Quantifying the Emissions and Spatial/Temporal Distributions of Chemical Volatile Chemical Products (VCPs) in the Greater Houston Area

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AQRP Workshop

Austin, TX

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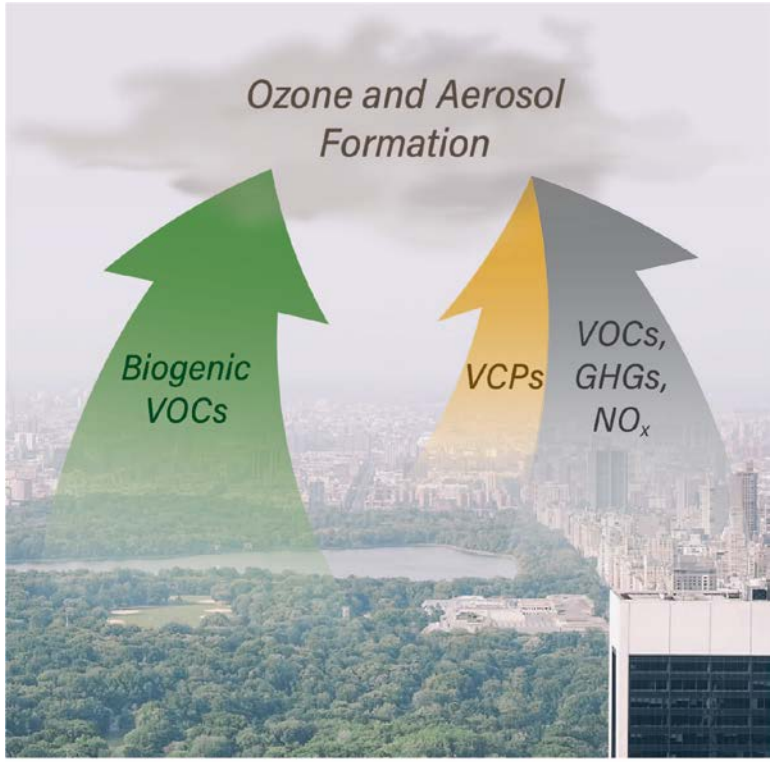
Air pollution and VOC

- **Volatile organic compounds (VOCs)** can lead to the formation of major atmospheric pollutants, such as photochemical **ozone (O_3)** and **particulate matter (PM)**
- Traditionally, VOCs generated in the urban environment comes from **traffic** and **tailpipe emissions**, **power plants**, and **residential combustion**
- **Traffic related VOC emissions have decreased** rapidly during recent years, leading to an **increase of the relative contribution of other types of VOCs such as VCPs**



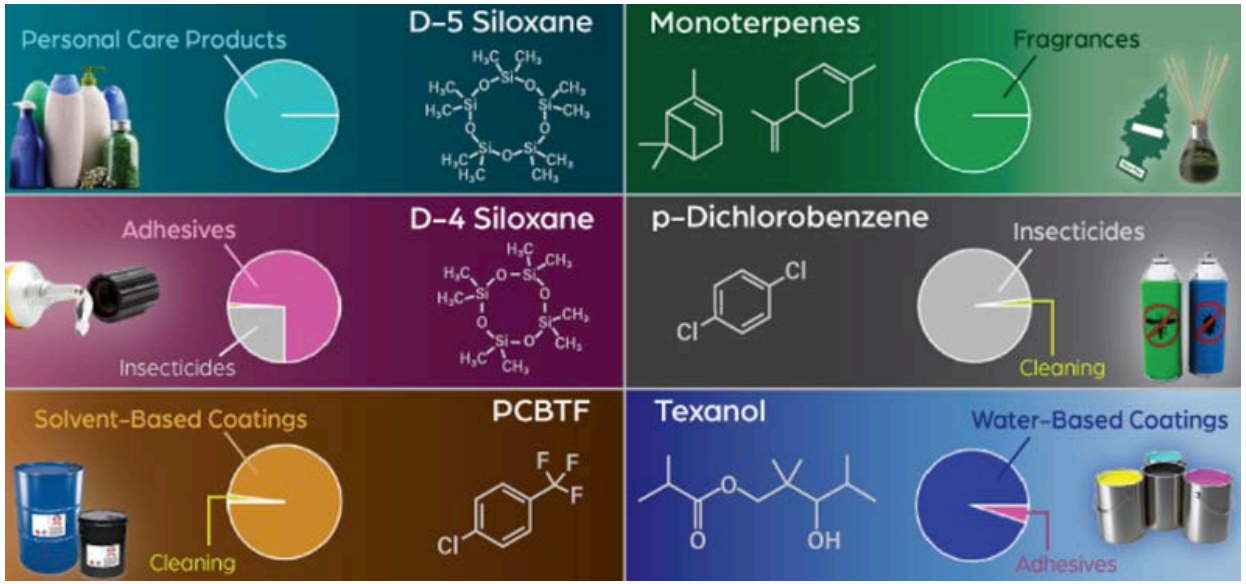
https://research.noaa.gov

What is VCP?

Volatile chemical products (VCPs):

- **Cleaning Products**
- **Personal care products**
- **Adhesives and sealants**
- **Paints and coatings**
- **Printing inks**
- **Pesticides**
- **Dry cleaning**

VCP tracer compounds:



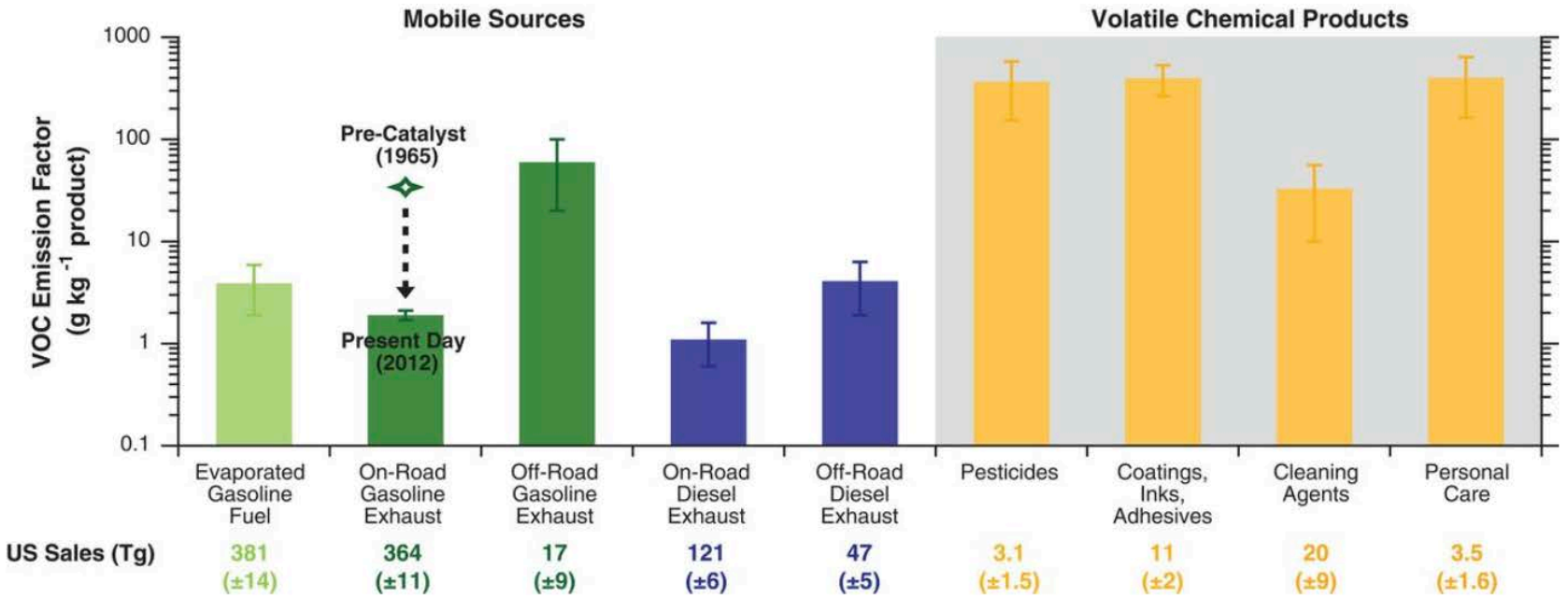
Compounds such as **D5-siloxane, ethanol**, **alkenes**, and **monoterpenes** are major VCP emission sources in the urban environment.

Gkatzelis et al., *Environ. Sci. Technol.* 2021

Impacts of VCP

VCP relative Contribution

- **The green bars and symbols and dashed arrow illustrate the large reductions in tailpipe VOC emission factors**
- **Yellow bars represent VCP emissions**

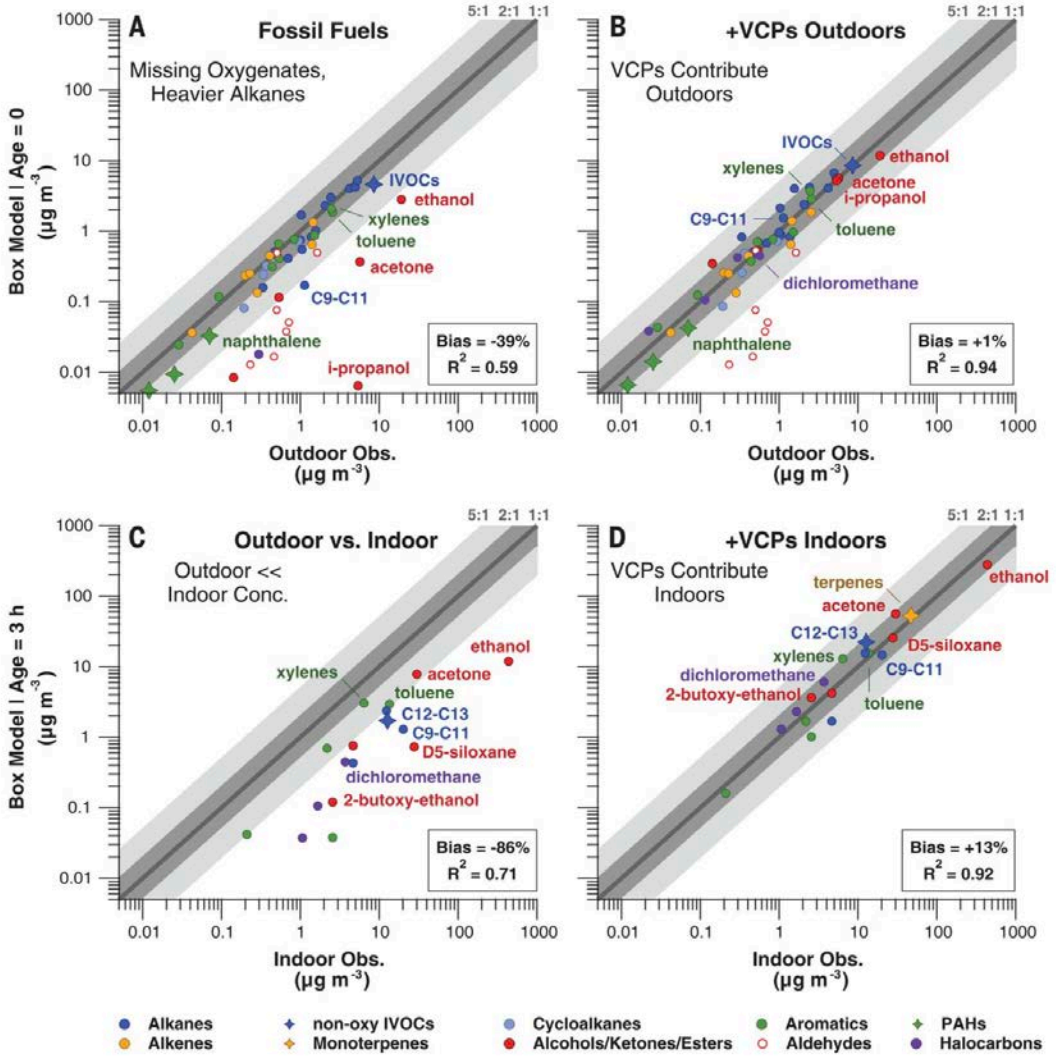


McDonald et al., *Science, 2018*

Impacts of VCP

VCP Model Results

- **Model results agree relatively well with outdoor measurement data**
- **Indoor measurement is about one order of magnitude higher than modeling results**

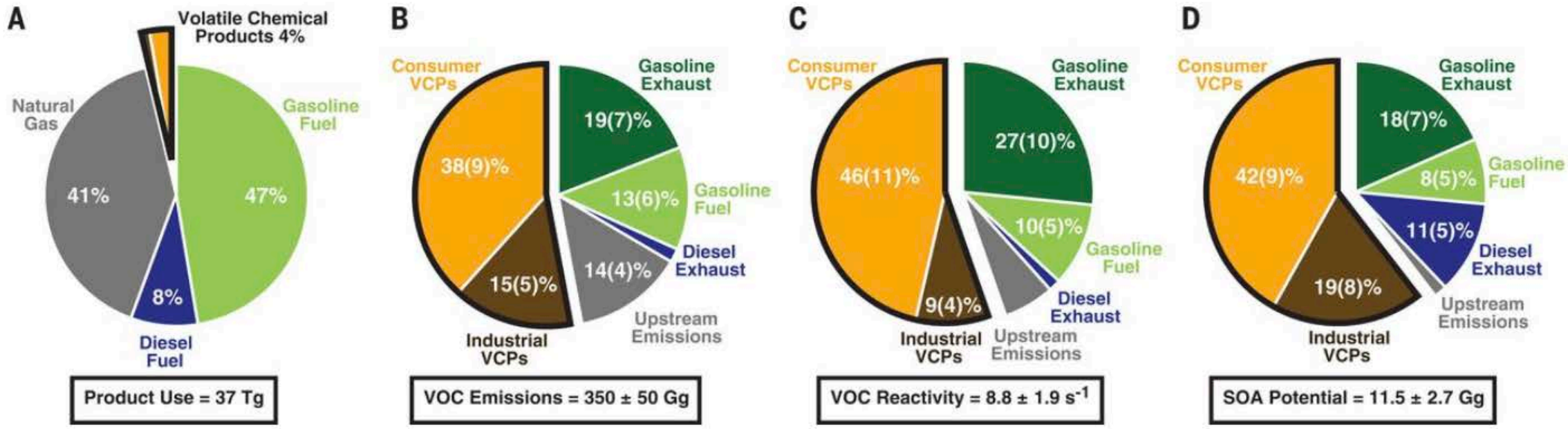


McDonald et al., *Science, 2018*

Impacts of VCP

VCP Model Results

- **Contribution of VCP to air quality**
- **VCP contributes a significant of ozone and SOA in Los Angeles**

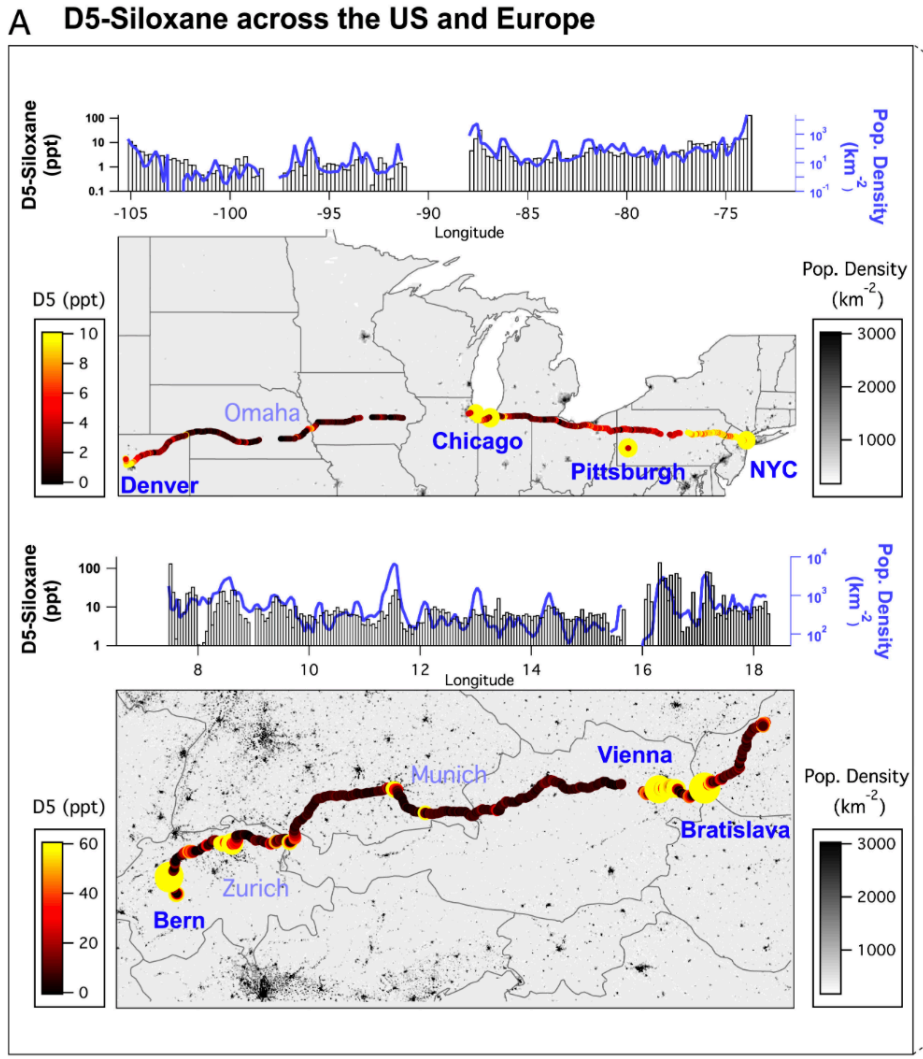


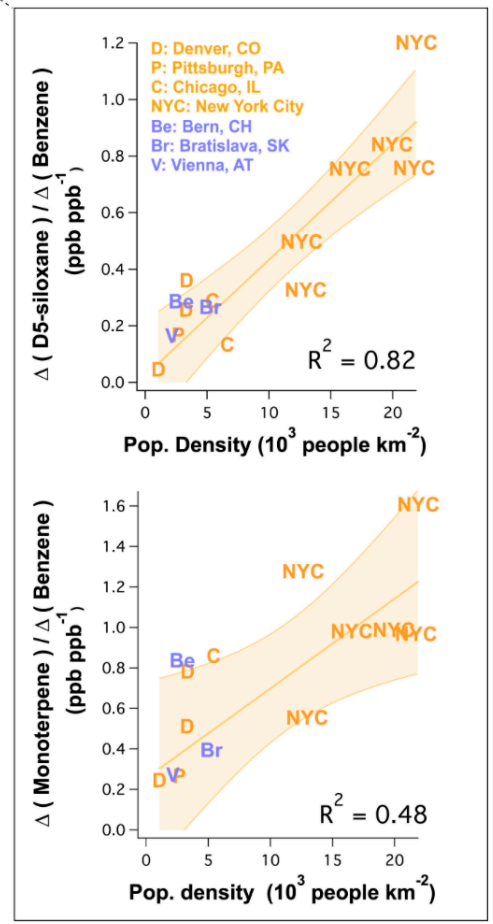
McDonald et al., *Science, 2018*

Impacts of VCP

VCP Mobile Results

- **VCP Mobile Sampling in North America and Europe**
- **High concentration of D5-Siloxane in major cities**
- **High concentration of certain VCPs correlates with population density**





Coggon et al., *PNAS, 2021*

Scientific Objectives

Primary hypothesis: the VCPs in the Greater Houston Area account for a significant portion of the total VOC emission and have important implications on the regional ozone concentrations that were previously not captured by the emission inventory and models.

- **Task 1:** Determine the spatial and temporal distribution of VCPs in the Greater Houston Area
- **Task 2:** Characterize the Seasonality Difference of VCP in the Houston Area
- **Task 3:** Assess the effects of urban VCPs on air quality, including summertime MDA8 O_3 and monoterpene SOA

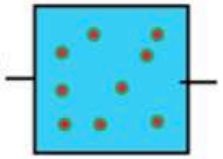
Research approach

Objective 1
VCP Field Measurmentn and Quantification

Mobile Lab

Vocus 2R CIMS | SP-HR-ToF-AMS

Laboratory Calibration and Quantification



Calibration of VCP standards and Field Deployment of the TRAM van for VCP Measurement

Objective 2
Seasonal Concentration and Emission of VCP

Measurement/Model Validation

Summer Time

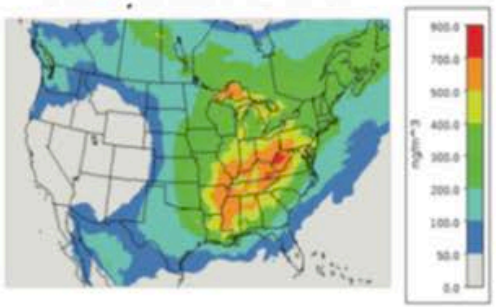
Winter Time

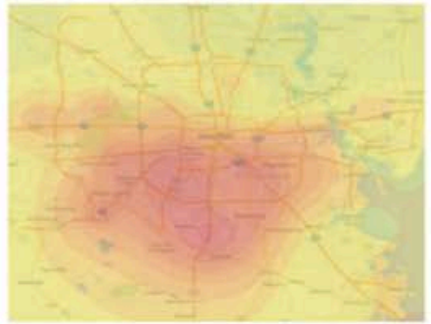
National Emission Inventory

VCPy Inventory

Season Difference of VCP Concentrations

Objective 3
VCP Contribution to Ozone

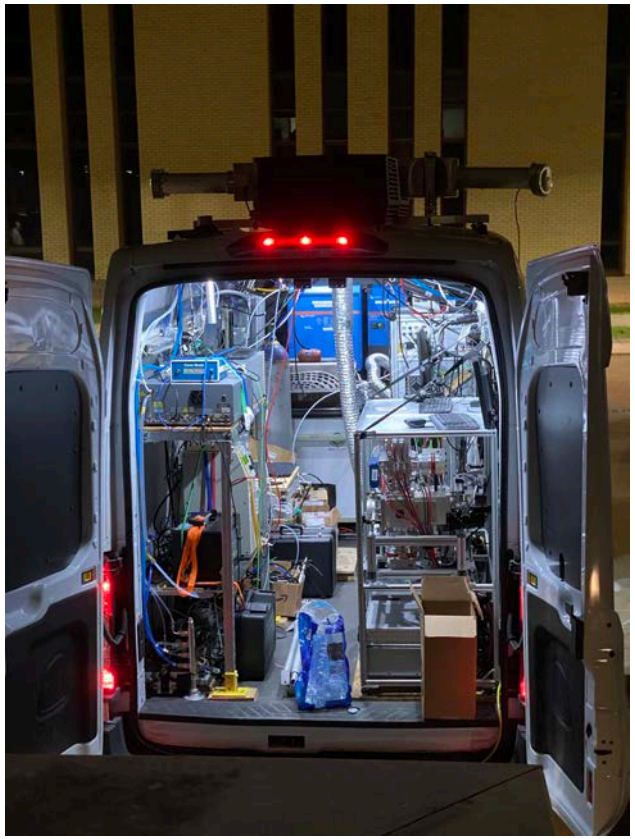




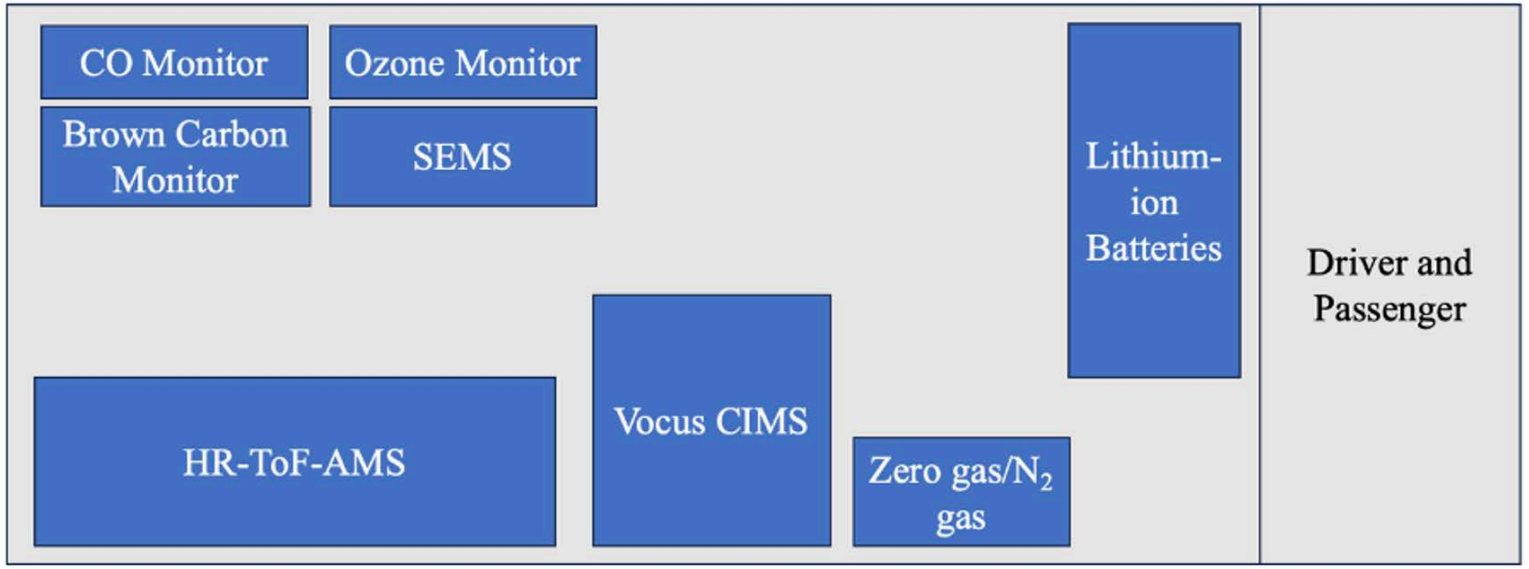
Estimate the Effects of VCP on Local Ozone Production

TRAM Van

The outside look:



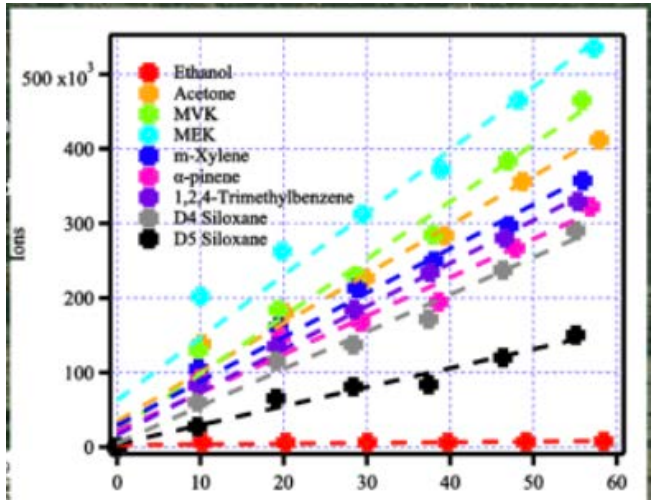
The inside structure:

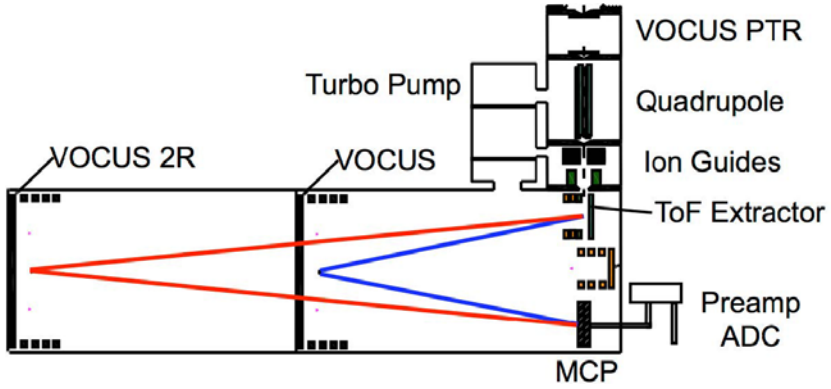


Vocus CI-MS

Vocus 2R Chemical Ionization Time-of-Flight Mass Spectrometer (Vocus CI-MS)

A combination of the regular Vocus CI-*MS* and AMS system will be able to detect the total amount of VCPs in the gas- and particle-phase species.



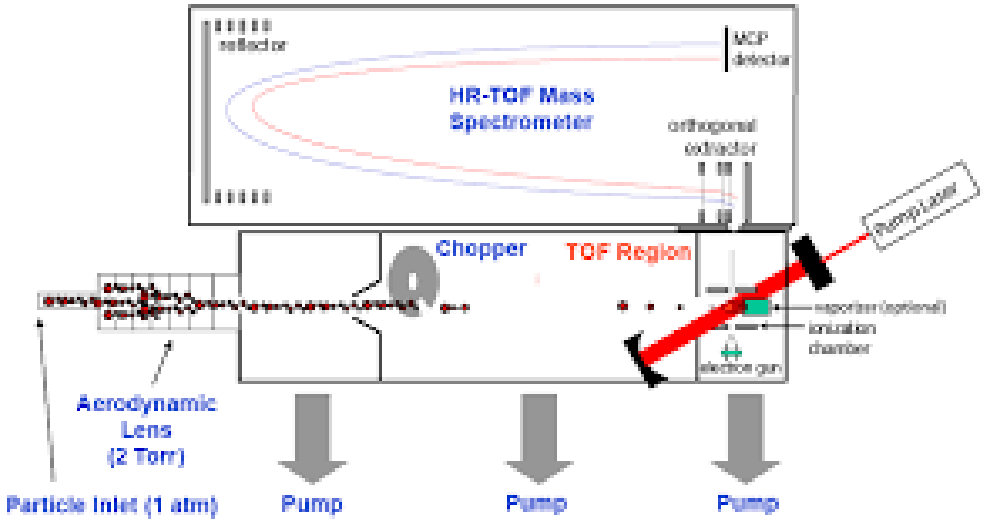


AMS

Soot Particle Aerosol Mass Spectrometer (SP-AMS)

Provides real-time, in situ measurements of black carbon containing particles

Measure aerosol mass loadings



(Credit: Aerodyne)

Summary of the Instruments

Instrument	Parameter	Data
SP-HR-ToF-AMS	peak area	VCP-derived Particle mass loading. The quantification of the VCP mass loading can be used to understand how much VCP can be oxidized in the atmosphere to form aerosols.
HR-ToF-Vocus CIMS Instruments	peak area	VCP concentration. The quantification of VCP can be used to calculate VCP emissions and chemical transformations in the atmosphere.
Aethalometer	Optical sensor signal	Total black carbon and brown carbon measured during selected time intervals
CO analyzer	Instrument peak area	CO concentration measured from the gas phase
NO_2 analyzer	Optical sensor signal	NO_2 concentration measured from the gas phase
Filters	Mass spectrometer signals	Organic species detected on the filters

Additional Collaborators

Dr. Raghu Bertha, Texas Tech University, aethalometer

Dr. Swarup China and Team, Pacific Northwest National Laboratory, filter analysis

Field measurement

In October-November 2022, January-February 2023, and August 2023, drive the TRAM van to circle around Houston and Corpus Christi, based on the blue- and green-shaded routes in the right Figure to capture additional VCP emission patterns (deliver 10-15 days of useful data deployment)

Factors being measured:

- **VCPs**
- **GPS location**
- CO concentration
- Temperature, relative humidity
- Aerosol mass loading
- NO_x, and other gas concentrations

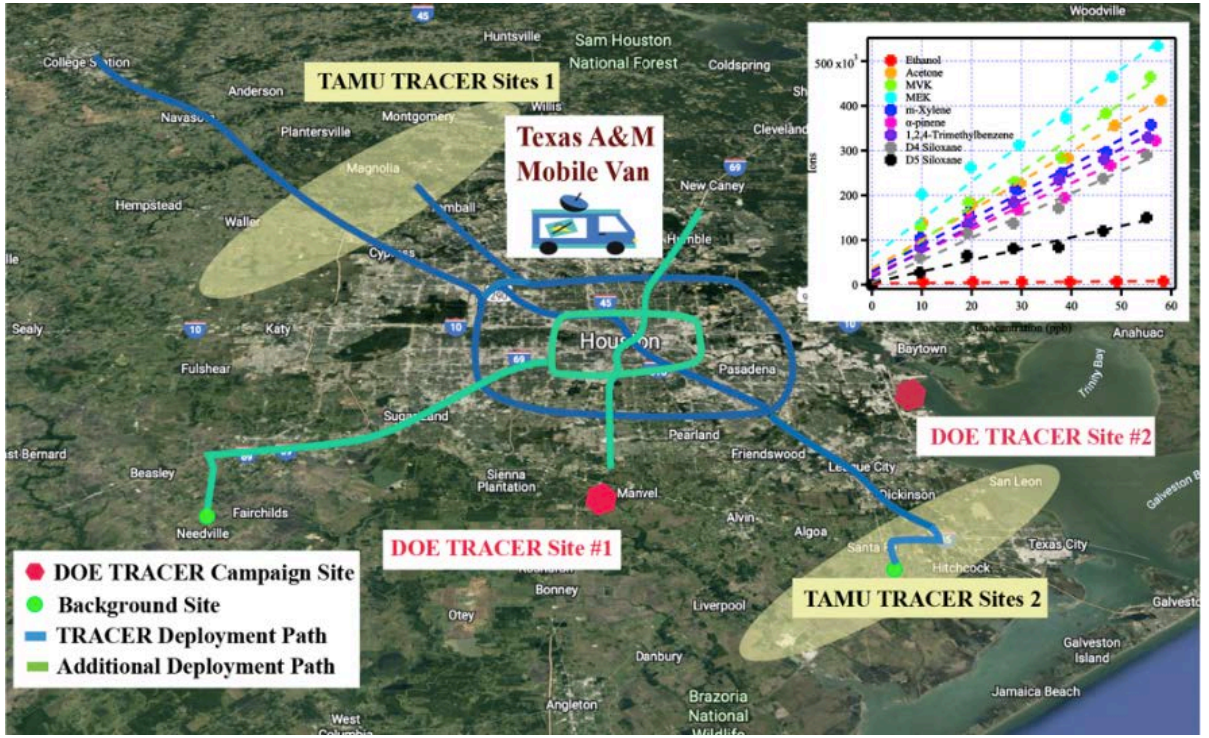


Figure. Field deployment map of the Texas A&M Mobile Van.

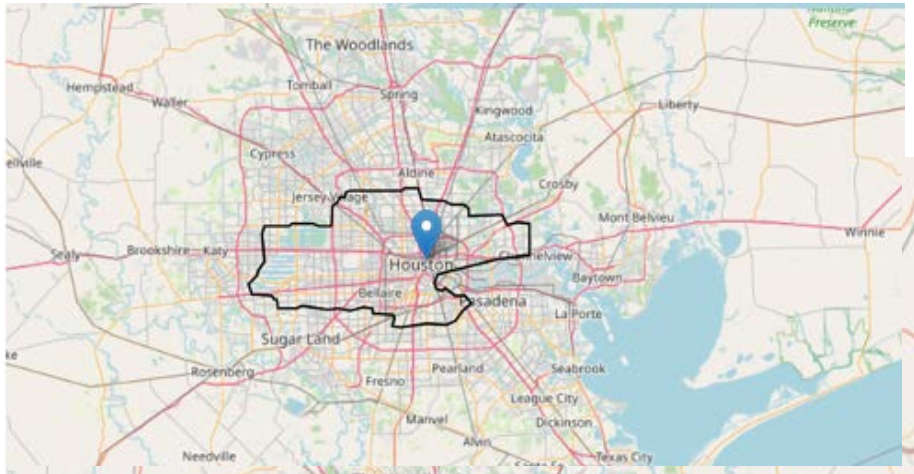
Field measurement schedule

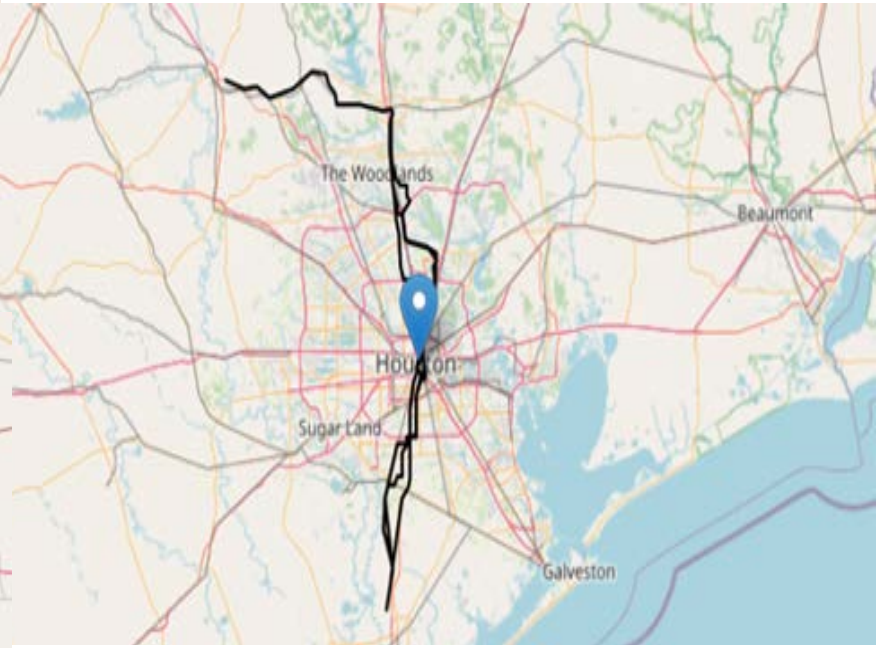
Fall			Winter		
Date	Route	Ionization Mode	Date	Route	Ionization Mode
10/30	Round	NH_4^+	1/12	North South	NH_4^+
11/02	East West	NH_4^+	1/13	Round	NH_4^+
11/04	Round	NH_4^+	1/14	Round	NH_4^+
11/05	North South	H^+	1/15	East West	NH_4^+
11/06	Round	H^+	1/17	Round	H^+
11/07	Round	H^+	1/18	Round	H^+
11/09	East West	H^+	1/19	North South	H^+
			1/21	East West	H^+
			1/22	North South	H^+
			1/23	Round	H^+
			1/24	North South	H^+

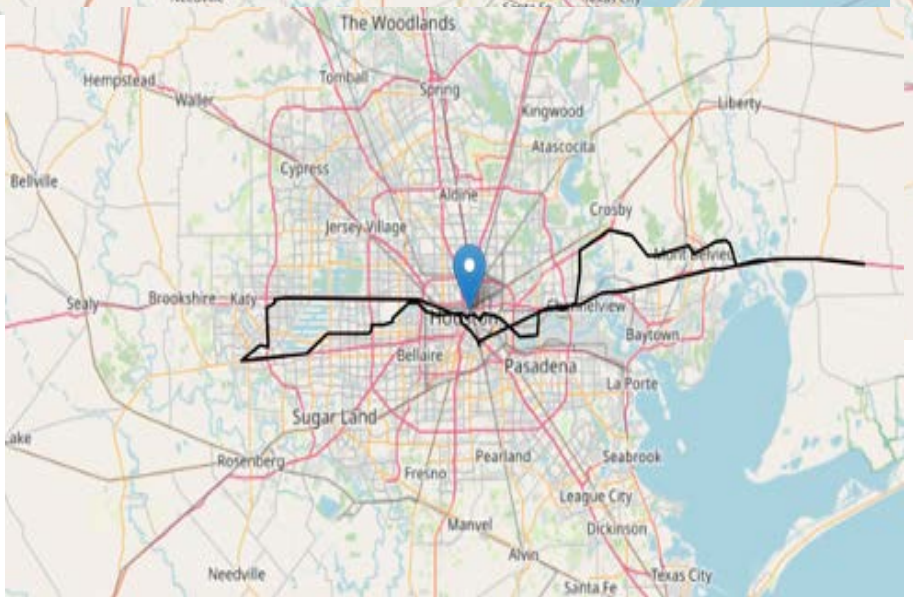
Field measurement routes

Three major routes

Circle
East-West
North-South



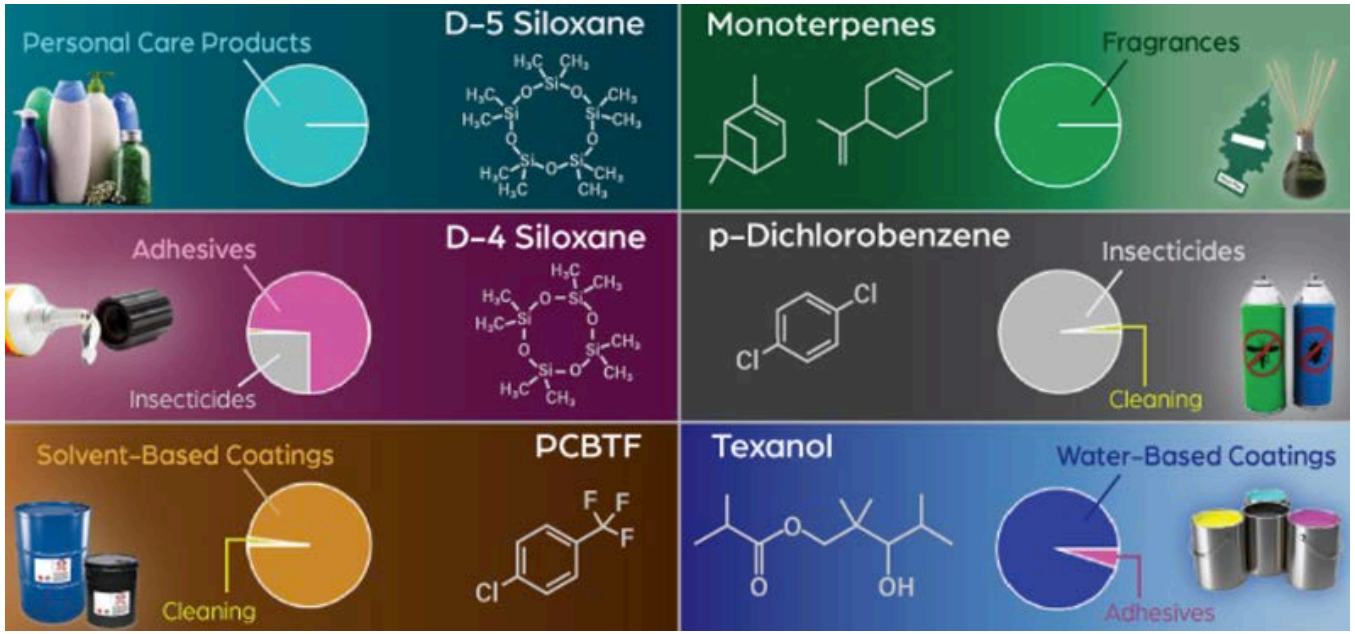




Measurement Data

Six major VCP precursors

- D-5 Siloxane
- D-4 Siloxane
- PCBTF (Para-Chlorobenzotrifluoride)
- Monoterpenes
- p-Dichlorobenzene
- Texanol

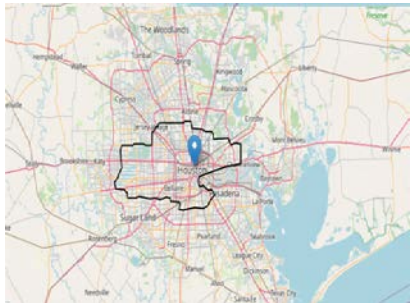


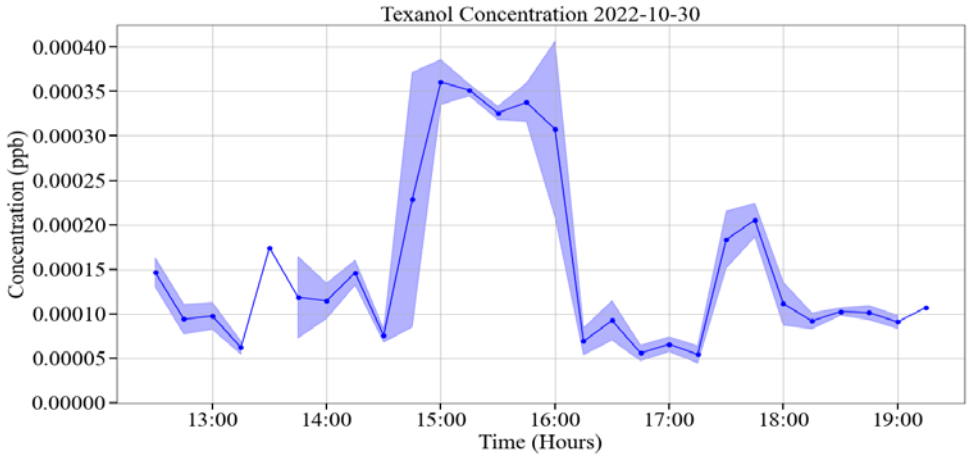
Fully calibrated before and during the field project using pure standard with Vocus CI-MS

Measurement Data

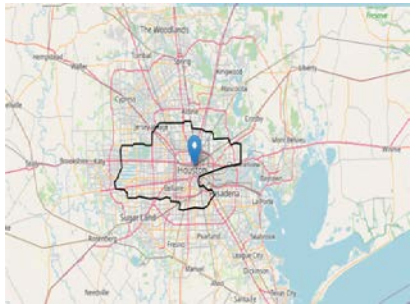
- Texanol

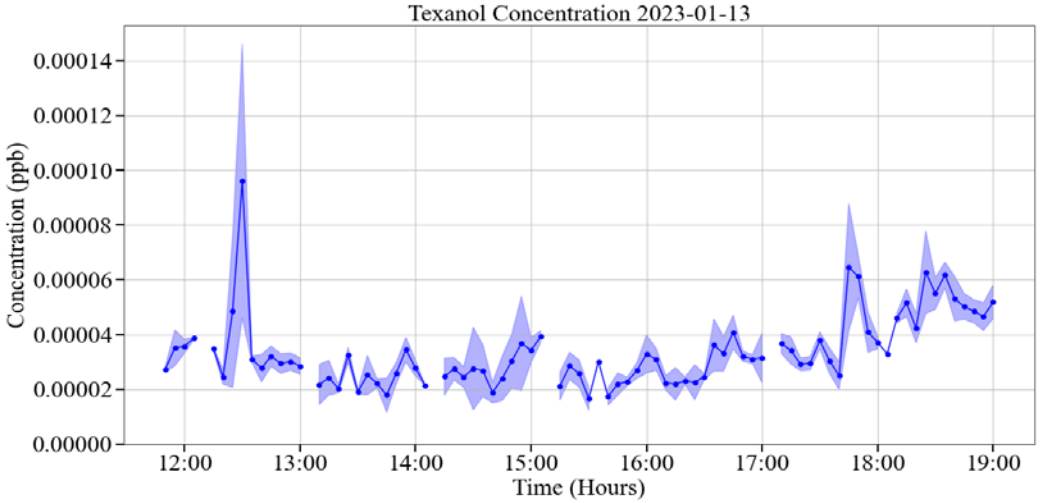
Fall





Winter

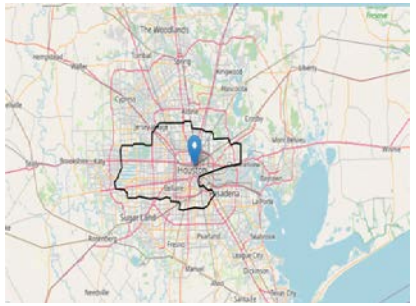


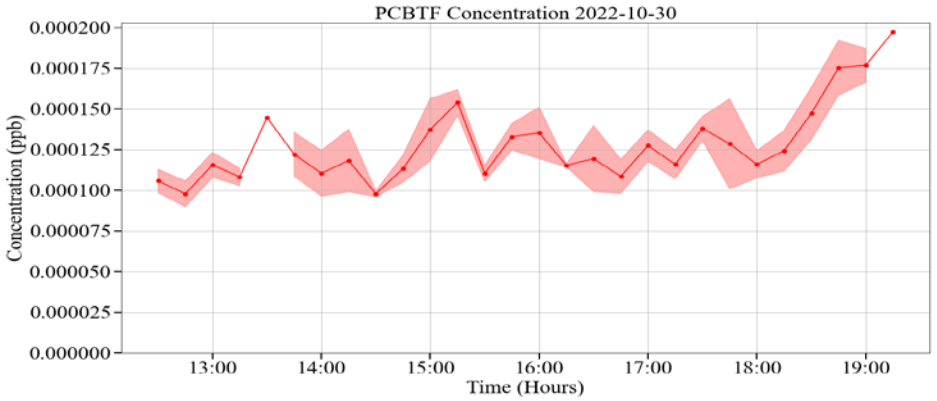


Measurement Data

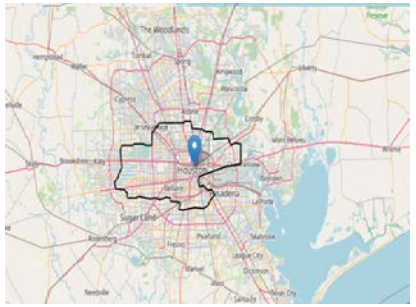
- PCBTF

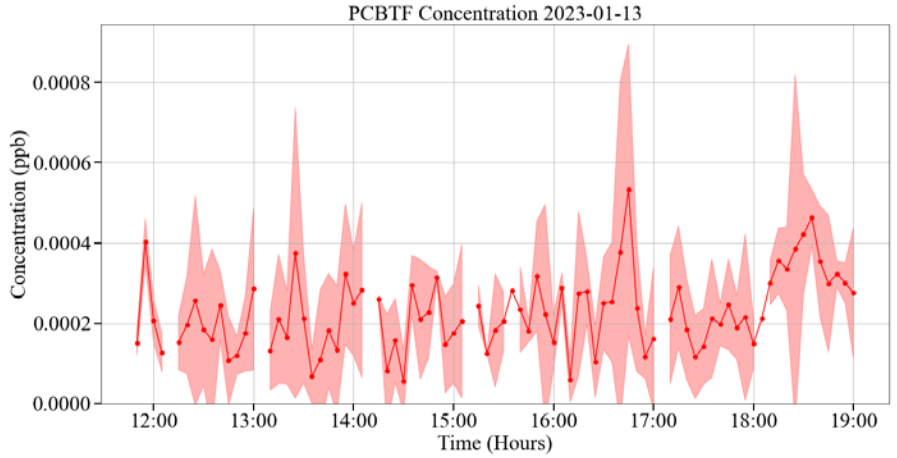
Fall





Winter

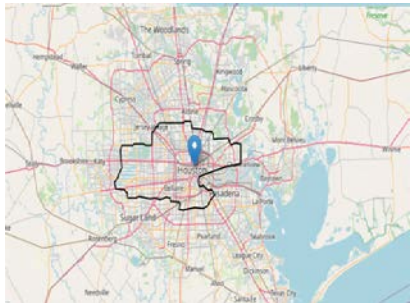


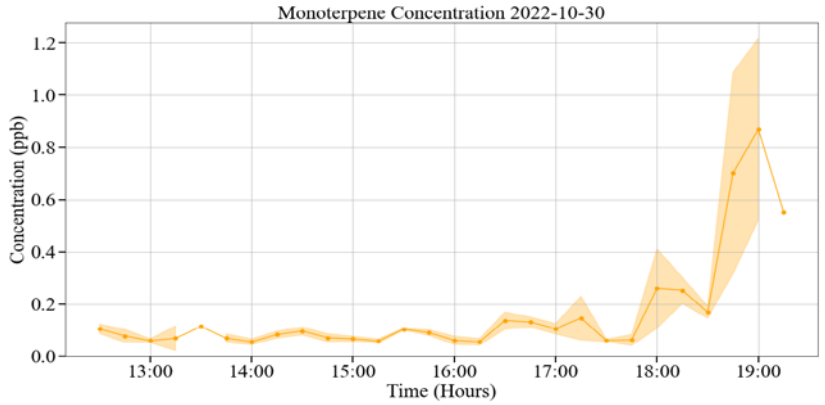


Measurement Data

- Monoterpenes

Fall





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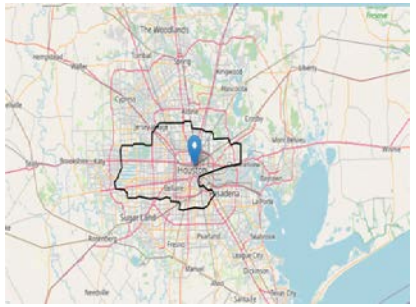
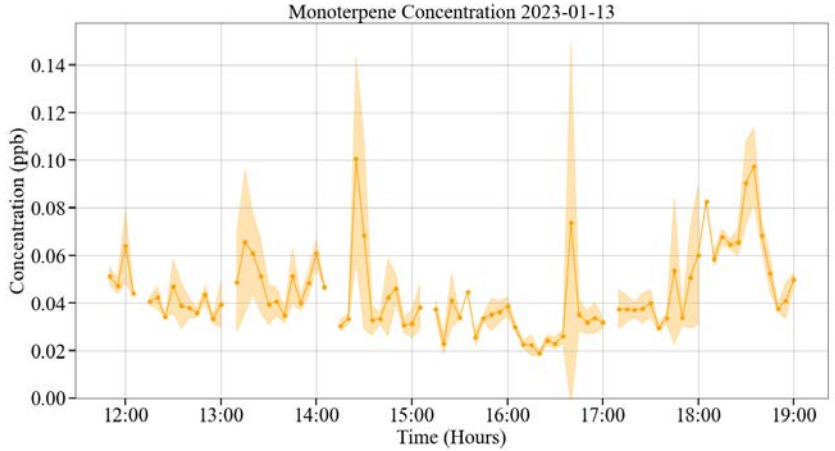
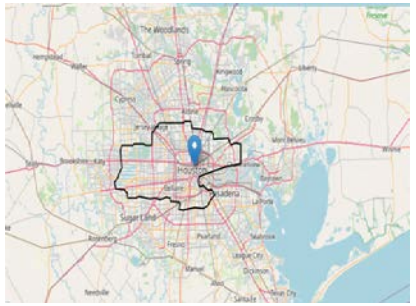


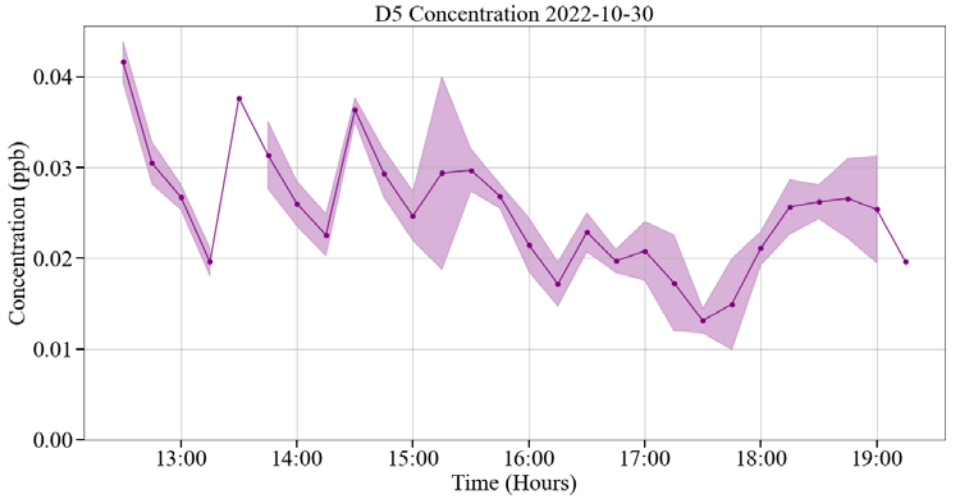


Measurement Data

- D5-Siloxane

Fall





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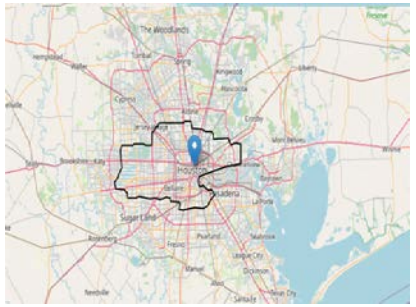
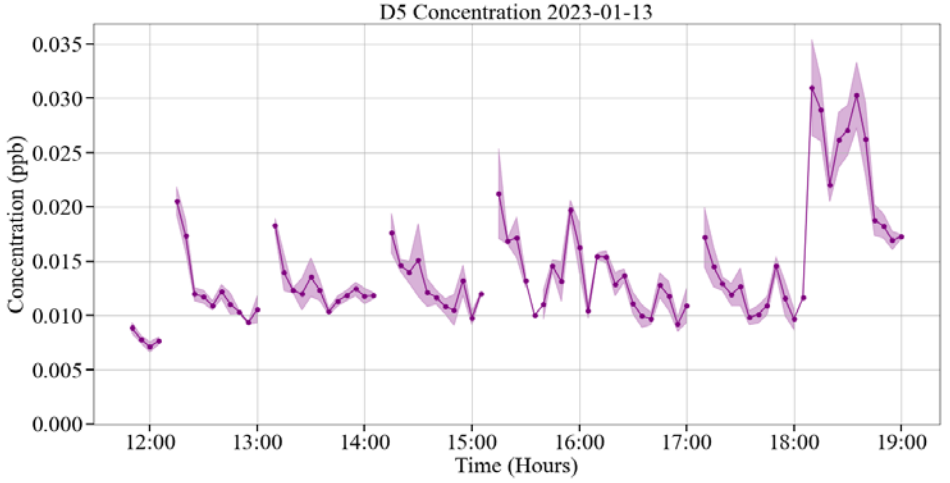
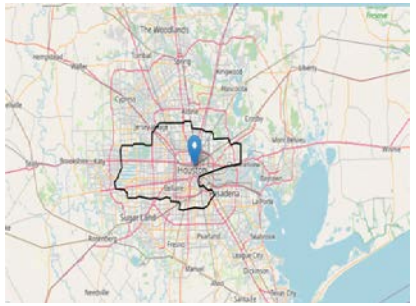


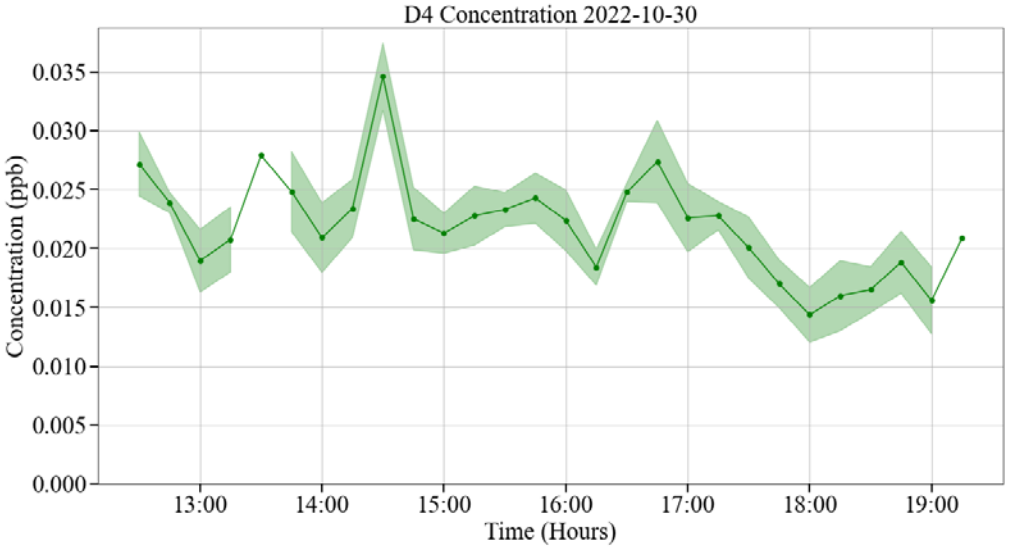


Measurement Data

- D4-Siloxane

Fall





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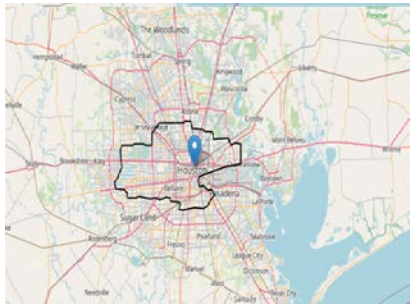
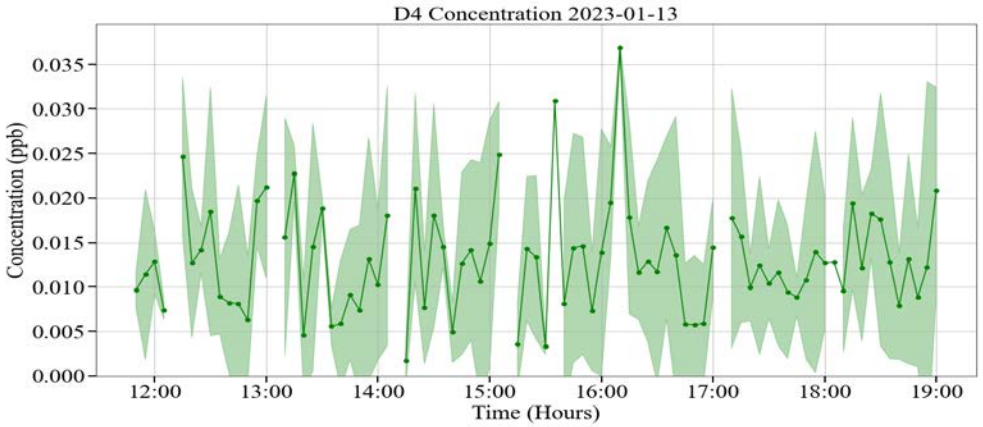
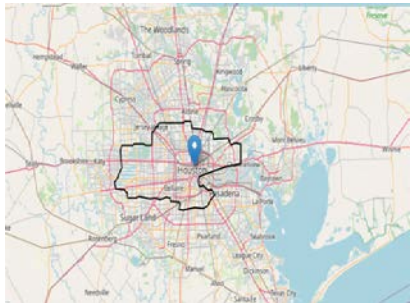


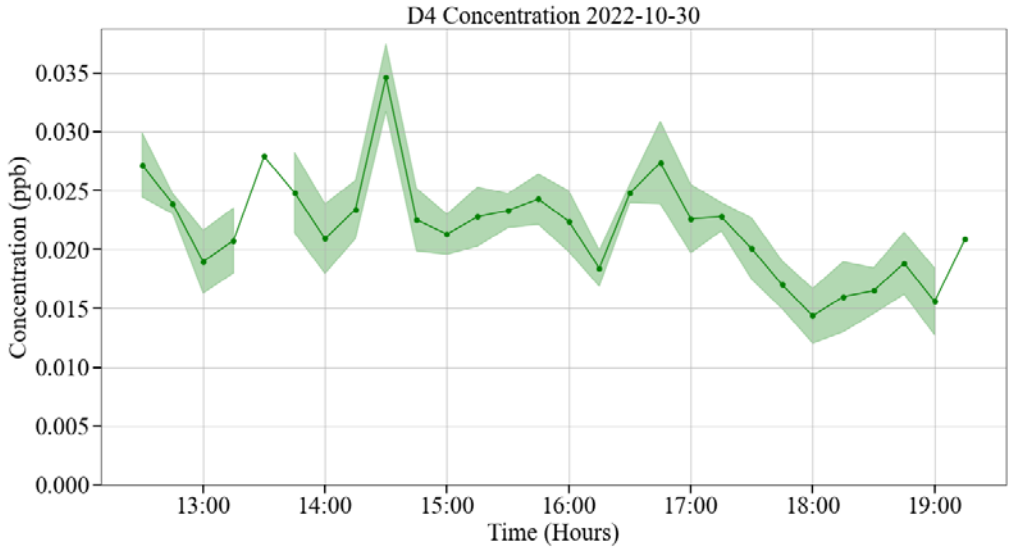


Measurement Data

- D4-Siloxane

Fall





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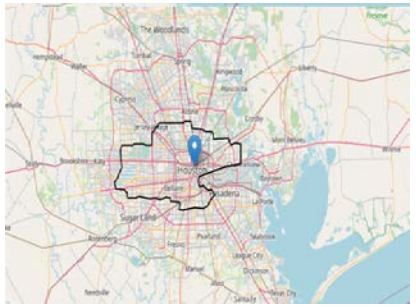
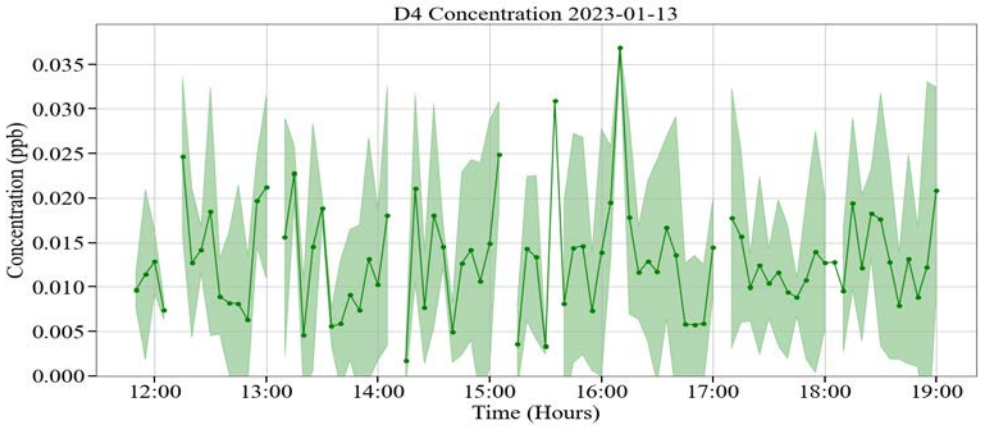
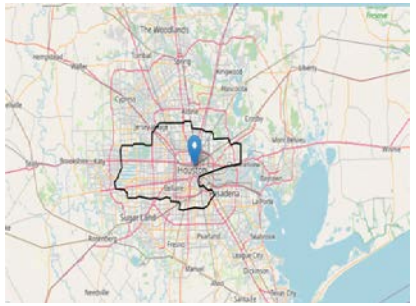


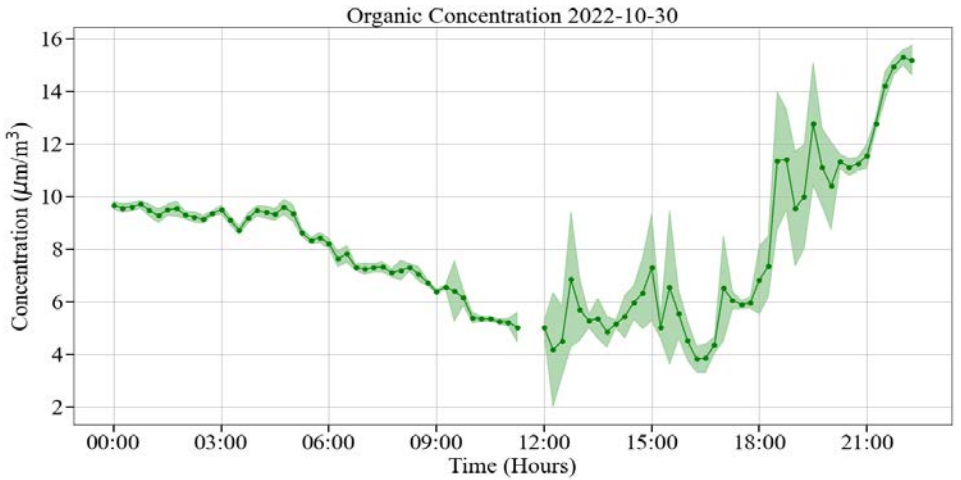


Measurement Data

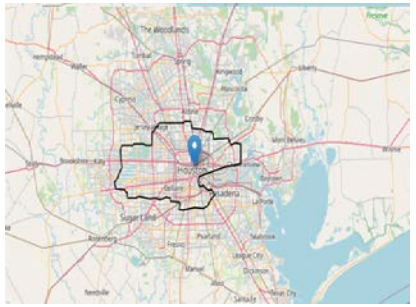
- Aerosol Measurement

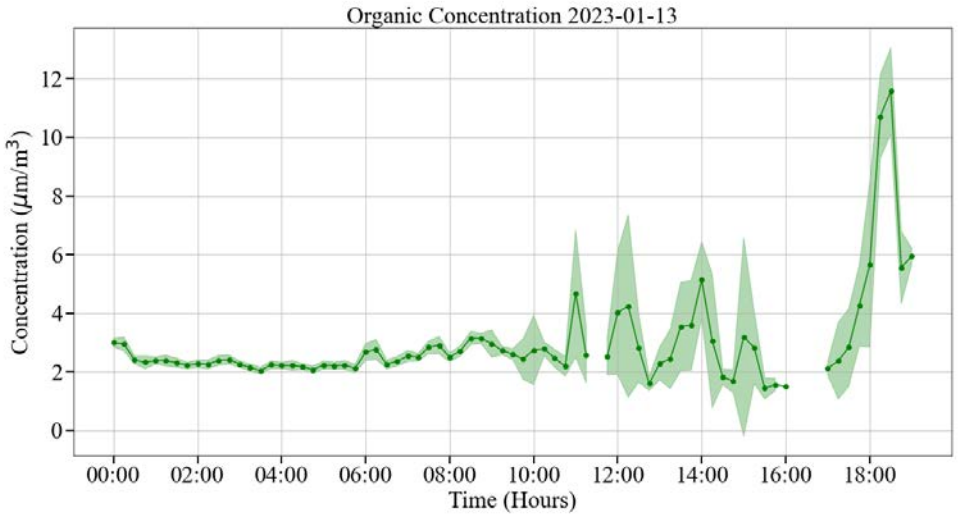
Fall





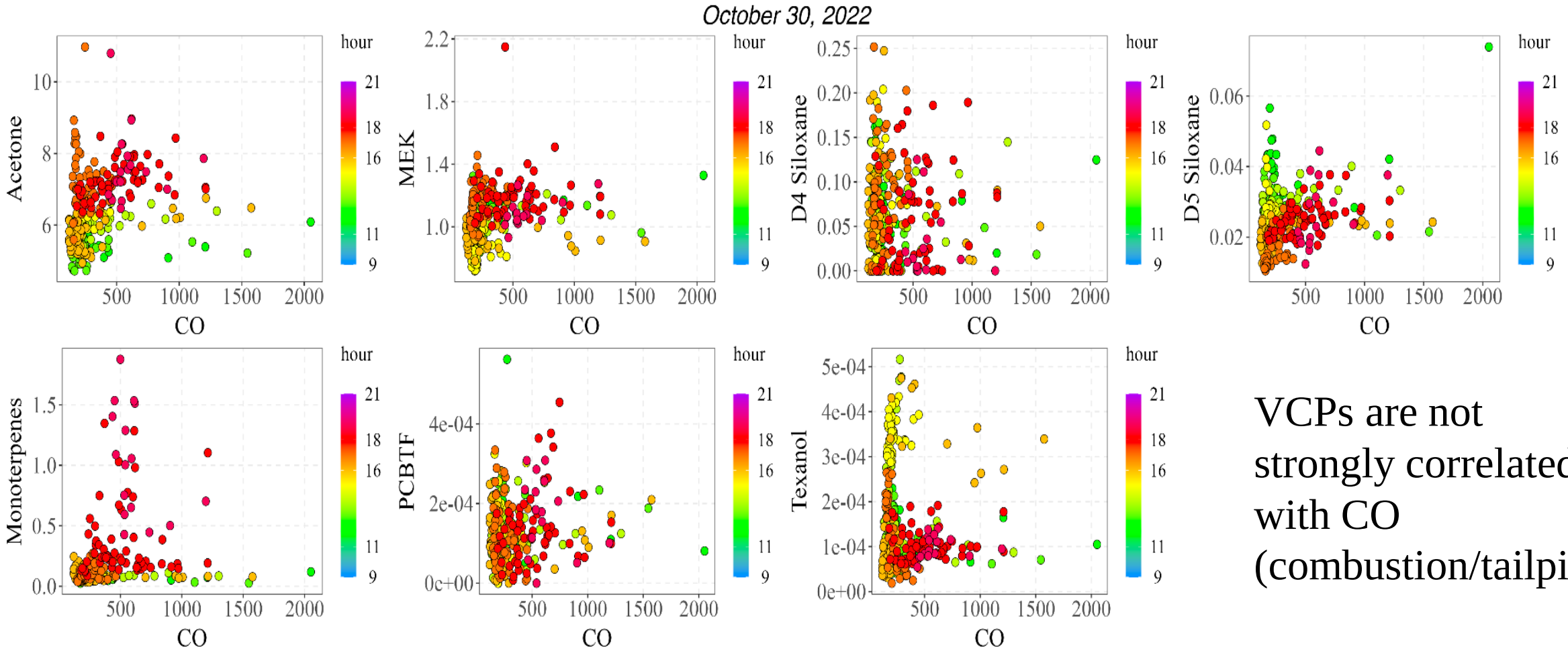
Winter





Measurement Data

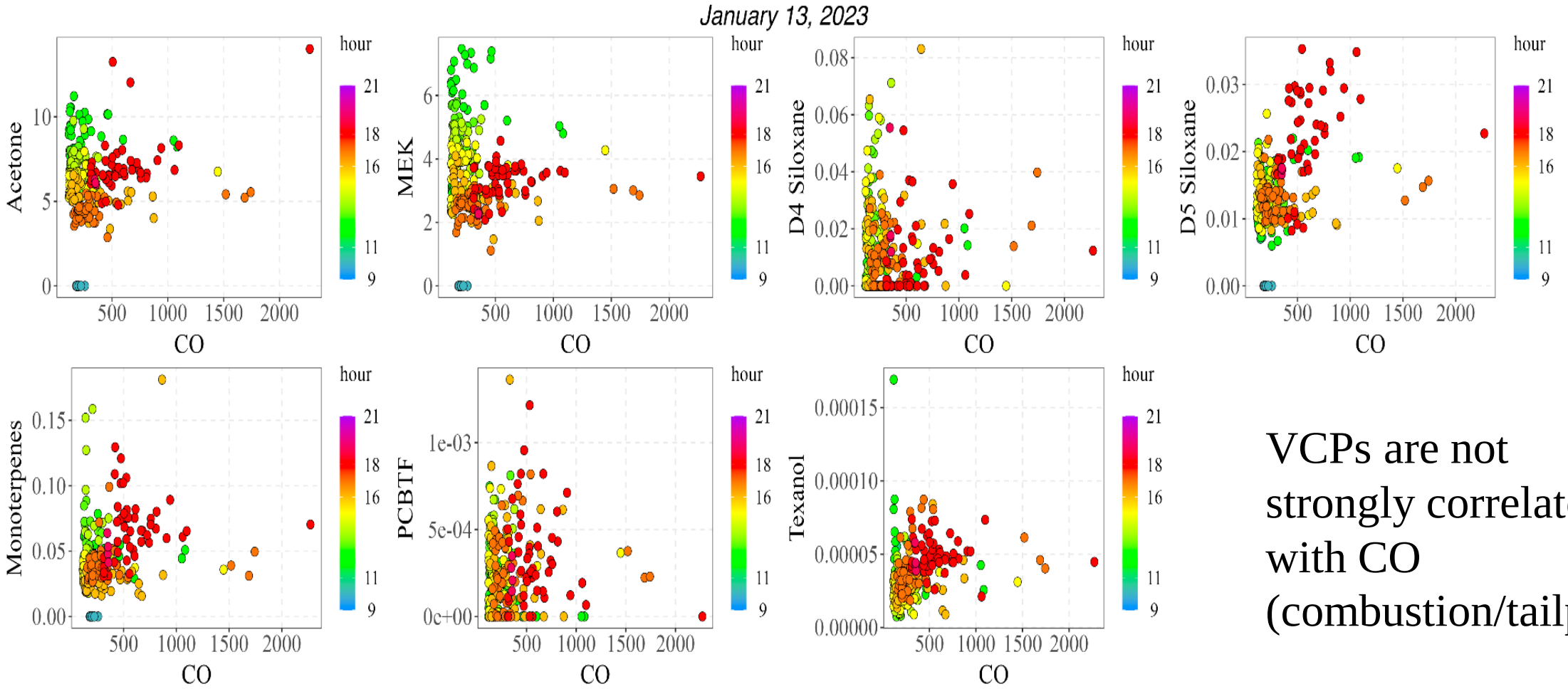
- VCP correlation with CO



VCPs are not strongly correlated with CO (combustion/tailpipe)

Measurement Data

- VCP correlation with CO



VCPs are not strongly correlated with CO (combustion/tailpipe)

Measurement Comparison

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- Averaged Seasonal Concentrations

	Acetone	MEK	D4-siloxane	D5-siloxane	Monoterpenes	PCBTF	Texanol
Fall NH_4^+	4.5625	0.6567	0.0198	0.0167	0.1187	0.0007	0.0004
Fall H^+	3.7724	0.8411	0.0007	0.0117	0.279	0.003	0.0006
Winter NH_4^+	7.3146	5.1618	0.0187	0.0132	0.0425	0.0002	0
Winter H^+	1.4651	0.3049	0.0003	0.0101	0.0872	0.0013	0.0003

Major VCPs in the Houston Area do not have a seasonal difference in its concentration, except for monterpenes.

Model Simulations

How does the field measurement serve to improve model simulations?

1. Three sets of VCP emissions from the traditional models will be compared with our field measured seasonal data:
   - First emission: National Emissions Inventory (NEI)
   - Second emission: VCPy emission inventory

2. Model performance statistics for O_3, NO_x, and $PM_{2.5}$ will be statistically evaluated to ensure that the model captures the general feature of air pollution during the study periods.

3. The inventory that leads to better overall model performance will be selected for further improvement to assess the impacts of VCPs on O_3 and SOA

CMAQ Modeling

Based on CMAQ v5.0.1 with updates of the gas and aerosol mechanisms to model SOA from monoterprenes

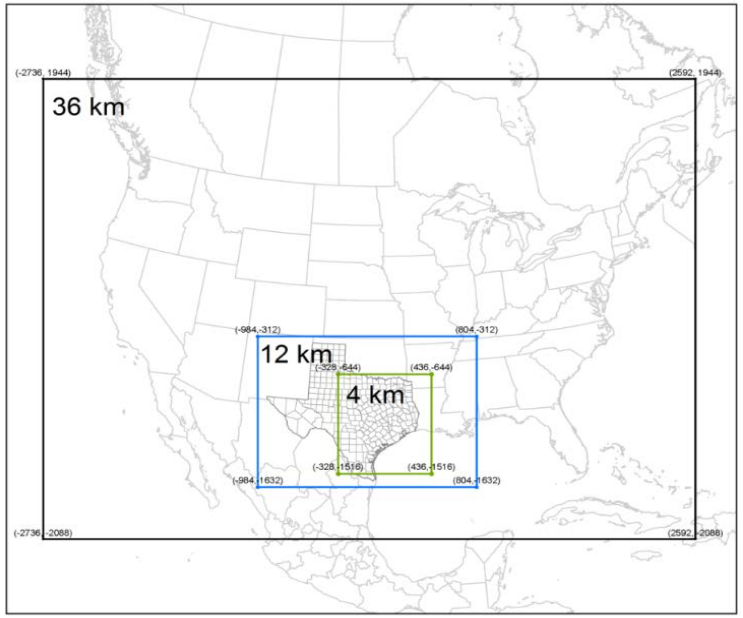
Gas phase chemistry – SAPRC-11D (SAPRC-11 but with the maximum reasonable number of emitted compounds represented explicitly)

- Suitable for studying oVCPs: The reactions of major oVCPs, including methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol, and acetone, are explicitly represented by the mechanism

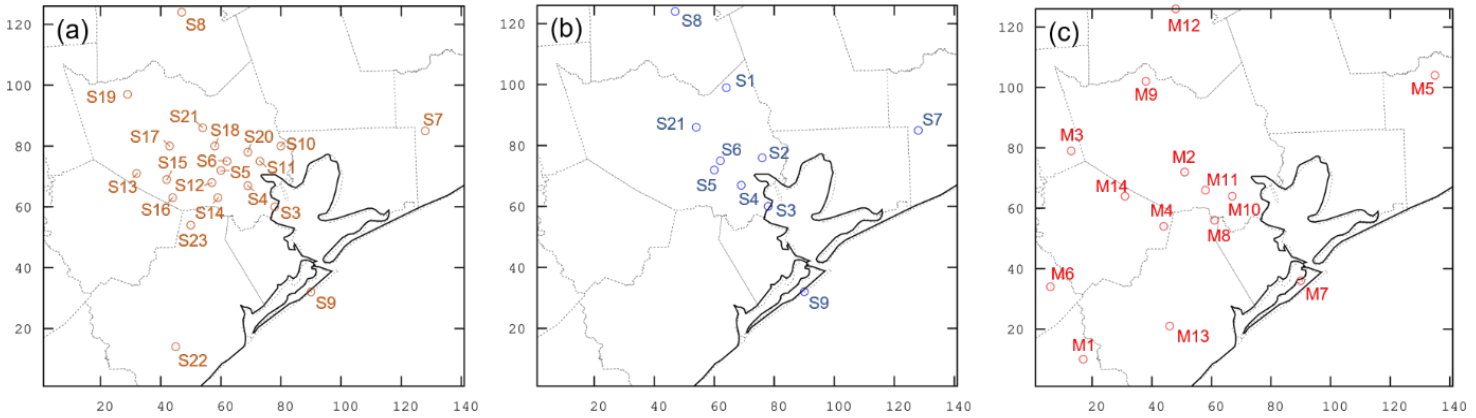
Emissions

- **Biogenic emissions** – MEGAN (Model for Emissions of Gases and Aerosols from Nature) v3.1. Modified to generate emissions of VOCs matching the detailed species in SAPRC-11D
- **Anthropogenic emissions** – 2019 Emissions Modeling Platform from US EPA
  - Based on 2017 NEI, updated to represent emissions in 2019. No further adjustments for 2022.
  - VOC speciation profiles were generated for the SAPRC-11D mechanism based on the latest **SPECIATE 5.2** speciation profile data base.
  - Non-point source solvent utilization emissions (cleaners, personal care products, adhesives, architectural and aerosol coating, printing inks, and pesticides) were derived using the using the **volatile chemical products in Python (VCPy) framework**

Model Domains and Episodes



- Four-level nested domains
- 36-km, 12-km and 4-km resolution domains – based on TCEQ 8-hour ozone attainment modeling
- A finer resolution (1.33-km) domain was nested to provide the detailed spatial distribution of air pollutants in Houston
- Modeling episodes: October 16-21, 2022; **November 1-12, 2022 (this presentation)**.

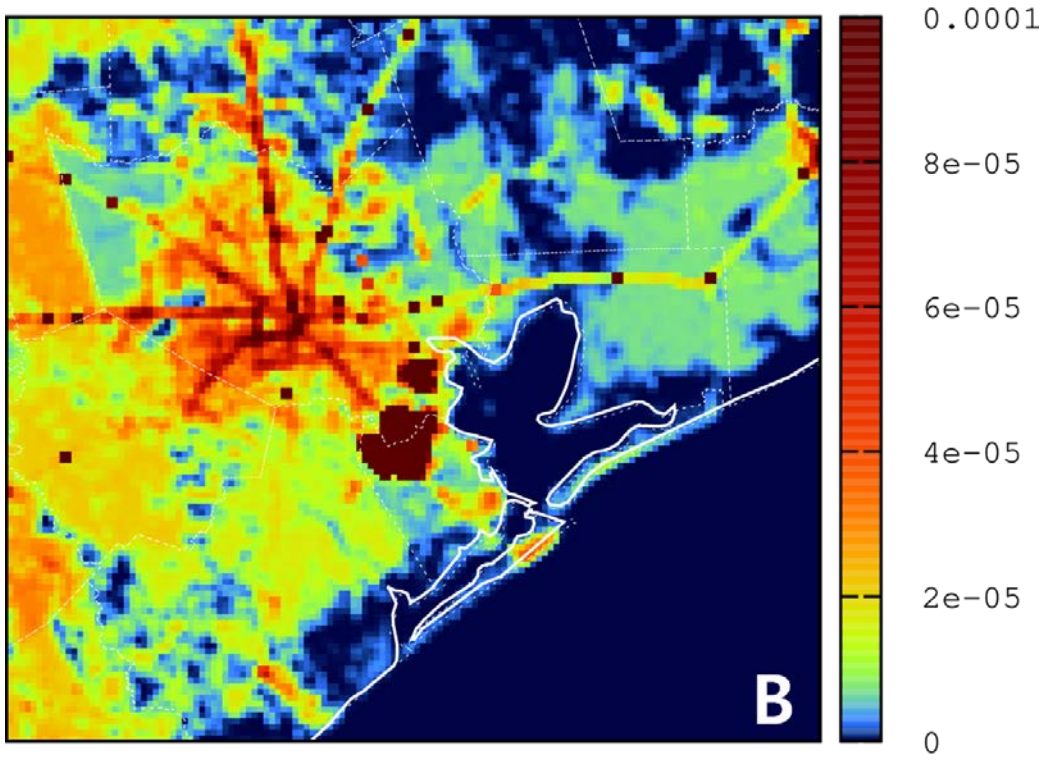


The observation sites for ozone (a), $PM_{2.5}$ (b), and (c) meteorological data within the 1.33-km domain

Emissions of n-hexane and d-limonene

n-hexane kg/h

D-limonene kg/h



Anthropogenic emission dominated

Significant contributions from biogenic emissions, with large anthropogenic emissions in the urban areas. The anthropogenic emission rates are probably too low.

Meteorological fields

Generated using WRF v4.4

Inputs

European Centre for Medium-Range Weather Forecasts (ECMWF) Reanalysis v5 (ERA5), with hourly reanalysis meteorological fields at 137 model levels with a resolution of 0.25x0.25 degrees

Model performance

Variable	MB	GE	RMSE
T (K)	-0.33	1.72	2.13
WD (°)	12.42	26.26	39.56
WS (m/s)	0.18	1.18	1.53
RH (%)	1.16	9.15	11.8

Model performance benchmark

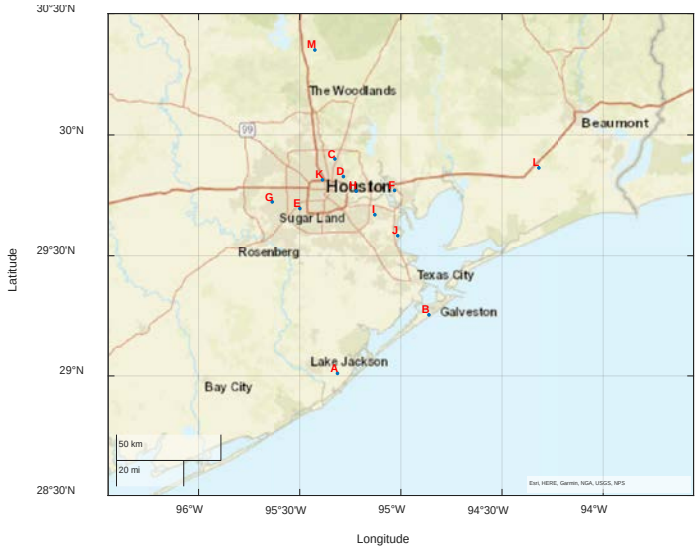
T: MB<± 0.5K, GE<2.0 K

WS: MB<± 0.5 m/s, GE<2.0 m/s, RMSE<2.0 m/s

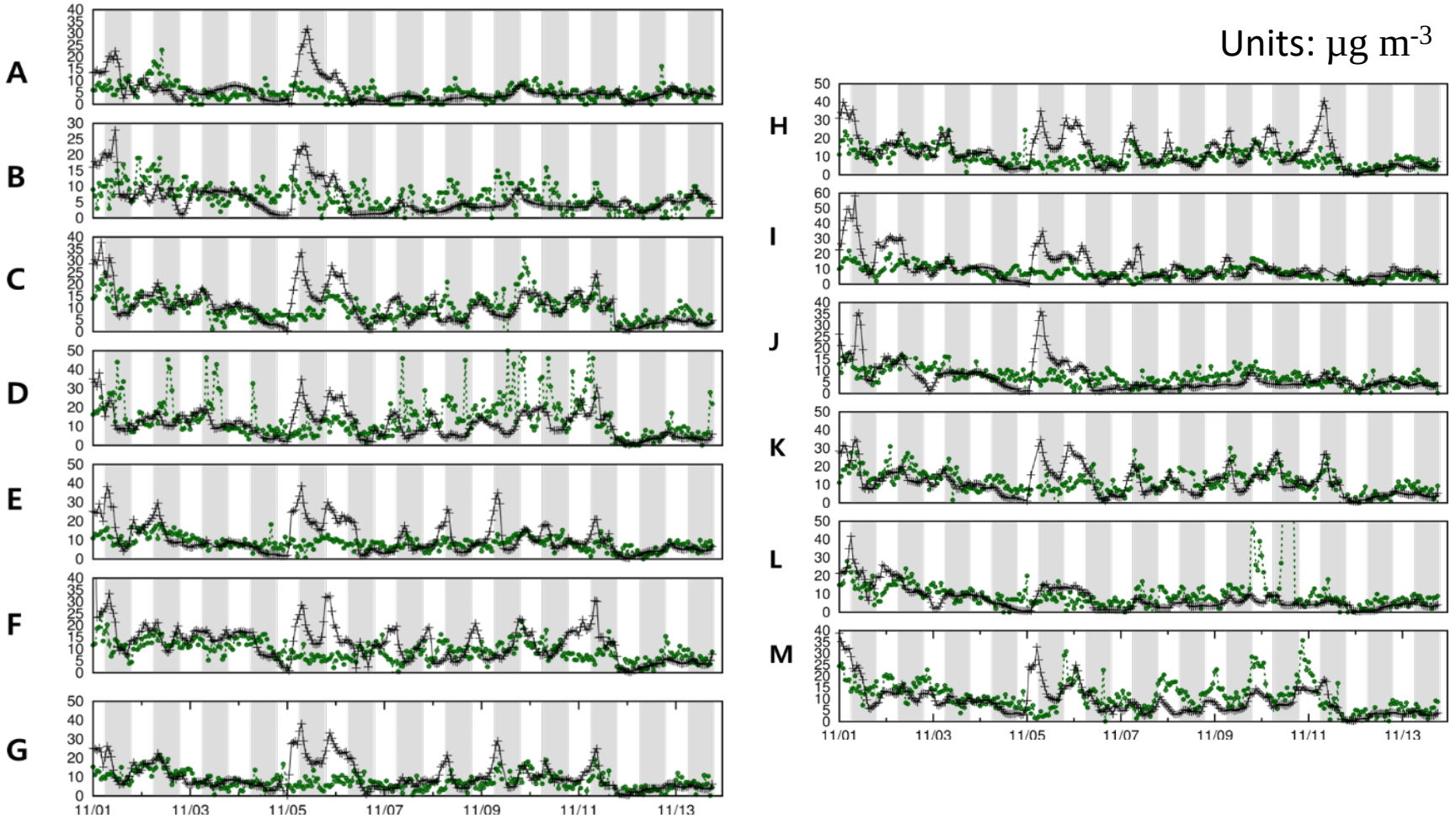
WD: MB<±10°, GE<30°

Meteorological model performance generally meets the suggested benchmark (Emery et al., 2001)

Modeled criteria pollutants – PM2.5

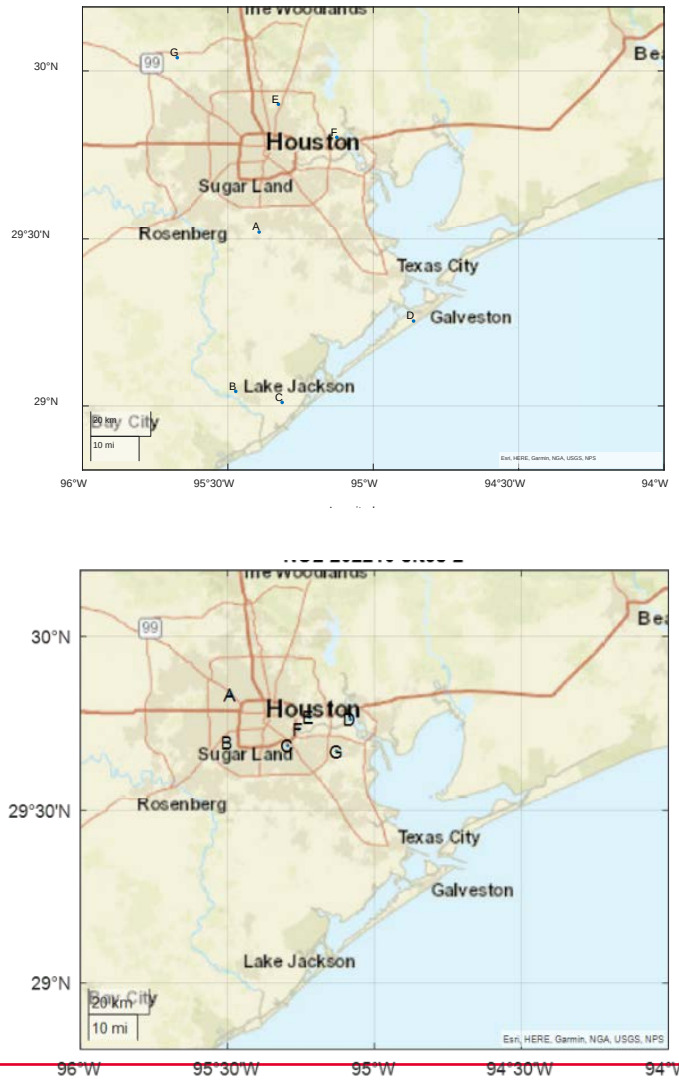


Units: µg m^{-3}



[Green: Observations; **Black**: Predictions]

Modeled criteria pollutants – NO_2



(top map)

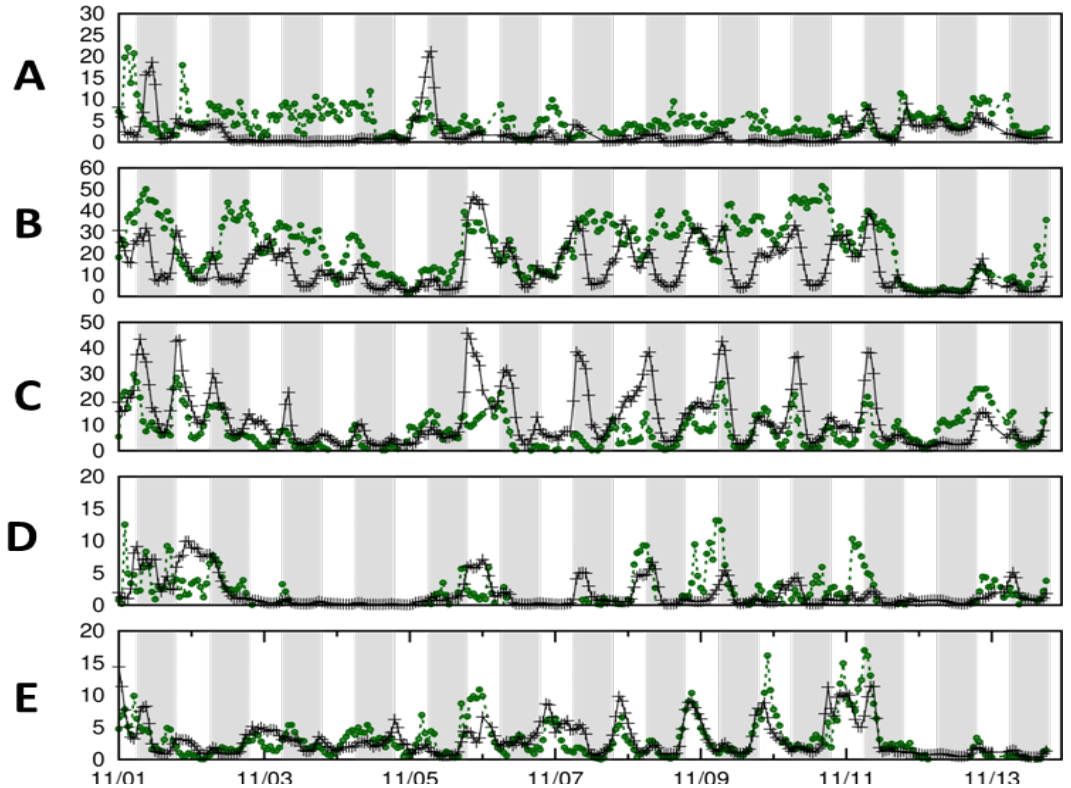
(bottom map)

Units: ppb

[Green: Observations; **Black**: Predictions]

Modeled criteria pollutants – NO_2

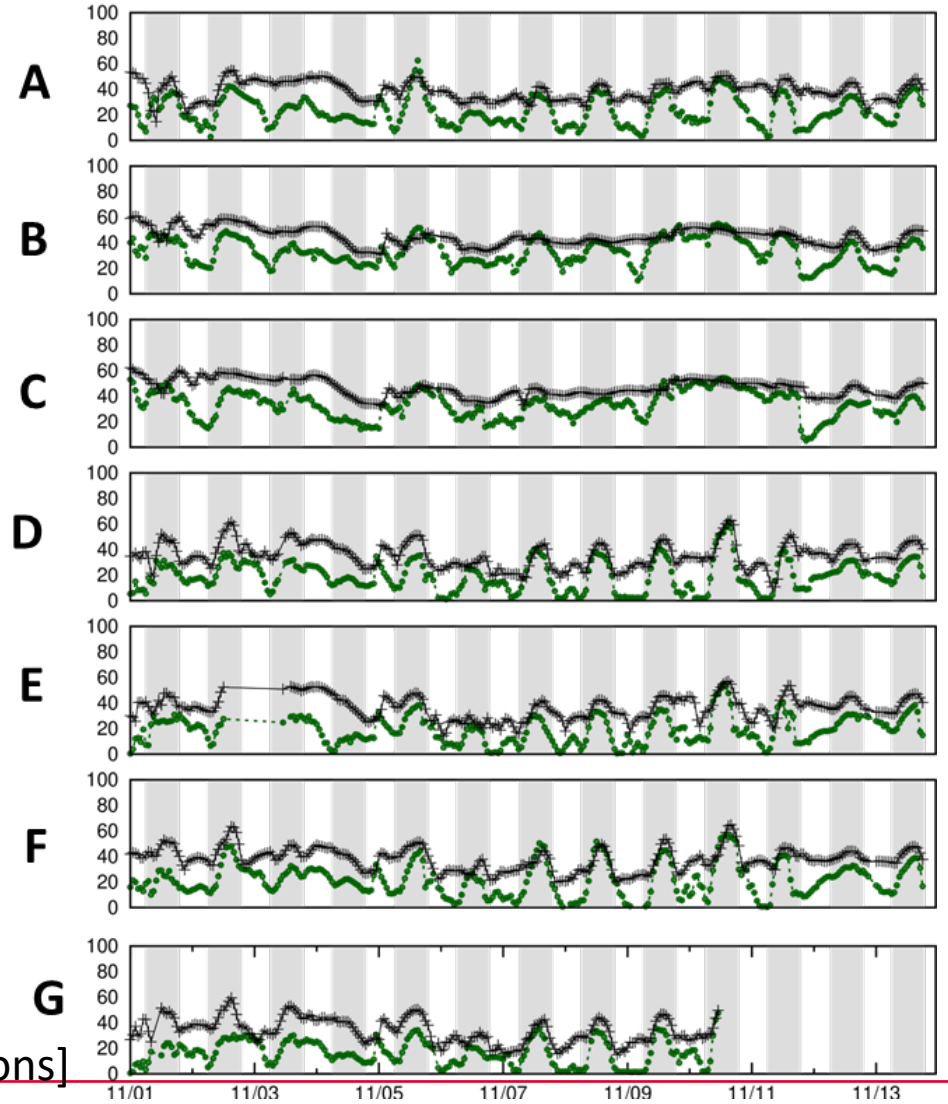
Units: ppb



[Green: Observations; **Black**: Predictions]

Modeled criteria pollutants – O_3

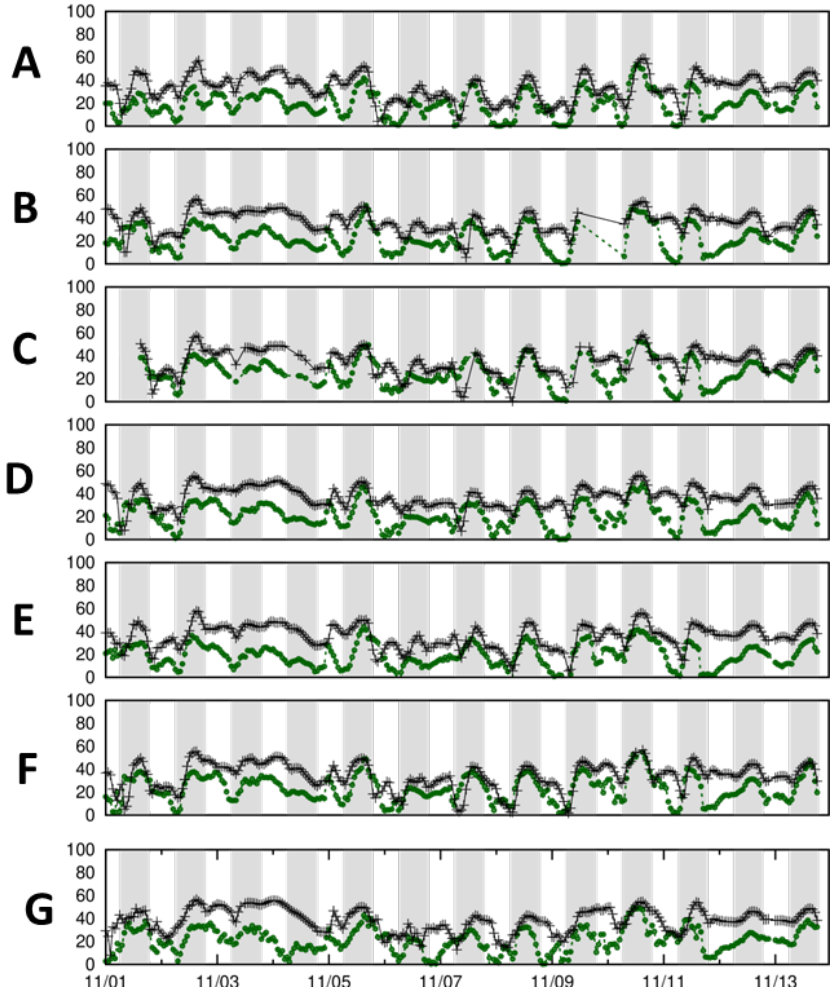
Units: ppb



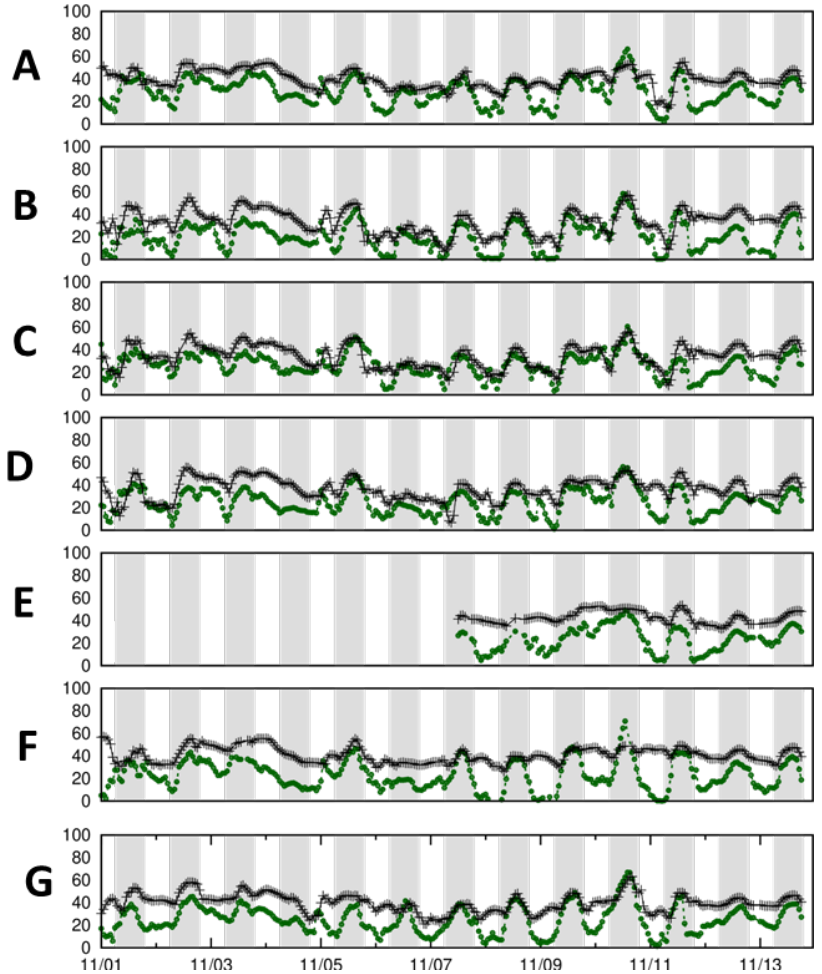
- Captured the higher O3 concentrations during the day
- Overpredicted the nighttime concentrations.
- Excess downward mixing in colder weather?

[Green: Observations; **Black**: Predictions]

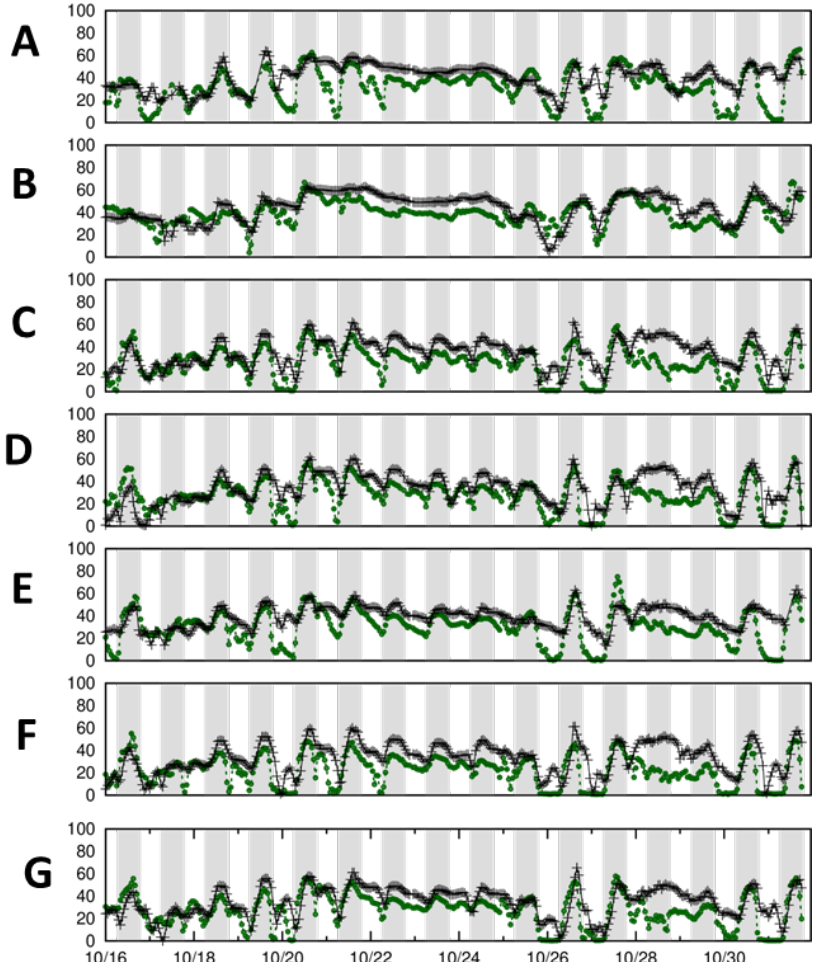
Modeled criteria pollutants – O_3



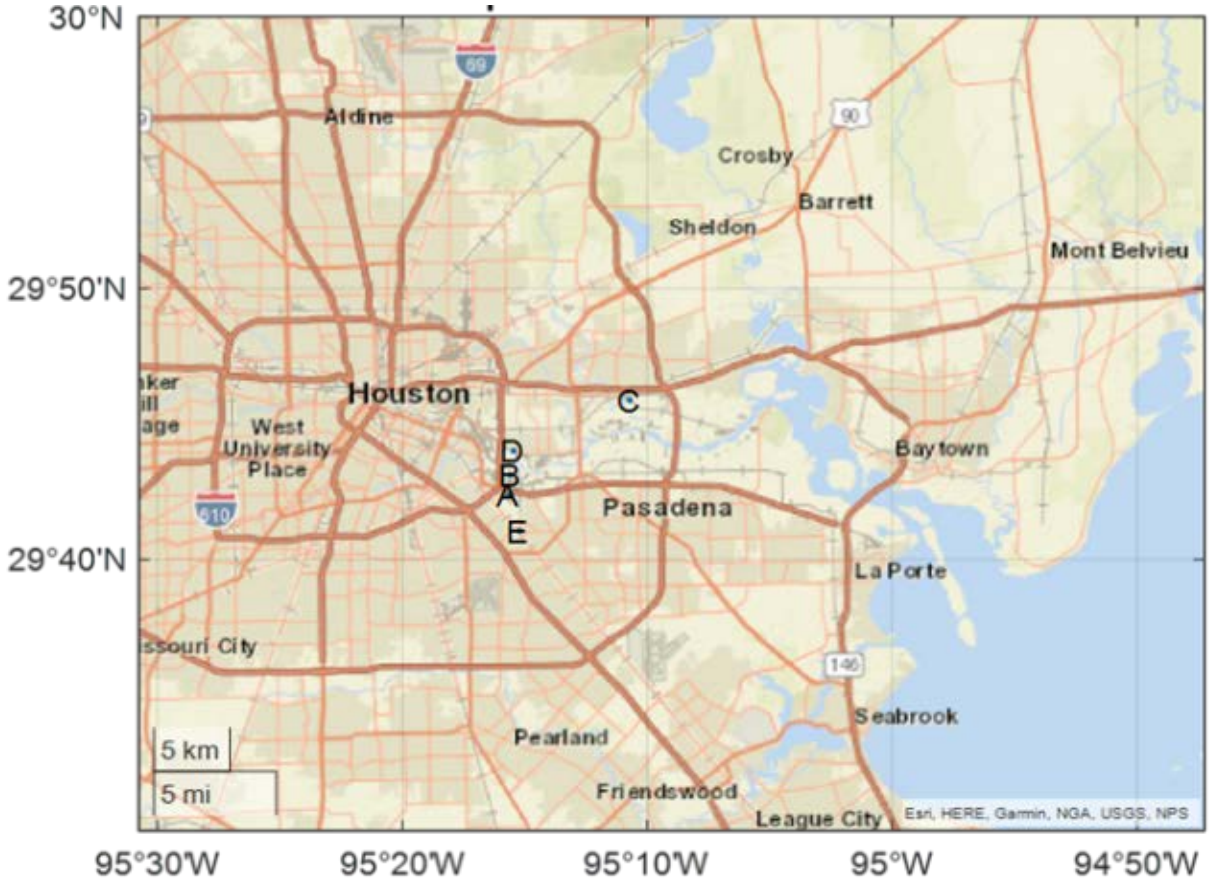
Modeled criteria pollutants – O_3



Modeled criteria pollutants – October O_3



Modeled Organic Compounds at Auto-GC sites



Major findings

- Larger alkanes (C6-C10) are better predicted than smaller alkanes (C3-C5)
  - Smaller alkanes have larger contributions from VCPs – VCP emissions are underestimated?
- Aromatic compounds are well represented

Modeled Organic Compounds at Auto-GC sites

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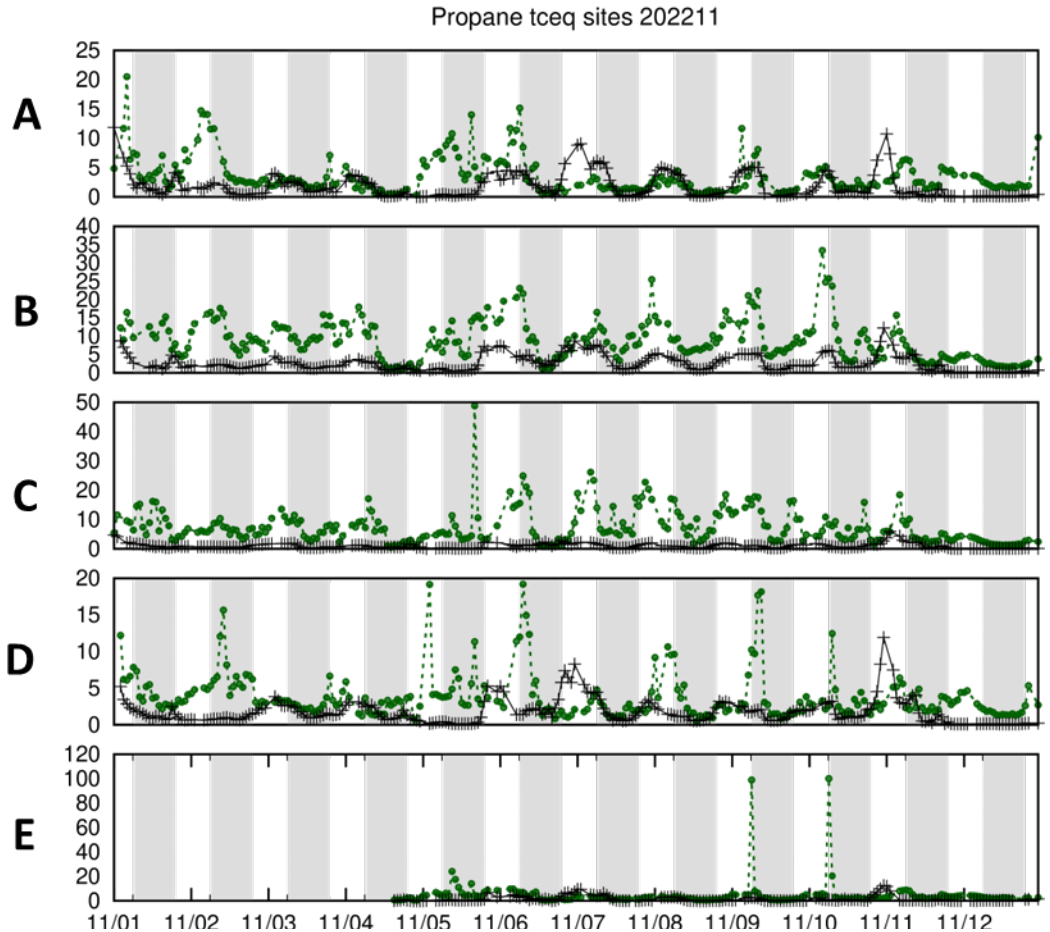
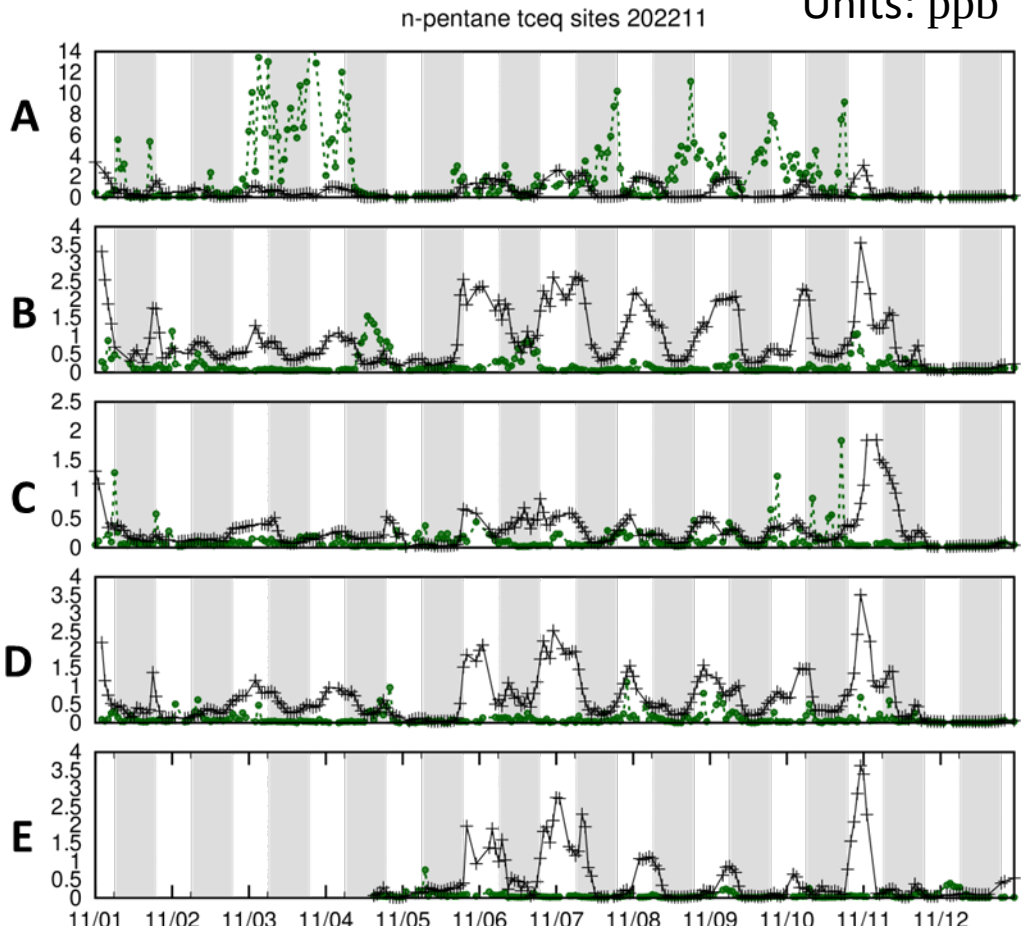
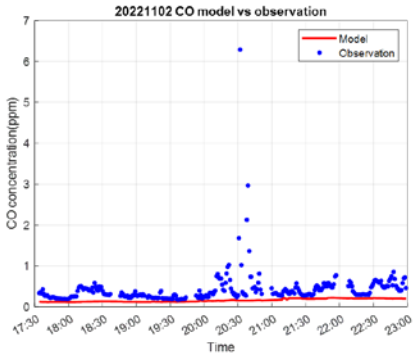
Units: ppb

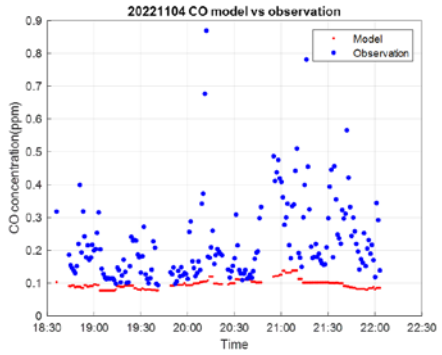


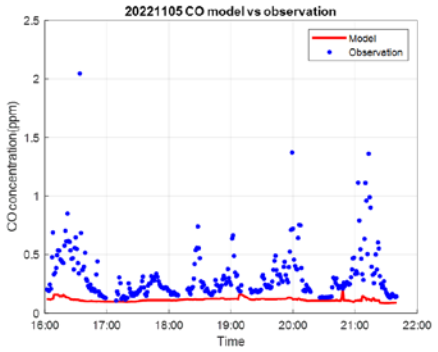


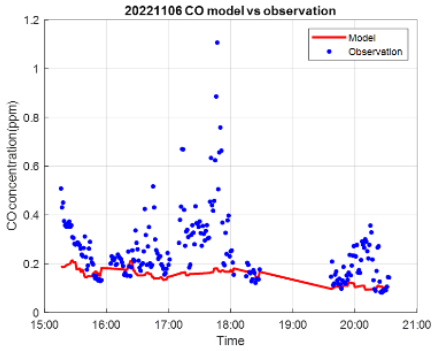
[Green: Observations; **Black**: Predictions]

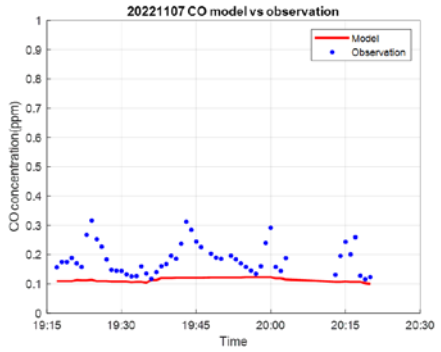
Compare with mobile platform measurements - CO

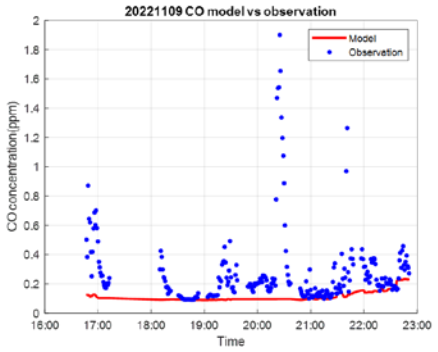


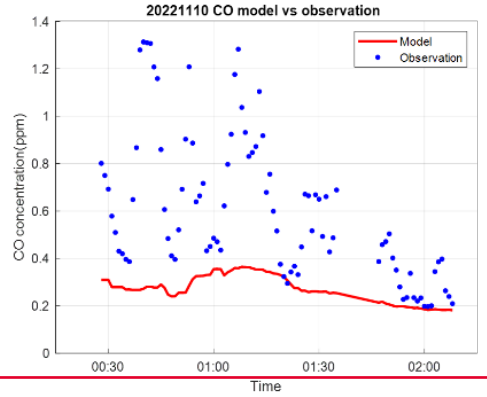








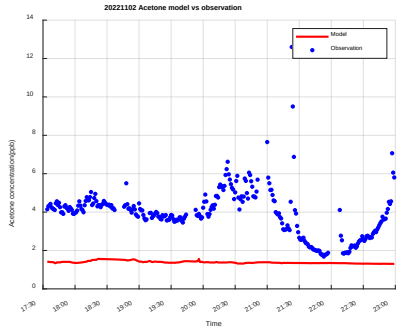


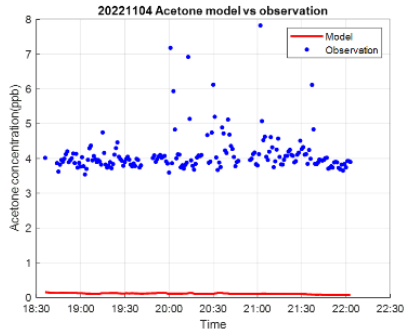


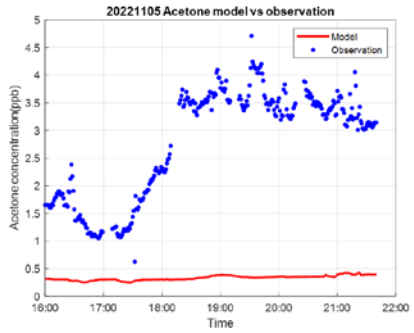
Major findings from the CO data

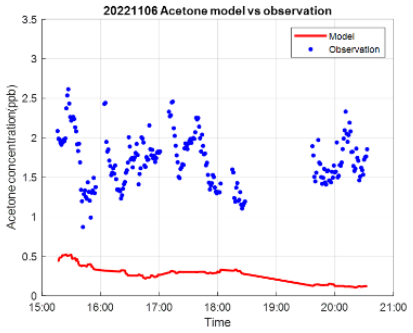
- The predicted concentrations are significantly lower than the observations
  - mobile platform is significantly influenced by the tailpipe emissions from on-road vehicles
- The lowest values in the observations matched the predictions
  - measurements were not affected by immediate tailpipe emissions

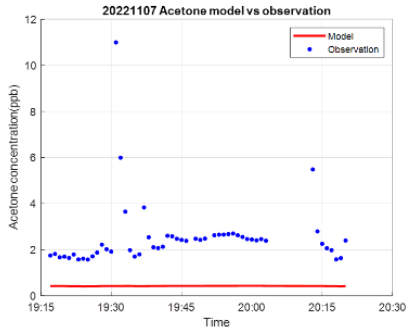
Compare with mobile platform measurements - acetone

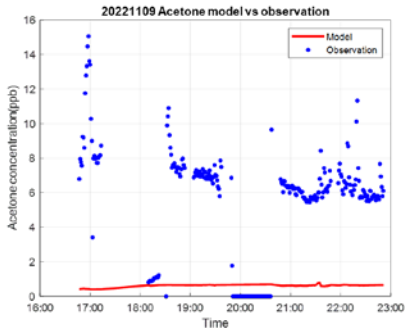


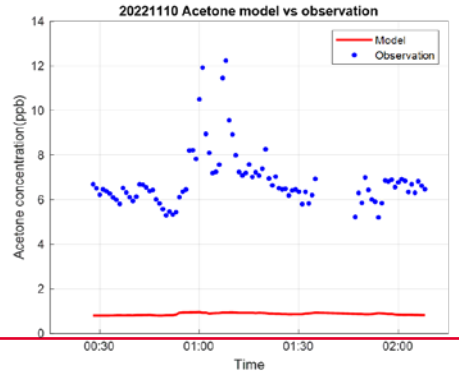






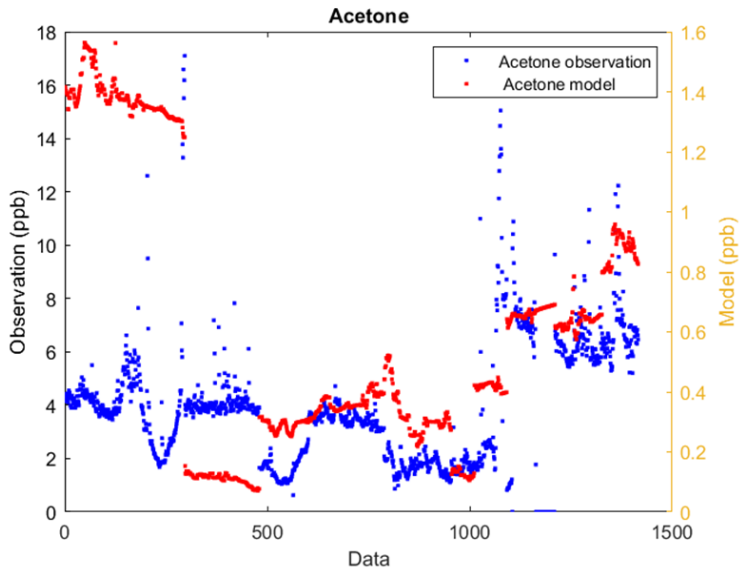




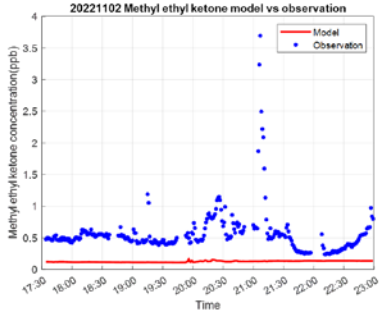


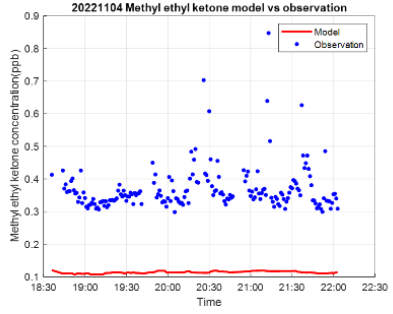
Major findings - acetone

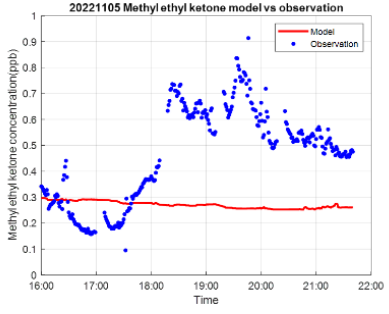
- Significantly under-predicted
- Except for the first day (11/2), the day-to-day variations of acetone was captured well
- Under estimation by a factor of 8-10
  - Adjust speciation profiles to fix the problem?

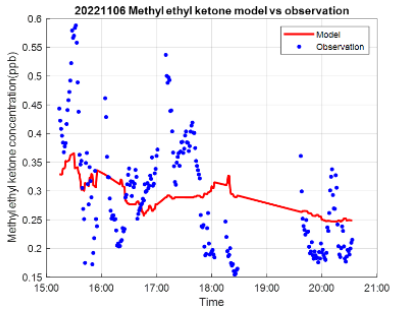


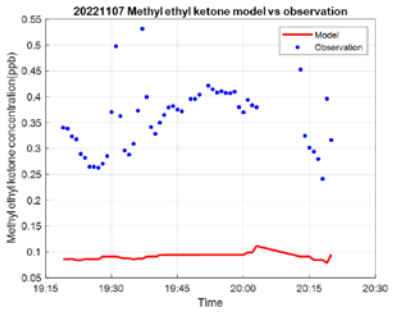
Compare with mobile platform measurements – methyl ethyl ketone

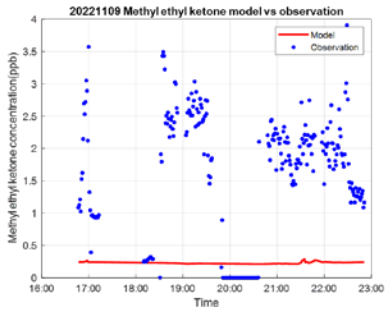


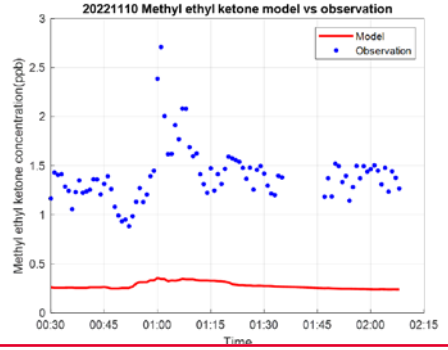






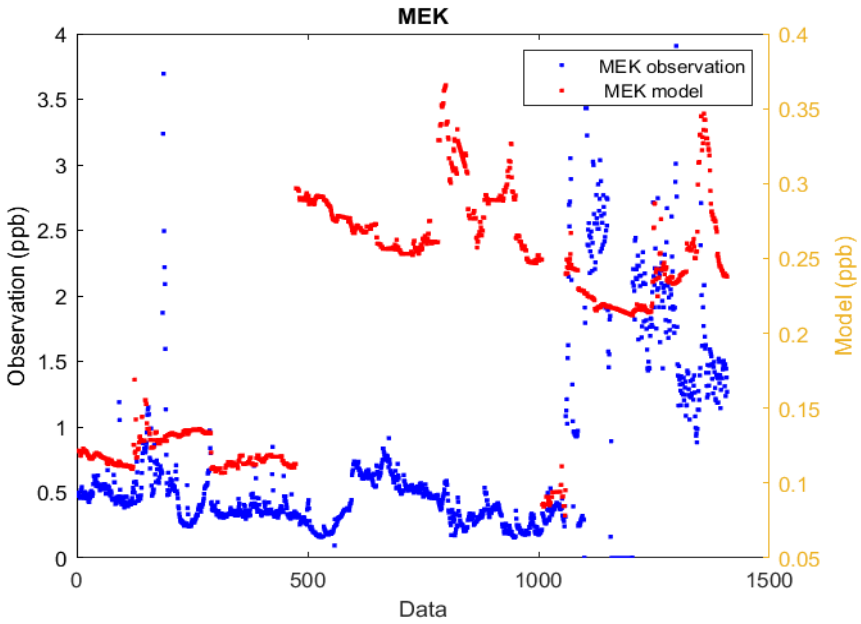






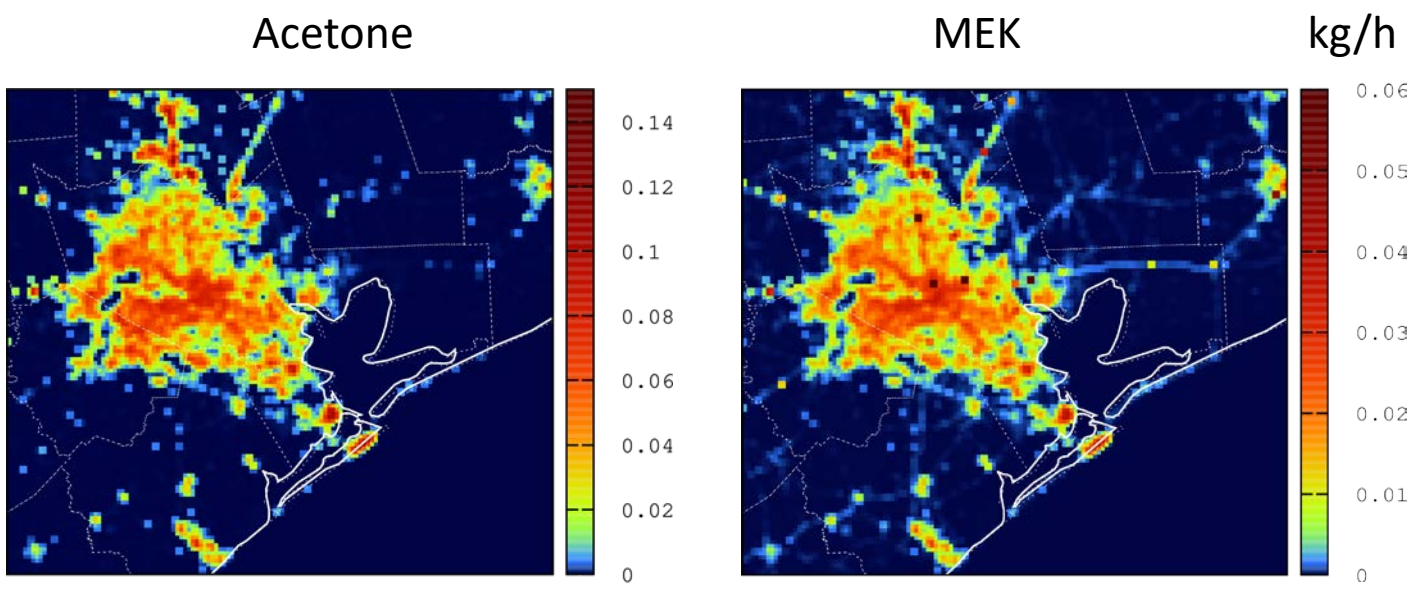
Major findings - MEK

- Significantly under-predicted
- Day-to-day variations of acetone was not as well captured as acetone
- Under estimation by a factor of 5-10



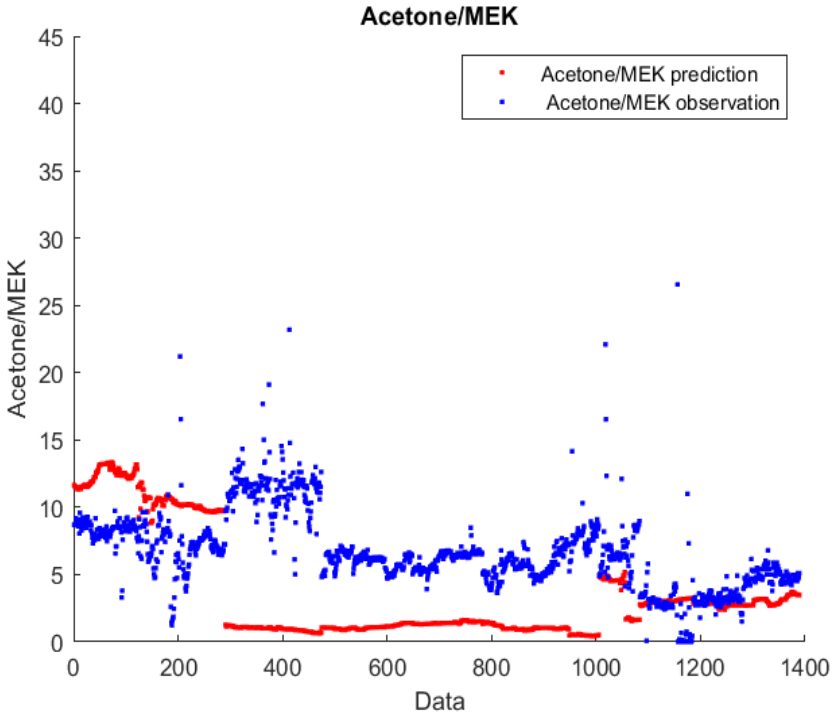
MEK and acetone

Emissions



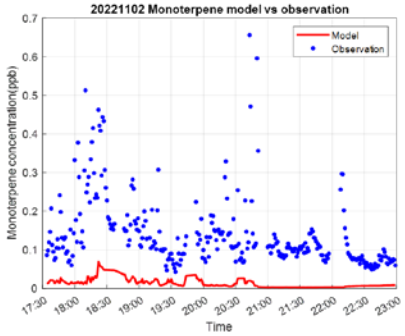
Emission ratio is approximately 2:1

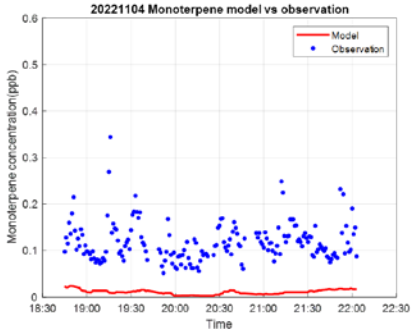
Concentration ratio

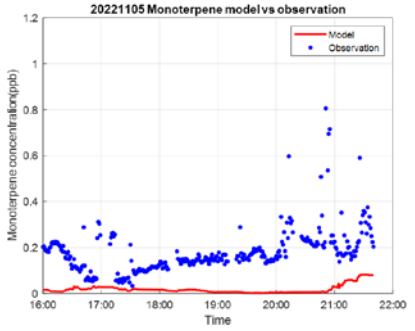


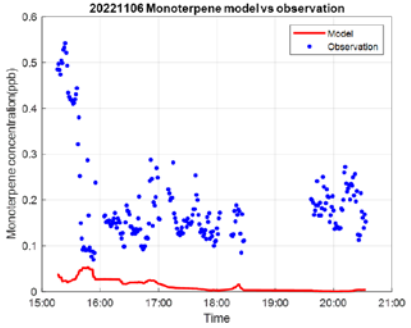
- Observation ratios ~ 5
- Modeled ratios match observations on some days
- Cause of the variations need to be investigated.

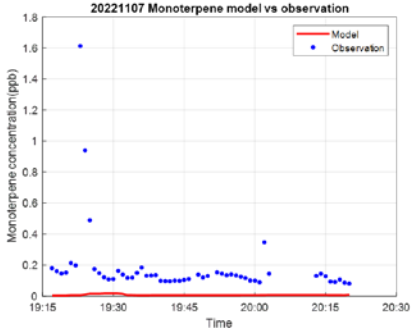
Compare with mobile platform measurements – Monoterpene

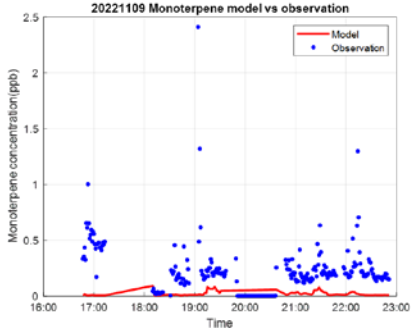


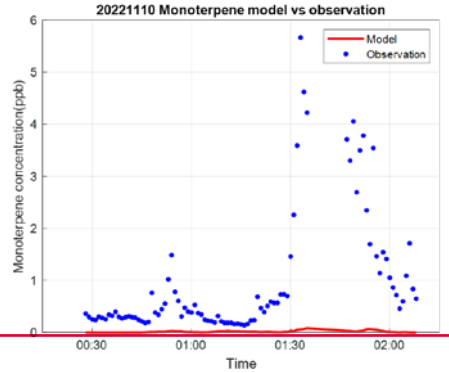












The predicted monoterpene concentrations are the sum of α-pinene, β-pinene, d-limonene, Δ3-carene, and sabinene

- Significant under-prediction
- Emission are potentially underestimated

Conclusions

- All major VCPs were able to be detected by the Vocus CI-MS down to ppt-ppb levels
- Major VCP concentrations detected over Houston using two ionization modes do not show strong seasonal difference, except for monoterpenes
- CMAQ model has been used to estimate normal pollutants monitored by the TCEQ and VCP concentrations
- Regular criteria pollutants agreed with CMAQ modeling results better compared with VCP.
- Certain VCP concentrations seems to be underestimated by the CMAQ model.

Acknowledgement

Thank you!

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Questions?