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

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1 RJ Lee Group DELIVERING SCIENTIFIC RESOLUTION

2 EPA United States Environmental Protection Agency

3 syft™ Technologies

Fenceline monitoring

- A method to measure air quality surrounding VOC-emitting facilities in efforts to assess neighboring community exposures.
- Traditional VOC testing methods include the collection of an air sample using a media, and its subsequent analysis in the lab
  - Such methods are TO-15 (summa canister) and TO-11/TO-17 (sorbent tubes)
- Instrumentation that can provide online real-time VOC measurements is one of the most effective ways for high temporal resolution
  - PTR-ToF-MS
  - SIFT-MS
  - UV-DOAS
  - Auto-GC
- The use of such equipment in mobile platforms can also provide high spatial resolution

Field campaign

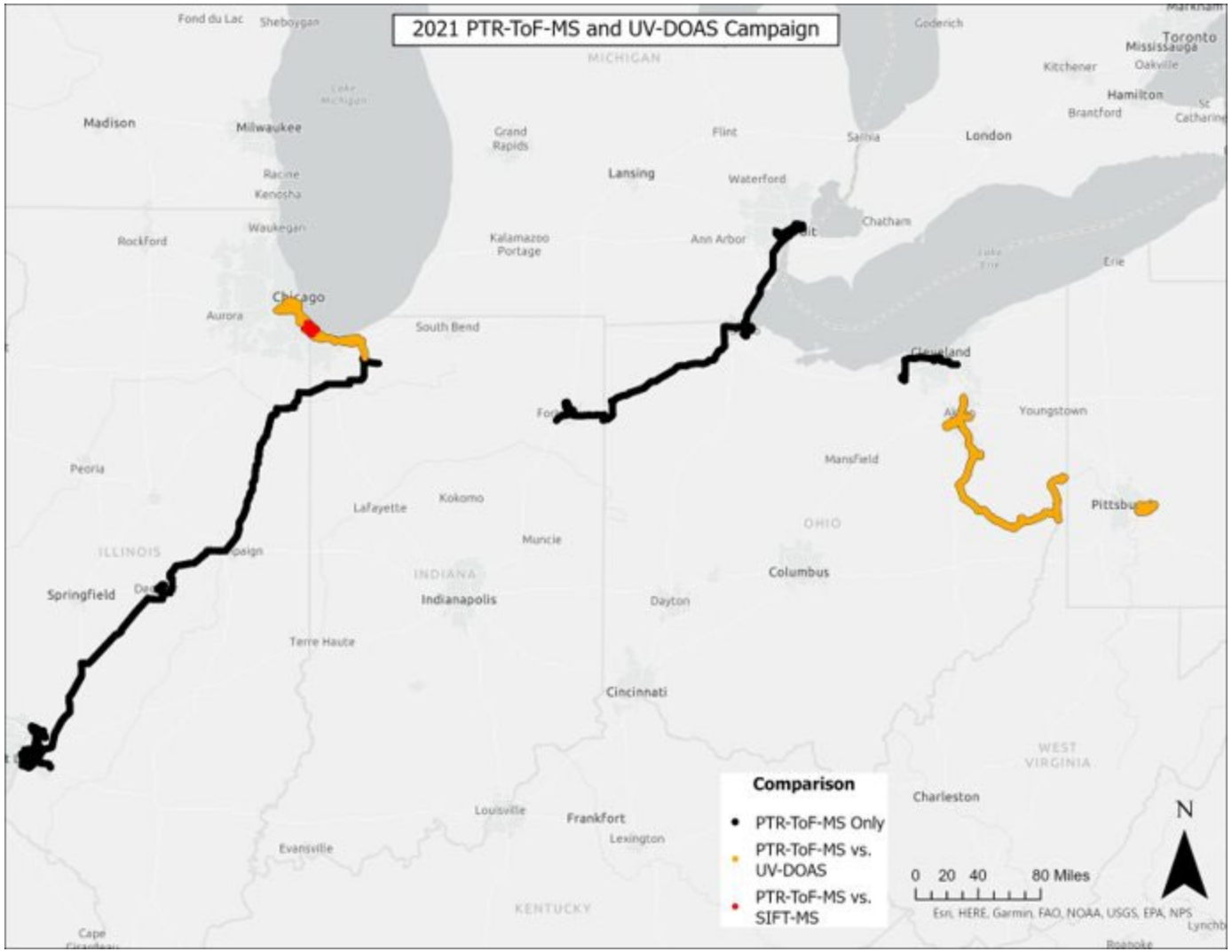
- Fenceline monitoring was completed around facilities across six states (PA, WV, OH, MI, IN, IL)
  - Chemical plants
  - Coke plants
  - Metals recycler/auto shredder
  - Paint and coating plants
  - Hazardous waste incinerator
  - Wastewater treatment plants

- Stationary comparisons were also conducted at a Missouri DNR PAMS site – Blair St. Site

Objectives

- Conduct fenceline monitoring around VOC-emitting facilities
- Comparison of PTR-ToF-MS with an EPA approved method (TO-15)
- Comparison of the PTR-ToF-MS with other instrumentation
  - UV-DOAS
  - SIFT-MS
  - Auto-GC-FID

Mobile measurements



- 11 days of measurements during August 2021
- Measurements were conducted in 6 states and around 50 facilities
- Intercomparison measurements were conducted around 11 facilities in 4 states

The study was focused on the measurement of 18 compounds

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

Instrumentation

Three mobile platforms were used during the 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. Summa cannisters (method EPA TO-15)

B) RJ Lee Group Mobile laboratory

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

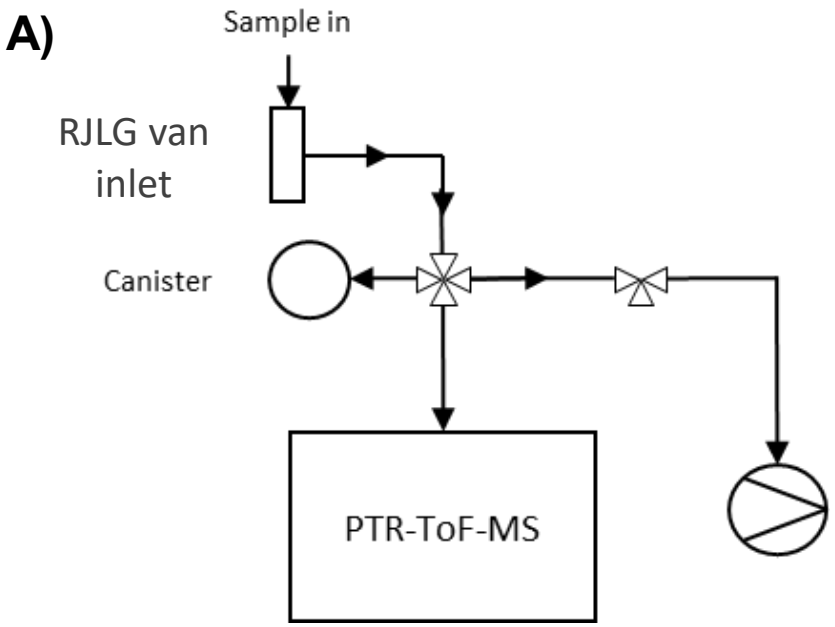
C) Syft Technologies Mobile Laboratory

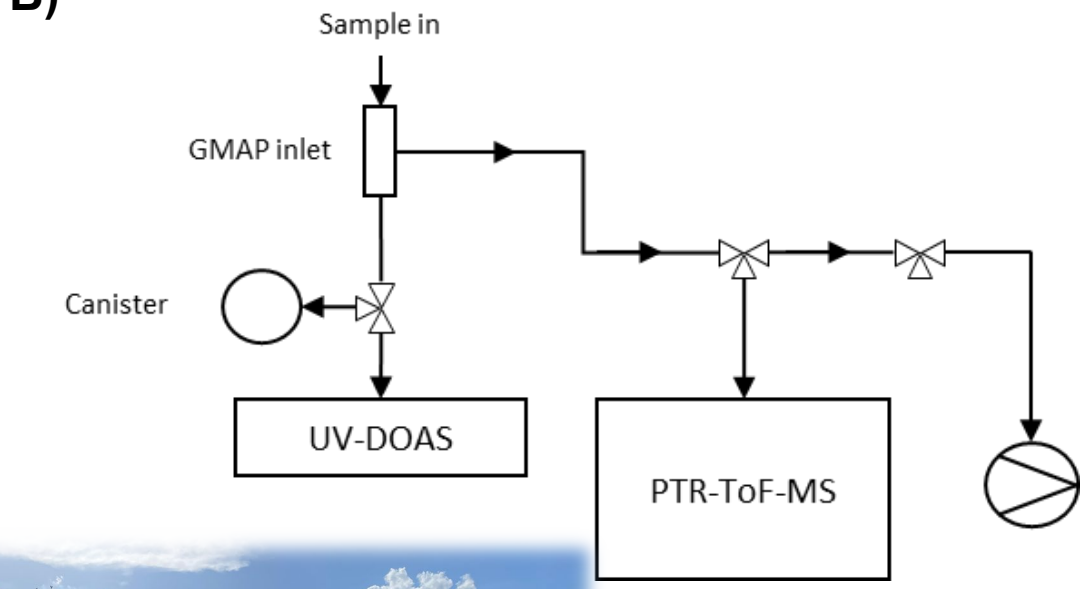
1. SIFT-MS (Voice200ultra)
2. GPS-Weather Station

PAMS Monitoring Site (MDNR)

Auto-GC-FID (Chromatec)

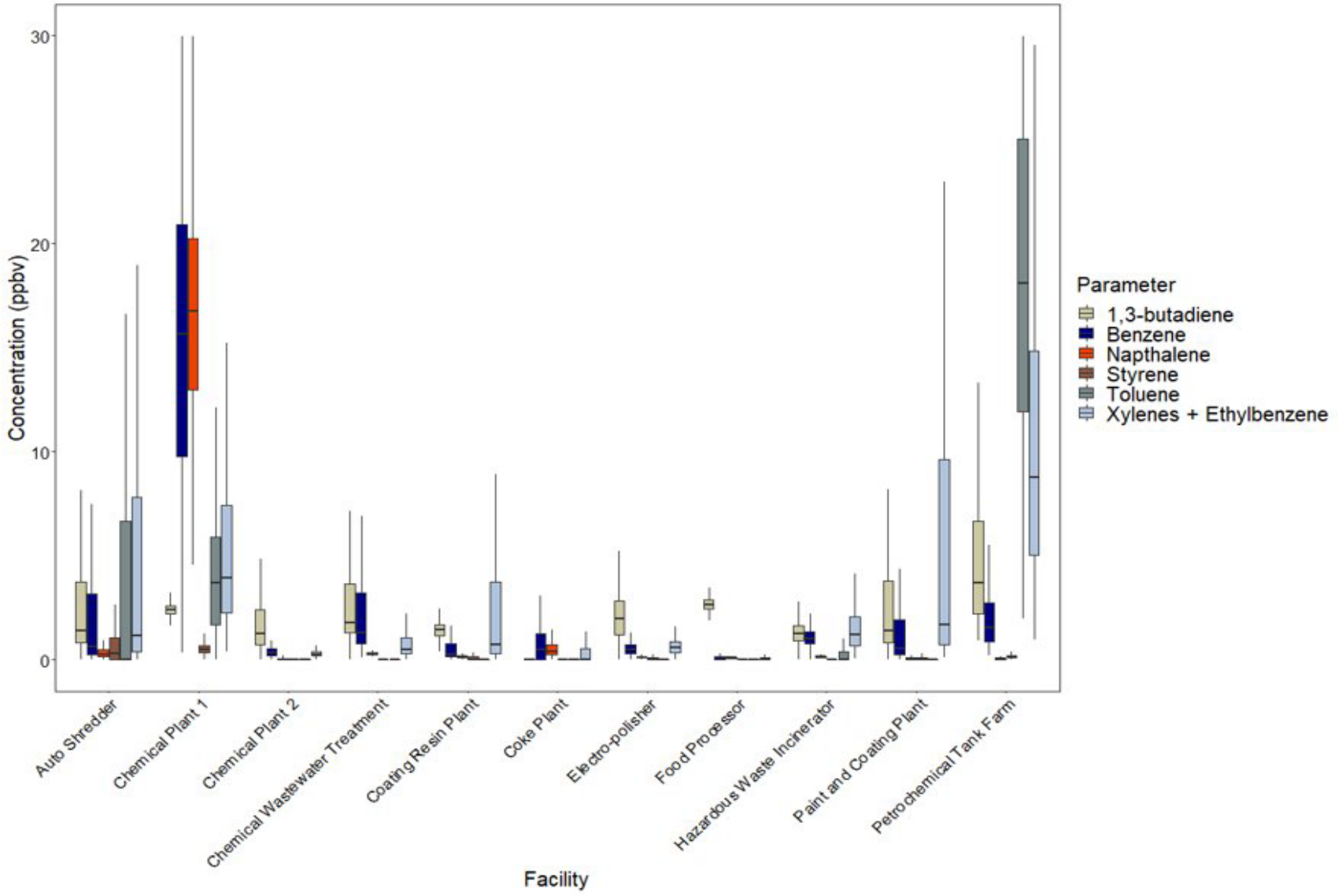
Measurement Setup



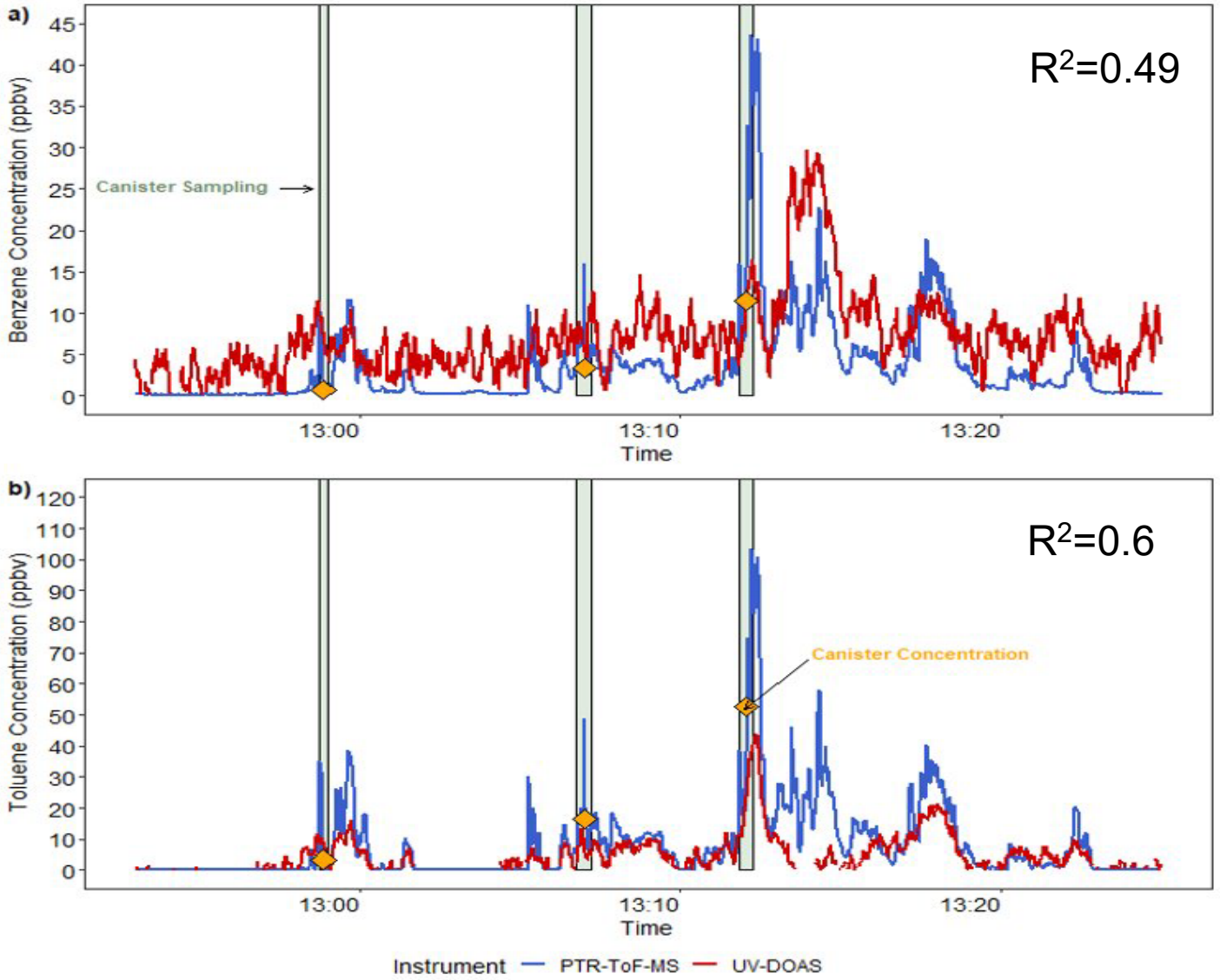


Average stationary VOC concentration per facility
(PTR-MS measurements)

- During the campaign, the highest concentrations were observed at a chemical plant and petrochemical tank farm
- 1,3-butadiene, toluene, and xylenes were observed at many of the facilities
- More unique compounds (e.g., naphthalene) were only observed at a handful of facilities

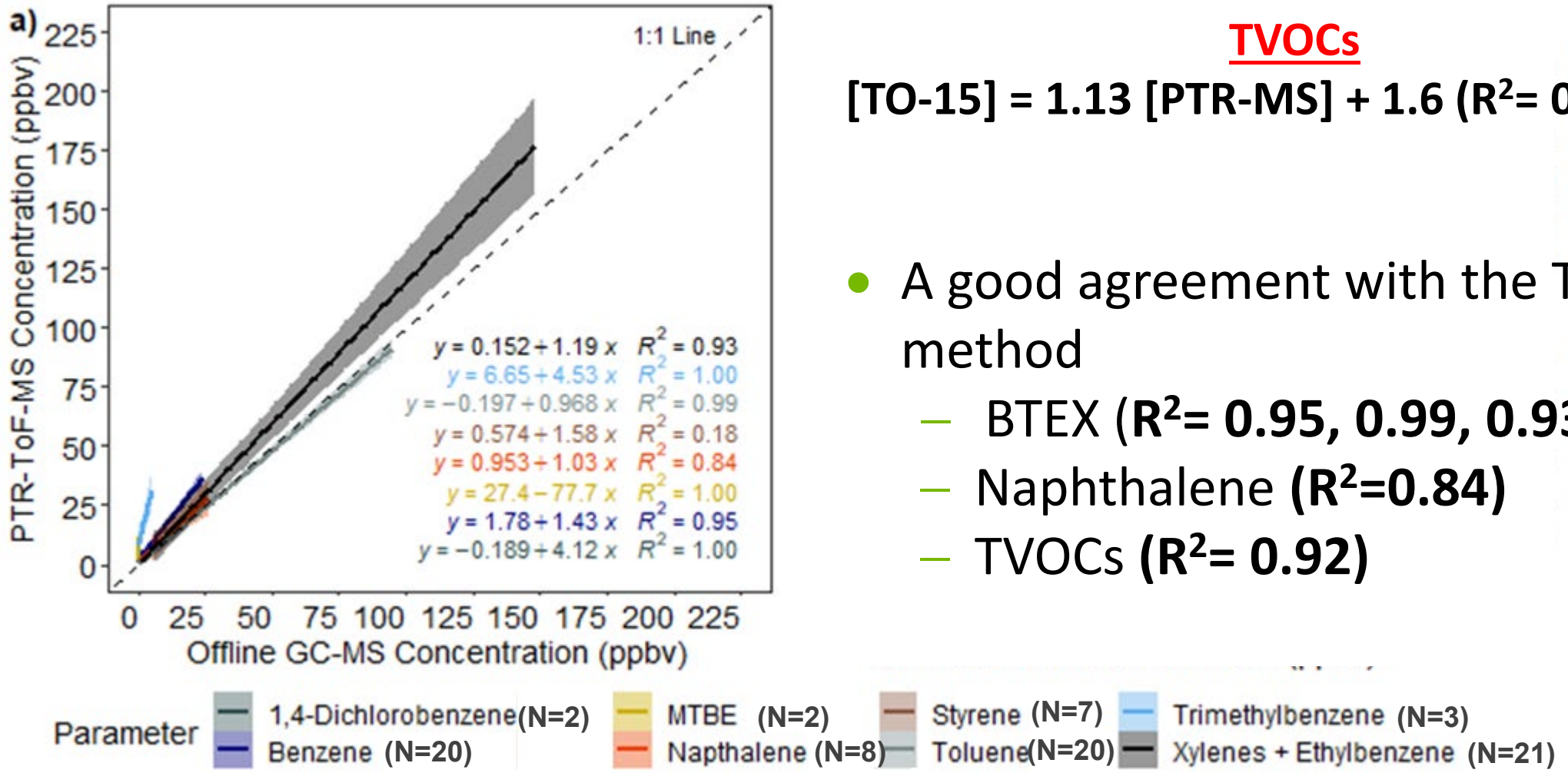


Fenceline measurement timeseries



- All the intercomparison samples were collected during stationary measurements
- 21 summa canister samples were collected in total
  - The summa canister sample collection ranged from 15-30 seconds
- Generally, the signal observed on the UV-DOAS mirrored that of the PTR-ToF-MS measurements

Comparison of PTR-ToF-MS with TO-15 (stationary measurements)

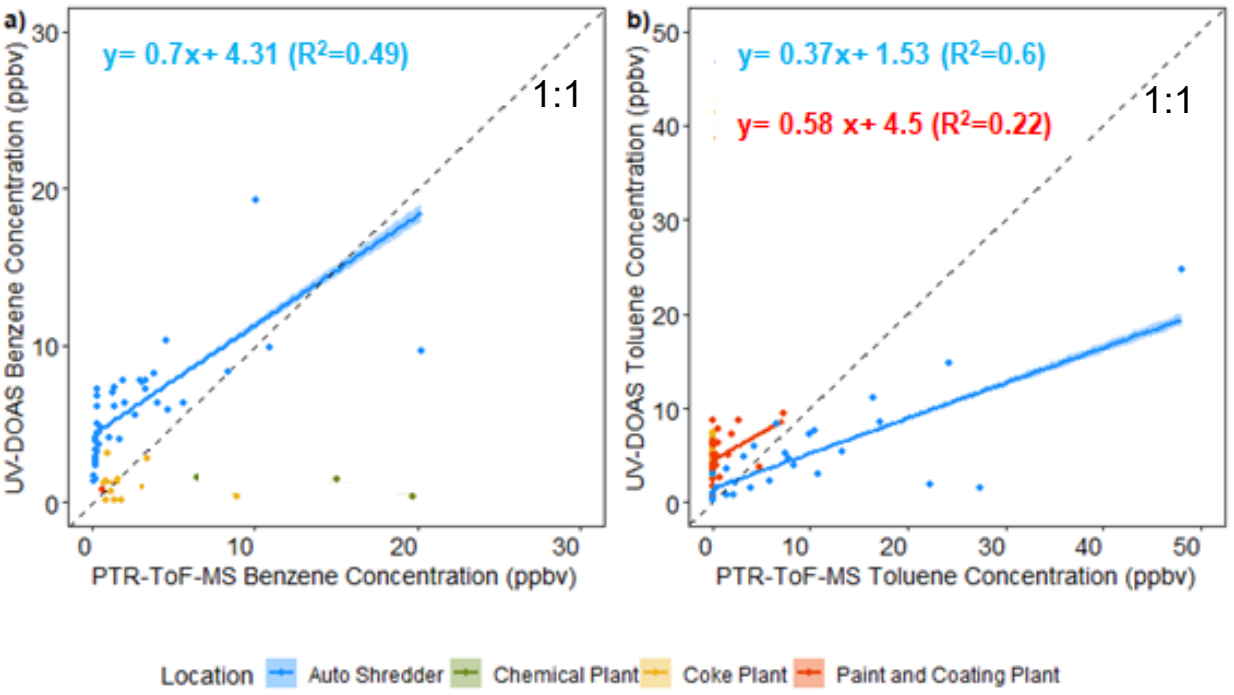


TVOCs

[TO-15] = 1.13 [PTR-MS] + 1.6 (R^2= 0.92)

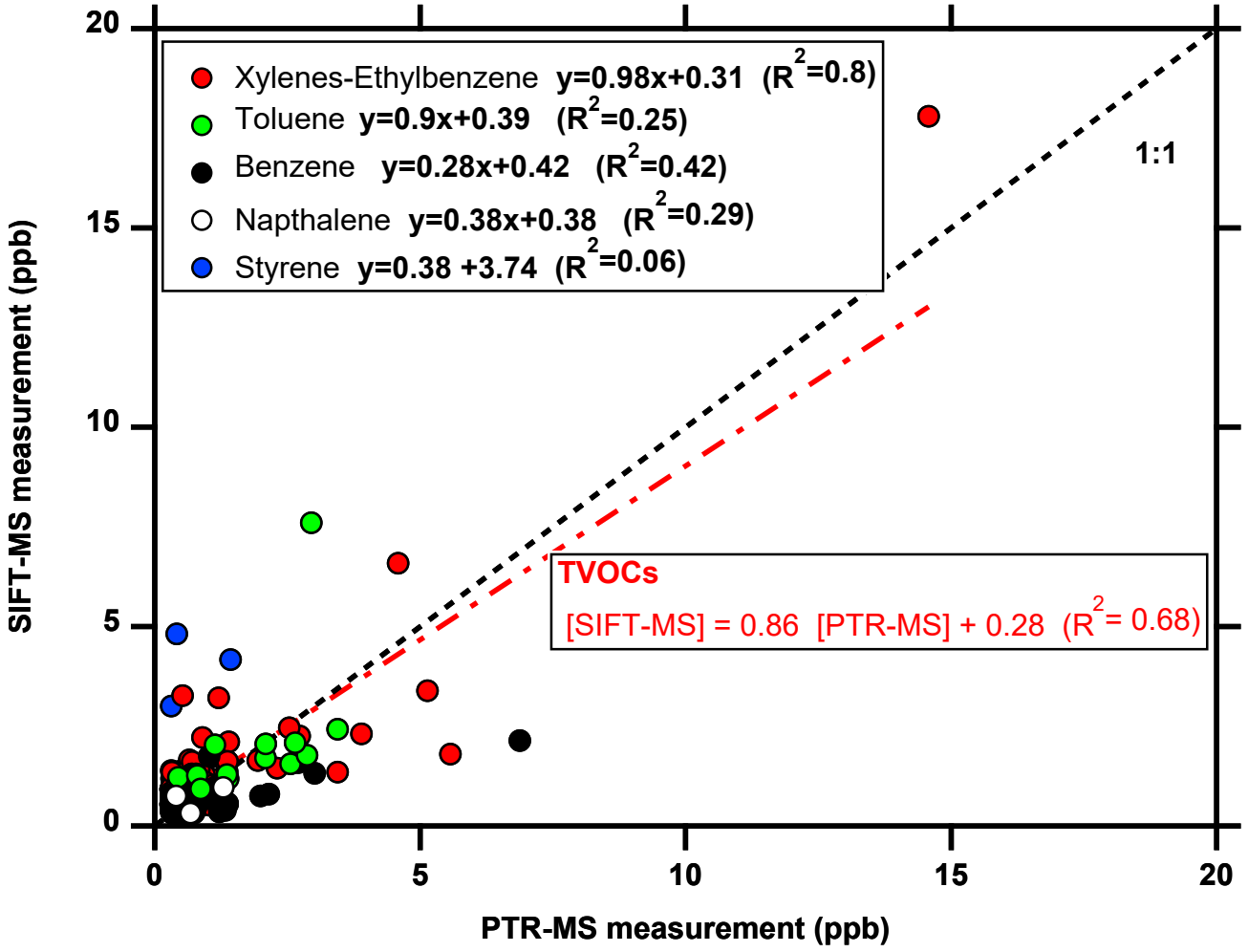
- A good agreement with the TO-15 method
  - BTEX (**R^2= 0.95, 0.99, 0.93)**
  - Naphthalene **(R^2=0.84)**
  - TVOCs **(R^2= 0.92)**

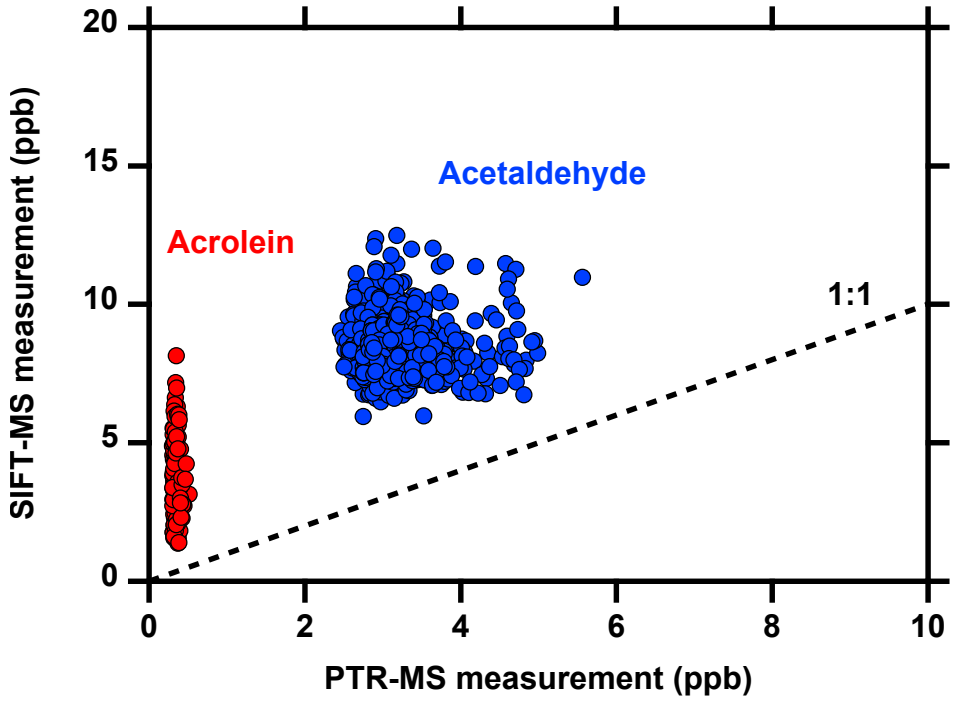
Comparison of PTR-ToF-MS with UV-DOAS (stationary measurements)



- In the Chemical Plant and the Coke Plant, the UV DOAS BTEX measurements were not accurate
  - High concentration of naphthalene can create interferences at overlapping wavelengths
- Better agreements in benzene and toluene were found during measurements at the Auto Shredder and the Paint and Coating Plant

Comparison of PTR-ToF-MS and SIFT-MS (mobile measurements)

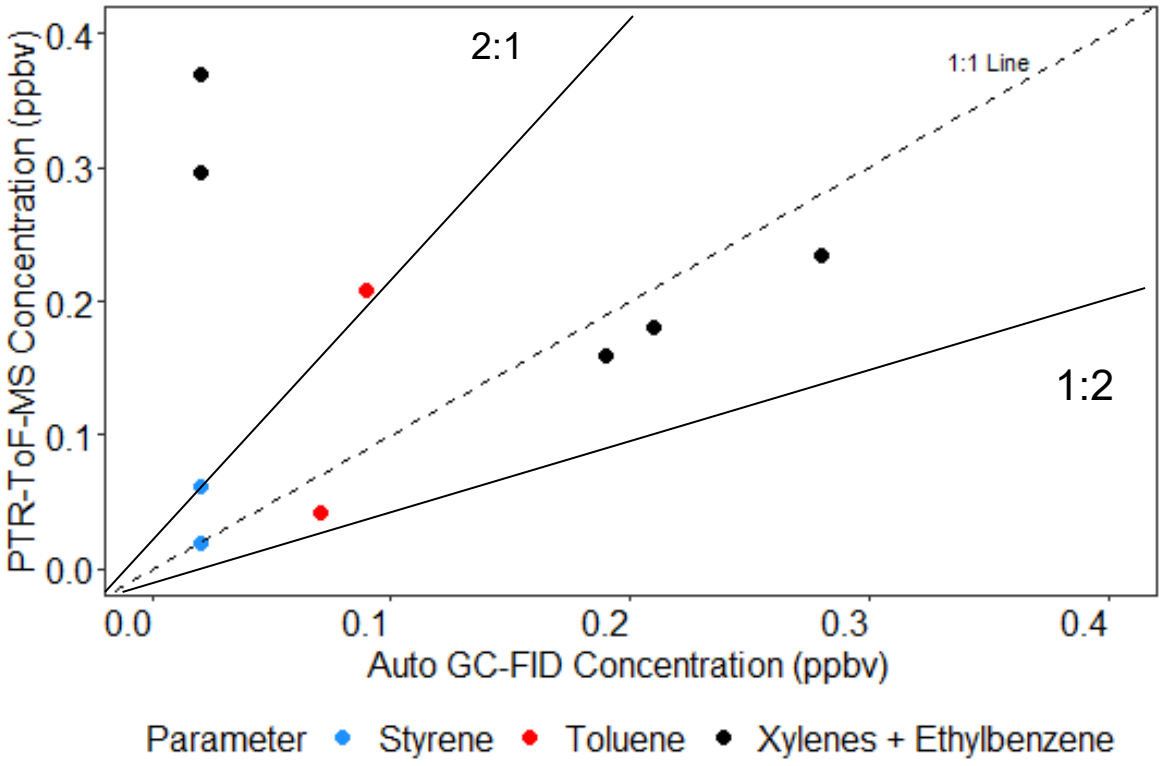




Acetaldehyde: possible interferences with CO_2

Acrolein: possible interferences with water clusters, butene

Stationary comparison against Auto-GC-FID



- The PTR-ToF-MS was compared with an Auto-GC-FID
- 5 hours of intercomparison measurements took place (1-hour averages)
- Not a good agreement in the measurements of aromatics.

Conclusions

- A VOC measurement study took place during a fenceline monitoring campaign over 11 days
- The highest concentrations were measured at
  - Chemical Plant
  - Auto Shredder
  - Coke Plant
  - Paint and Coating plant
  - Petrochemical tank farm
- 18 compounds were monitored during the fenceline campaign. The compounds that had the highest concentrations were
  - 1,3 Butadiene
  - BTEX
  - Styrene
  - Naphthalene

Conclusions

- **The PTR-ToF-MS showed a good agreement with the TO-15 method (slope=1.13; R^2=0.92)**
  - Toluene and naphthalene measurements by the two methods were similar within 3%
  - The measurements of xylene were similar within 19%
  - The PTR-ToF-MS measured higher concentrations of benzene and styrene by 43% and 58%, respectively
  - Measurements of trimethylbenzene, dichlorobenzene and MTBE were overestimated by the PTR-ToF-MS

Conclusions

- Stationary PTR-ToF-MS measurements were compared against a UV-DOAS and an Auto-GC-FID.
  - High concentrations of naphthalene created interferences for BTEX measurements by the UV-DOAS
  - For some matrices, the UV-DOAS compared well for benzene and toluene, albeit slight biases in both directions
  - 45% of the Auto-GC-FID measurements were similar to the PTR-ToF-MS measurements. Additional intercomparison measurements are suggested.

- Sift-MS was compared with the PTR-ToF-MS during mobile measurements.
  - The measurement of BTEX were similar
  - Discrepancies in the measurements of acrolein and acetaldehyde were found

Acknowledgements

- US EPA Region 5, Scott Hamilton, Robin Katz
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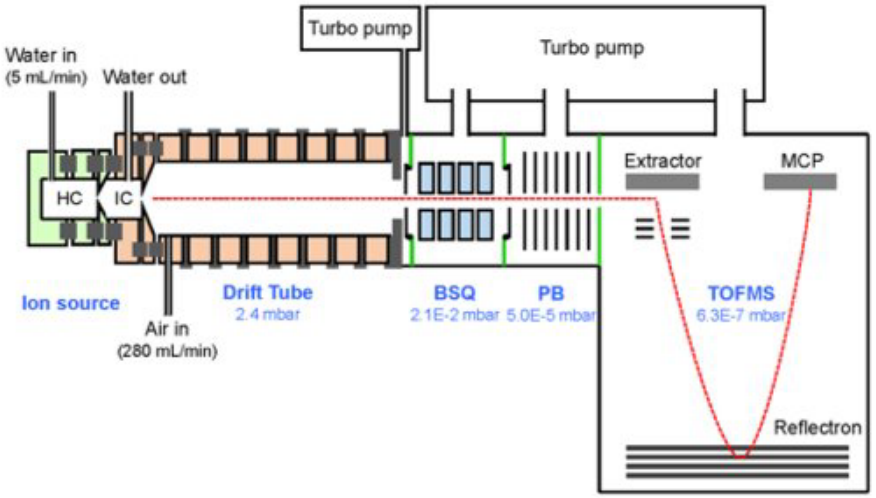
- Syft Technologies, Roadshow crew
- MDNR, Doug Thompson

Backup slides

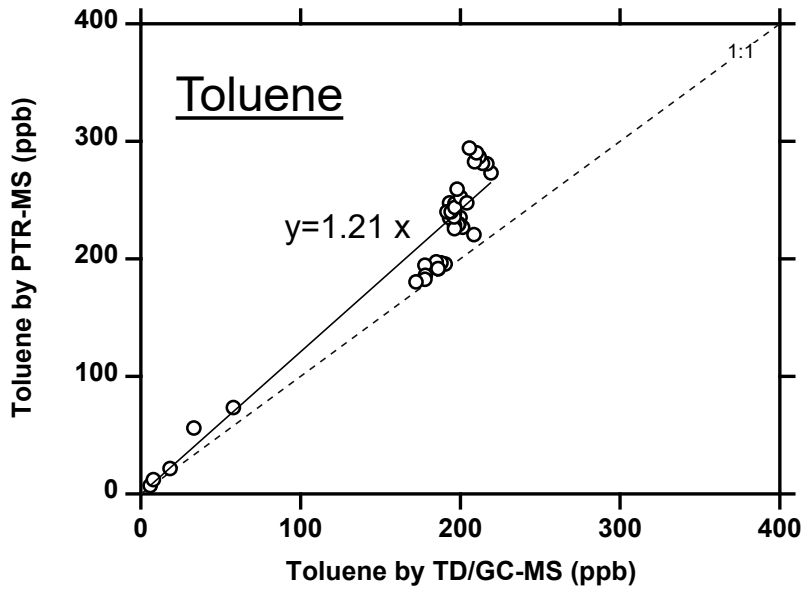
The proton transfer reaction mass spectrometer (PTR-ToF-MS)

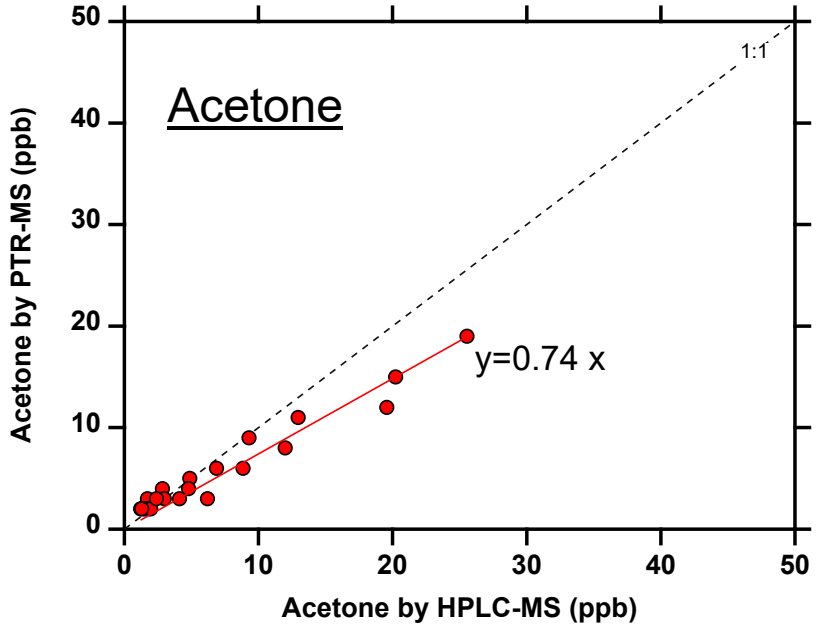


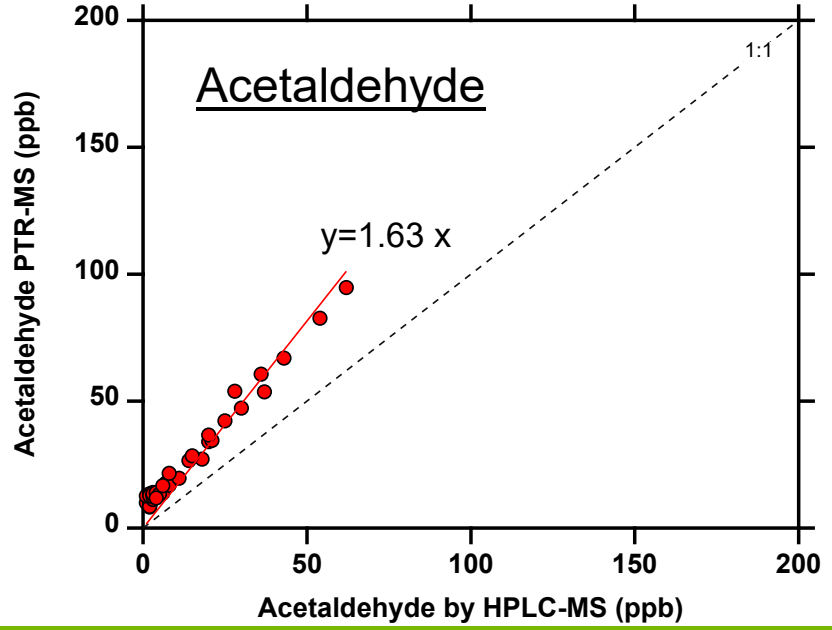
[Yuan et al. 2016]

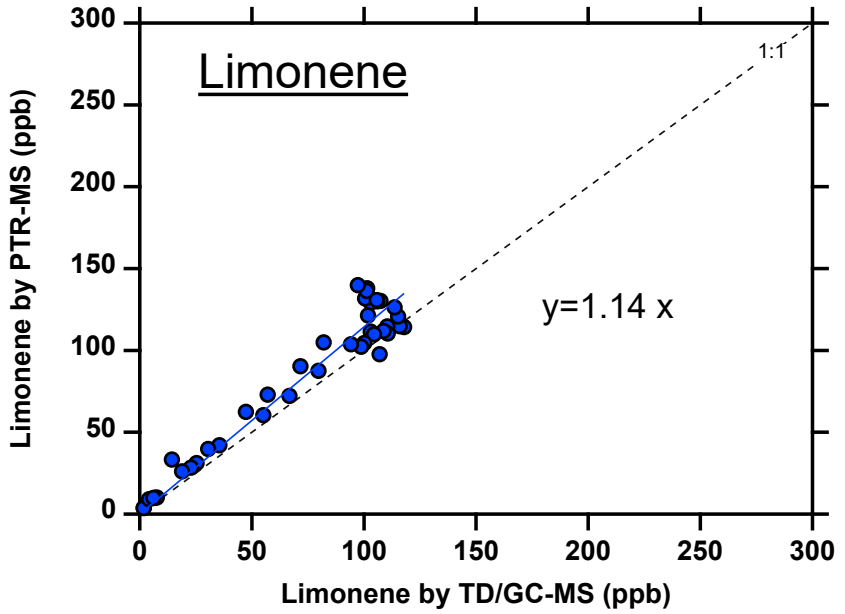
- The PTR-MS was developed in 1995
- Several studies have compared the PTR-MS with traditional techniques measuring VOCs
- De Gouw et al. (2006) found an agreement between the PTRMS and the GC measurements of aromatics within 3%-15%
- Ambrose et al. (2010) showed that the PTRMS has a small (13%) bias in the toluene measurements
- Yuan et al. (2017) using data from 58 publication concluded that accuracy of most published PTR-MS measurements is better than 20-27%

Comparison with standardized methods-controlled tests









- Six controlled tests in a large testing chamber
- Data were collected during 9 periods
- Sorbent tubes were used to collect VOCs for 10-15 minutes
- PTRMS measurements were compared with
  - HPLC-MS (ISO 16000-3)
  - TD/GC-MS (ISO 16000-6)