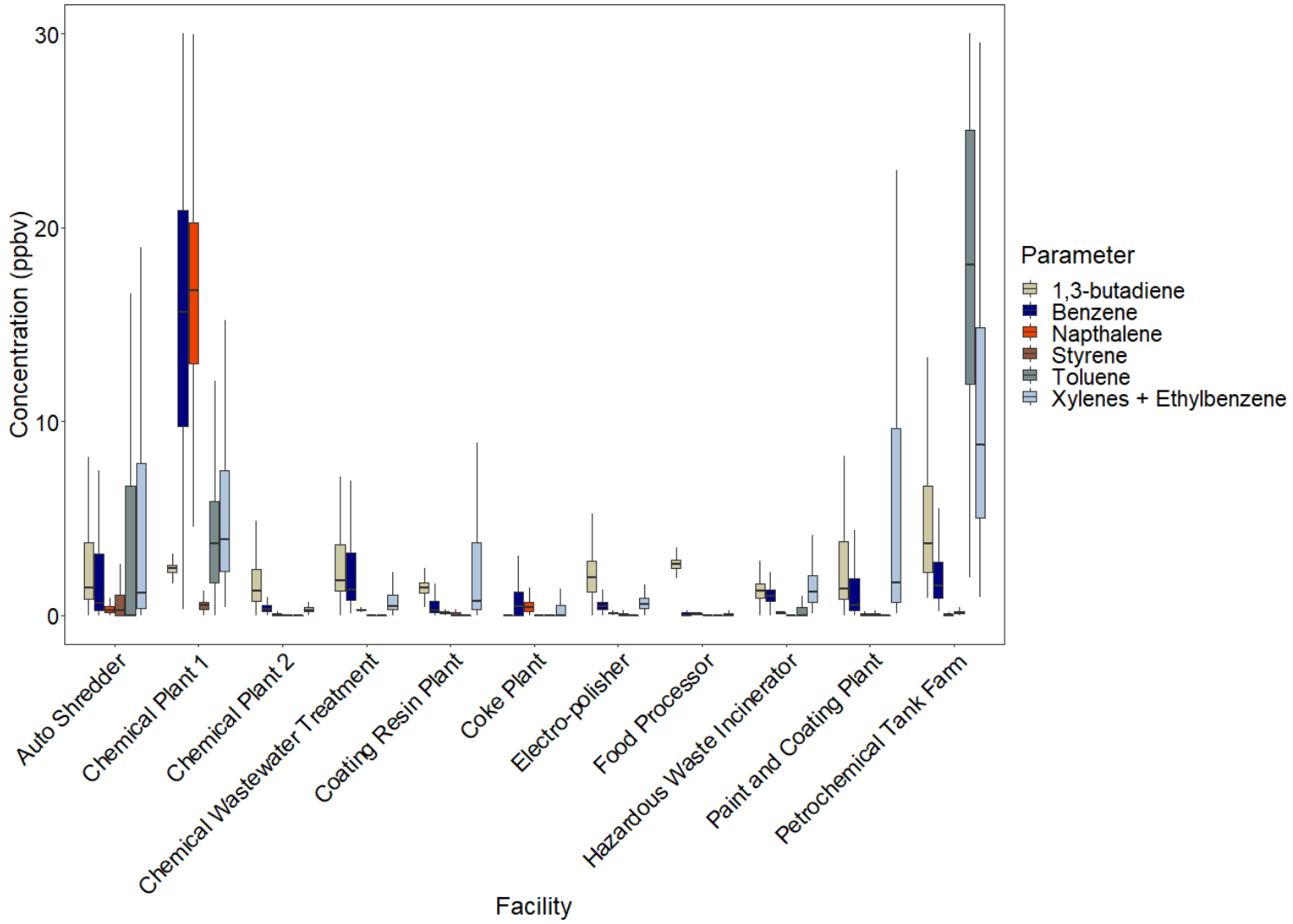
Stationary Measurement Setup





Stationary PTR-ToF-MS VOC Concentrations

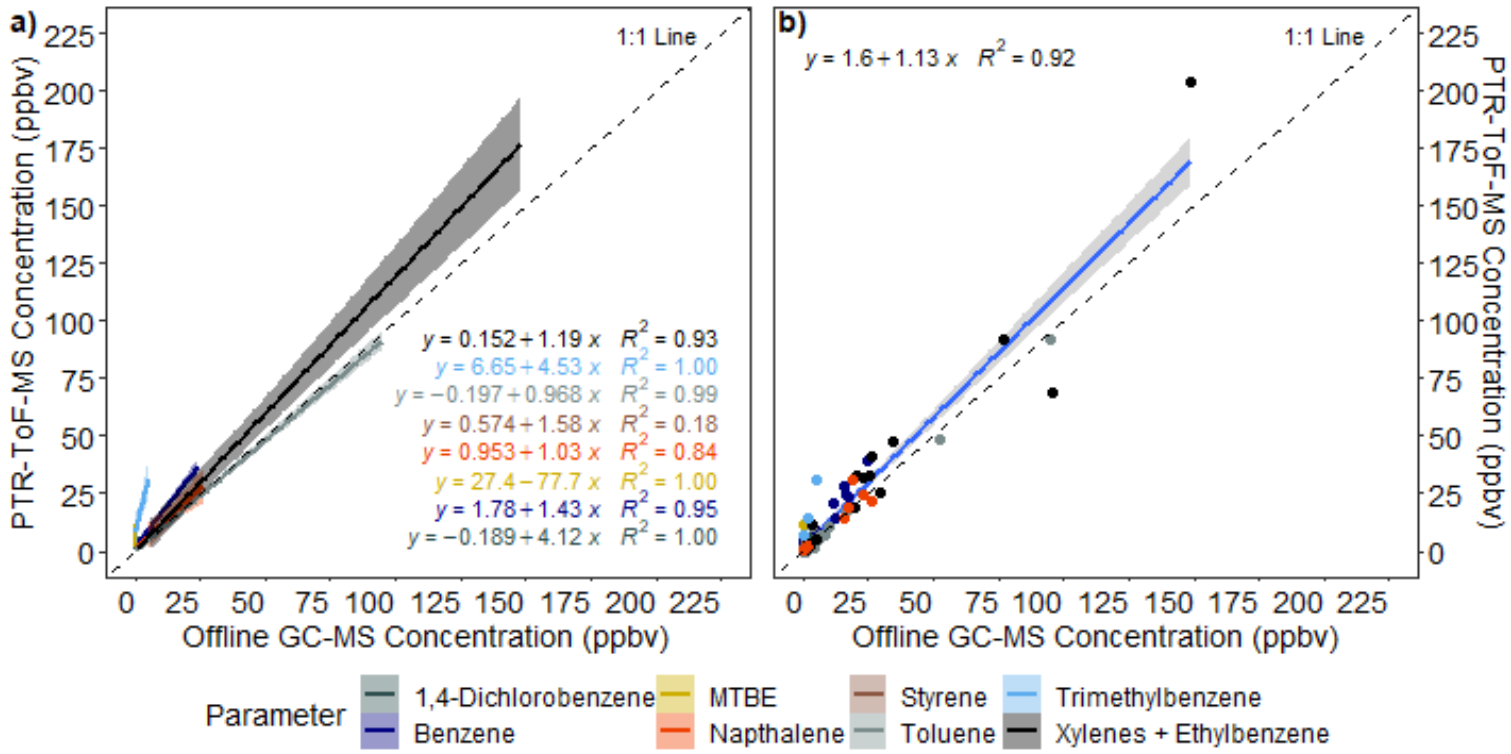
- During the campaign, the highest concentrations were observed at a chemical plant and petrochemical tank farm/auto body shop
- 1,3-butadiene, toluene, and xylenes were observed at many of the facilities
- More unique VOCs (e.g., naphthalene) were only observed at a handful of facilities
- Some outliers are not shown



Comparison of PTR-ToF-MS and Offline GC-MS

(stationary measurements)

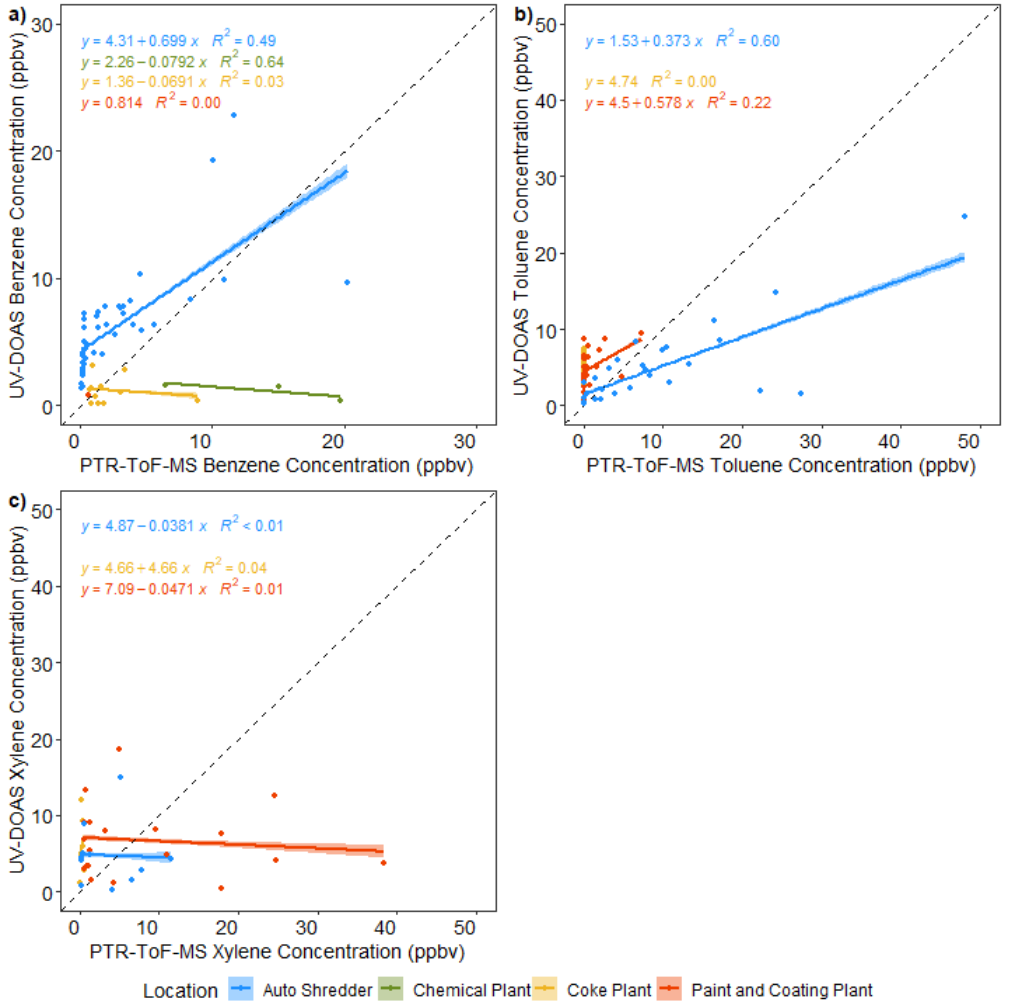
- Well-performing compounds:
  - Xylenes + Ethylbenzene
  - Toluene
  - Naphthalene
  - Benzene
- High magnitude slopes:
  - Trimethylbenzene
  - MTBE
  - 1,4-Dichlorobenzene
- Poor-performing compounds:
  - Styrene
- **Overall good agreement**
  - **R^2 = 0.92, slope = 1.13**



Comparison of PTR-ToF-MS and UV-DOAS

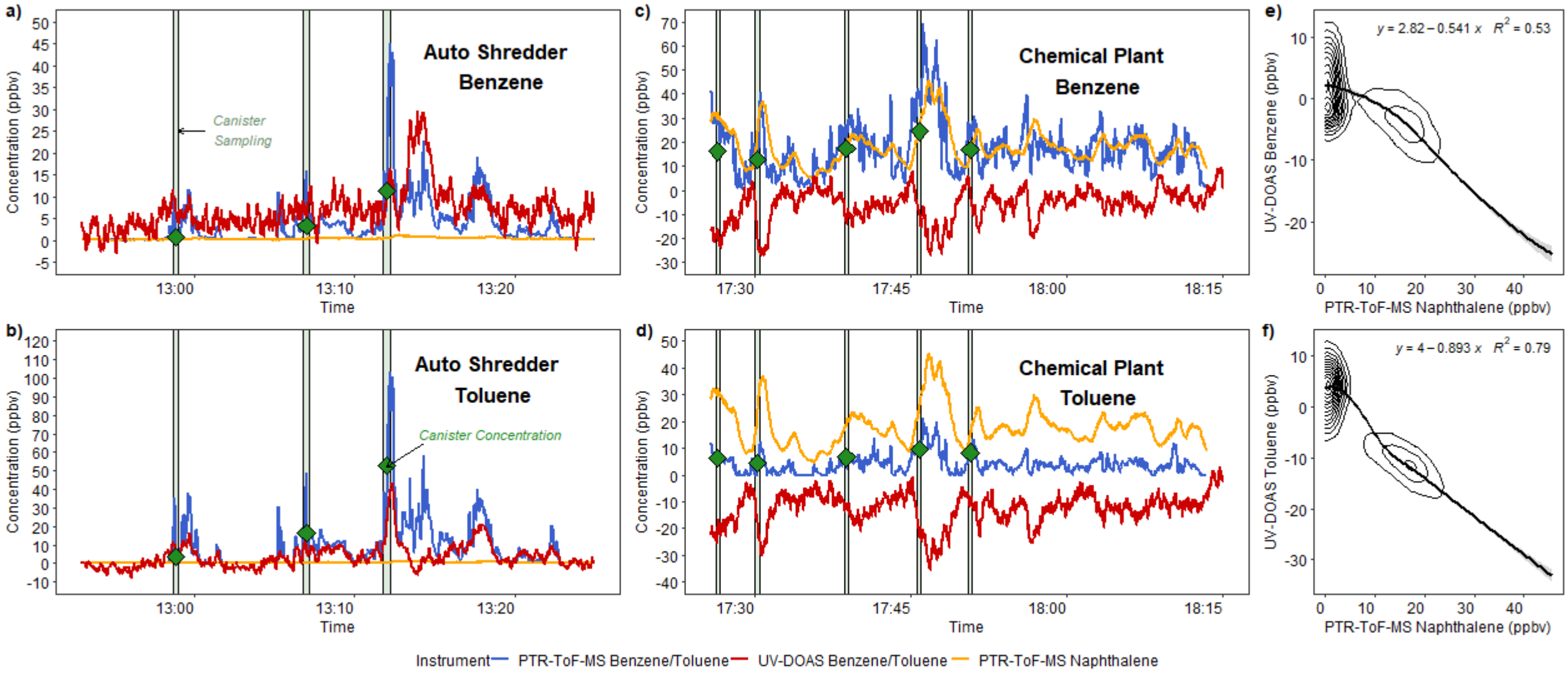
(stationary measurements)

- Two stationary comparisons performed well while the other two did not
- Auto Shredder/Paint and Coating Plant:
  - Benzene and toluene compared well
  - Xylenes did not compare well
- Chemical plant/coke plant:
  - No parameters compared well
- The inherent measurement method by the UV-DOAS can lead to measurement anomalies due to wavelength interferences
- Naphthalene was present at both the chemical and coke plants



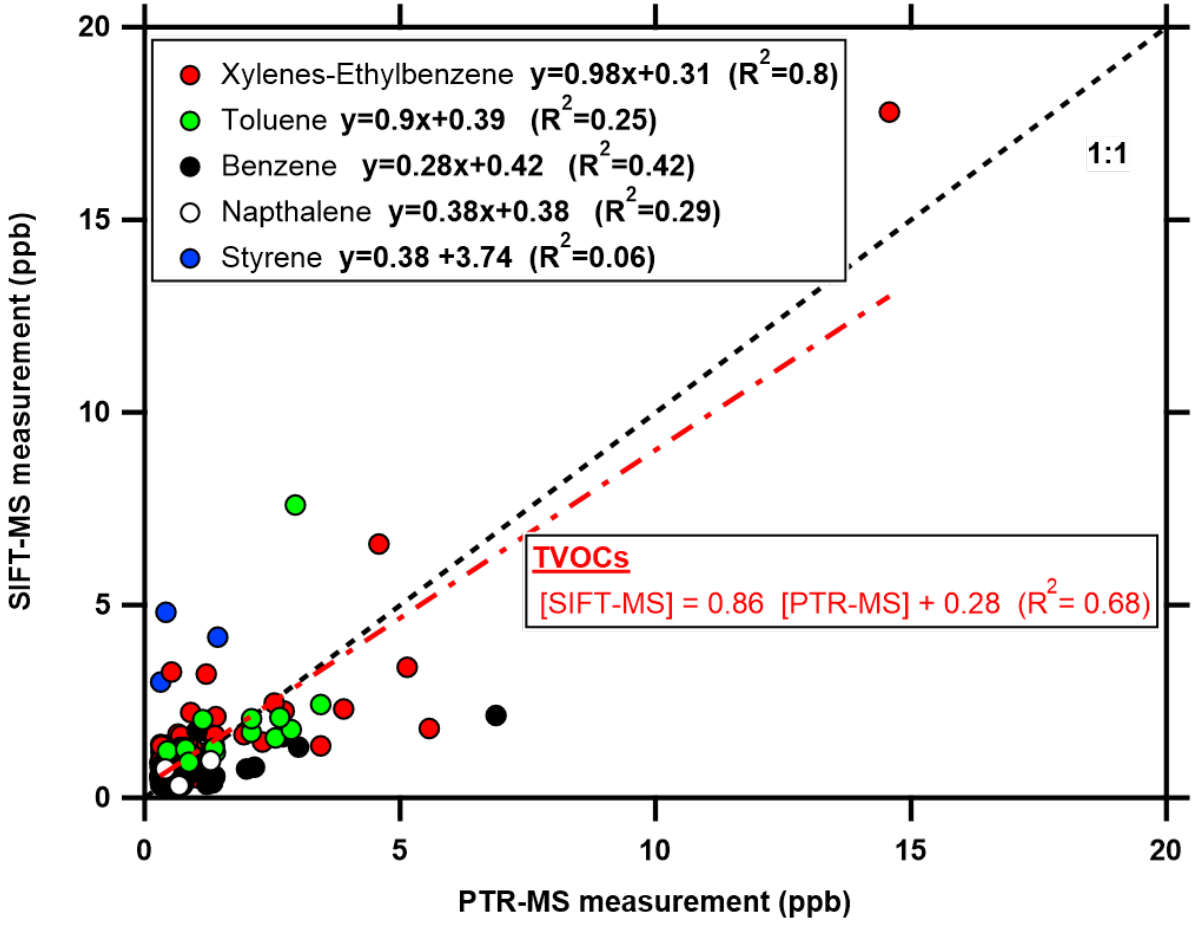
Measurement Time Series Comparison

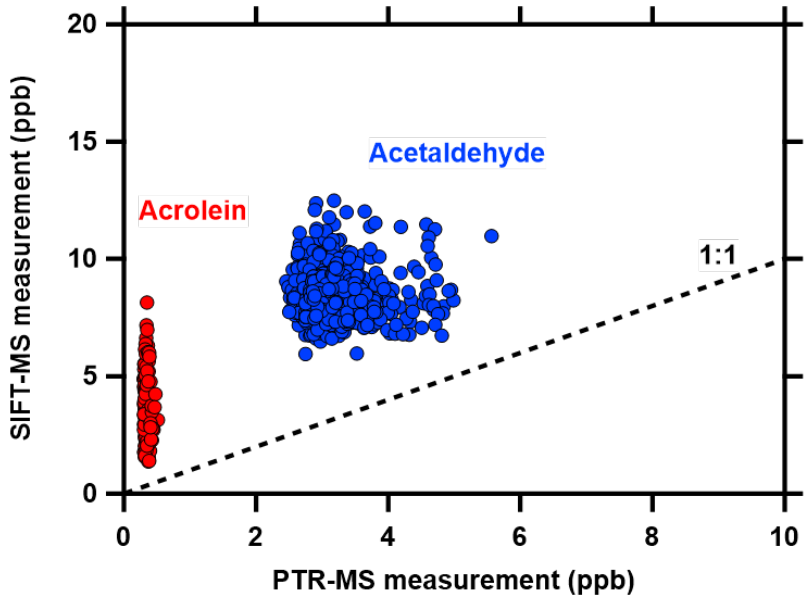
(PTR-ToF-MS vs. UV-DOAS vs. Offline GC-MS – stationary measurements)



Comparison of PTR-ToF-MS and SIFT-MS

(mobile measurements)



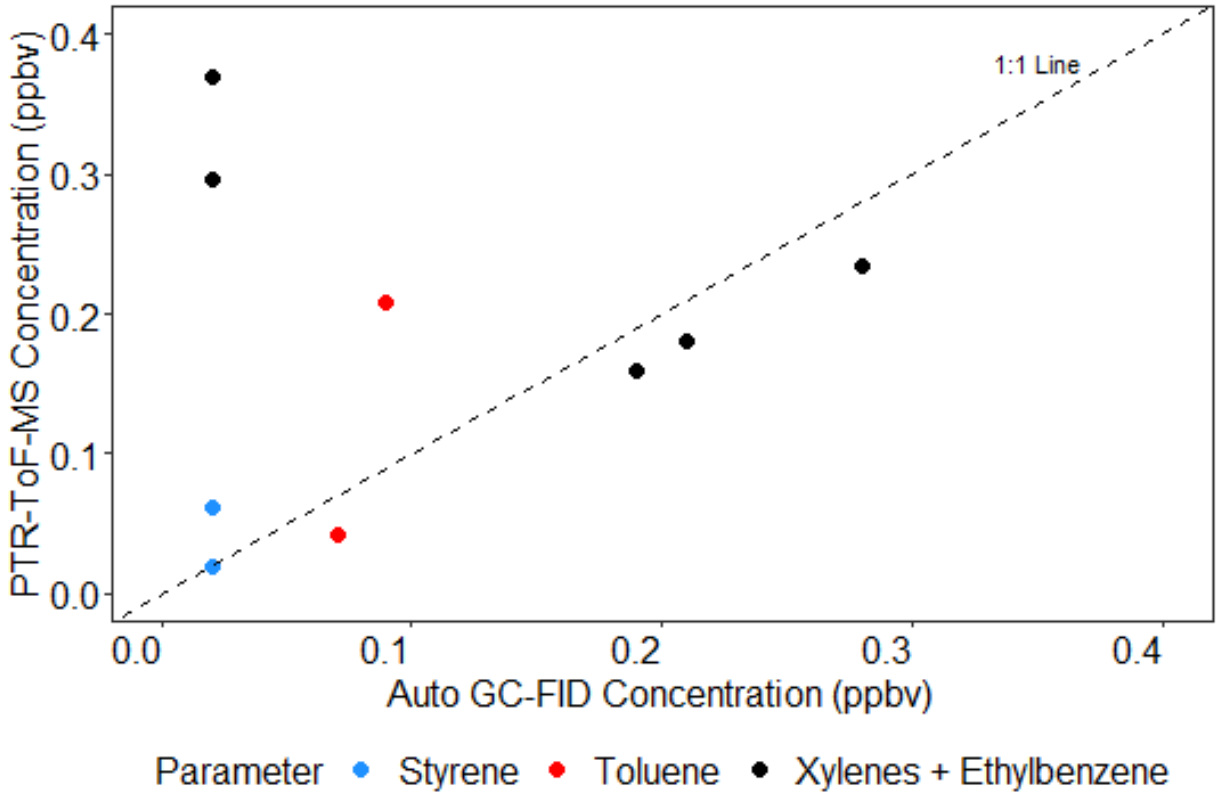


- Acetaldehyde: possible interferences with CO_2
- Acrolein: possible interferences with water clusters, Butene

Comparison of PTR-ToF-MS and Auto GC-FID

(stationary measurements)

- The PTR-ToF-MS was compared against an auto-GC-FID for five hours
- There was not good agreement in the aromatic measurements
- Concentrations were low for these measurements and were near the MDLs for the PTR-ToF-MS



Conclusions

- PTR-ToF-MS:
  - Good agreement with TO-15 method (r^2 = 0.92, slope = 1.13)
  - Toluene/naphthalene measurements within 3%
  - Xylenes within 19%
  - Measured higher for benzene and styrene (43% and 58%, respectively)
  - Trimethylbenzene, 1,4-dichlorobenzene, and MTBE had large discrepancies
- UV-DOAS:
  - Naphthalene caused large interferences
  - Very dependent on the ambient air matrix
- SIFT-MS:
  - BTEX measurements were very similar and showed good agreement
  - Acetaldehyde and acrolein had large discrepancies, likely due to interferences
- Auto GC-FID
  - Compared fairly well with the PTR-ToF-MS, but were near the latter's MDLs

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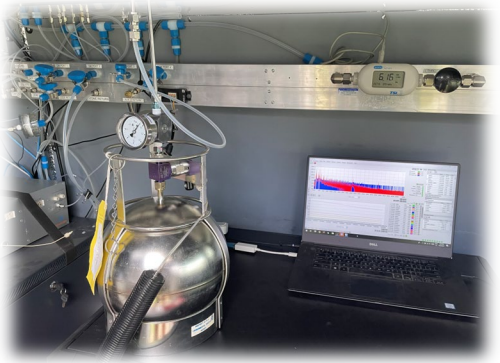

Session Q&A Discussion

Please submit your questions for the session speakers through Whova – on your mobile or desktop device.

Make sure to note WHOM your question should be addressed to.

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Thank You for joining us for the first Part 1 of the session.

Part 2 will begin momentarily.

Part 2 Speakers:

Leslie Silva, *Syft Technologies*

Dr Jean-Christophe Mifsud, *ELLONA*

Pami Mukherjee, *South Coast Air Quality Management District*

Steven Schill, *Sonoma Technology*

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