Apportioning the Sources of Ozone Production during the San Antonio Field Study

aka "SAFS"

University of Texas, San Antonio   Floresville TCEQ Monitoring Site   Corpus Christi State Park

AQRP Workshop, August 22, 2017

Project Team
AQRP 19-025

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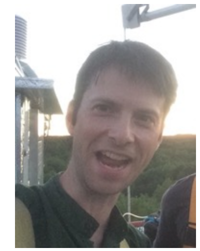

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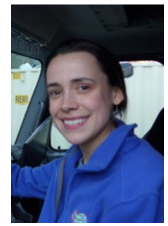
Drexel
(Separately funded)



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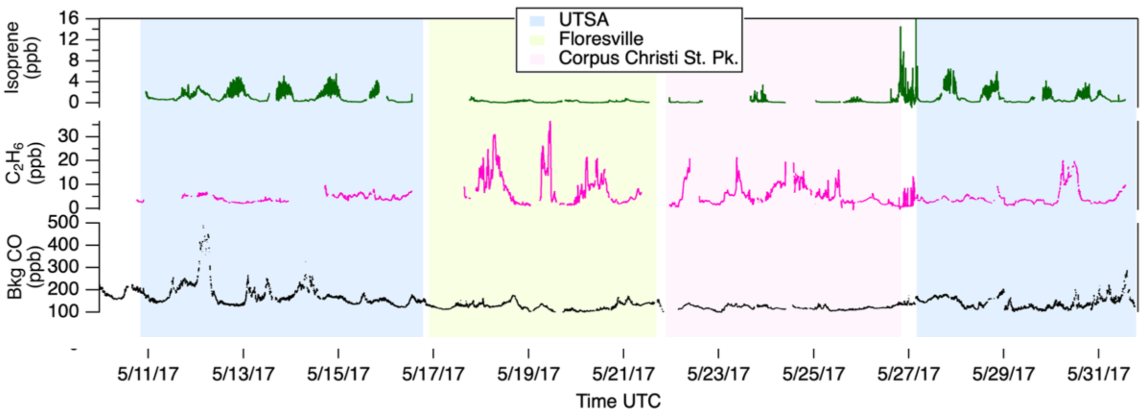
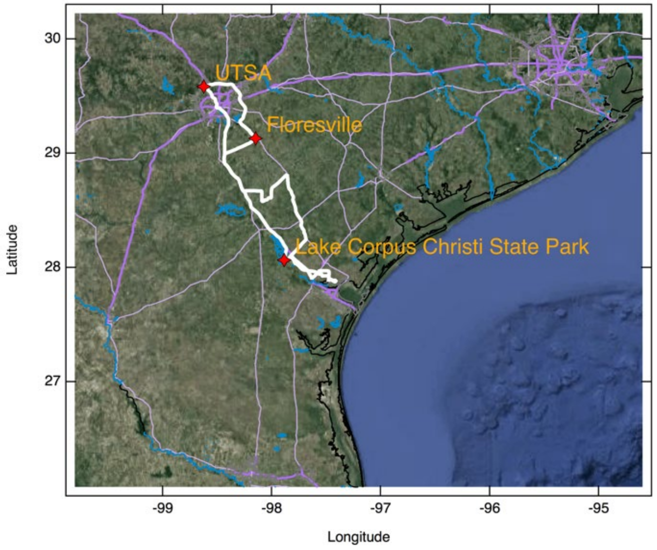
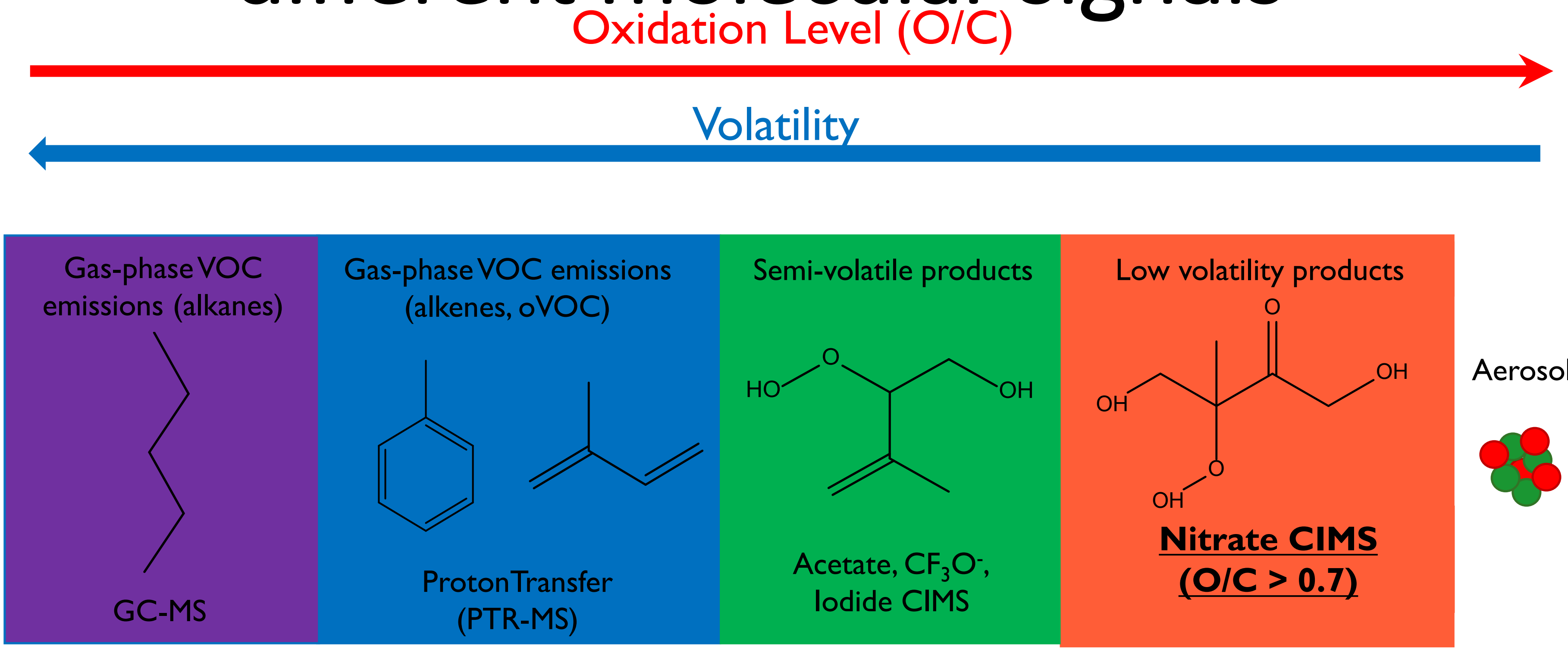
Overview of Time Series

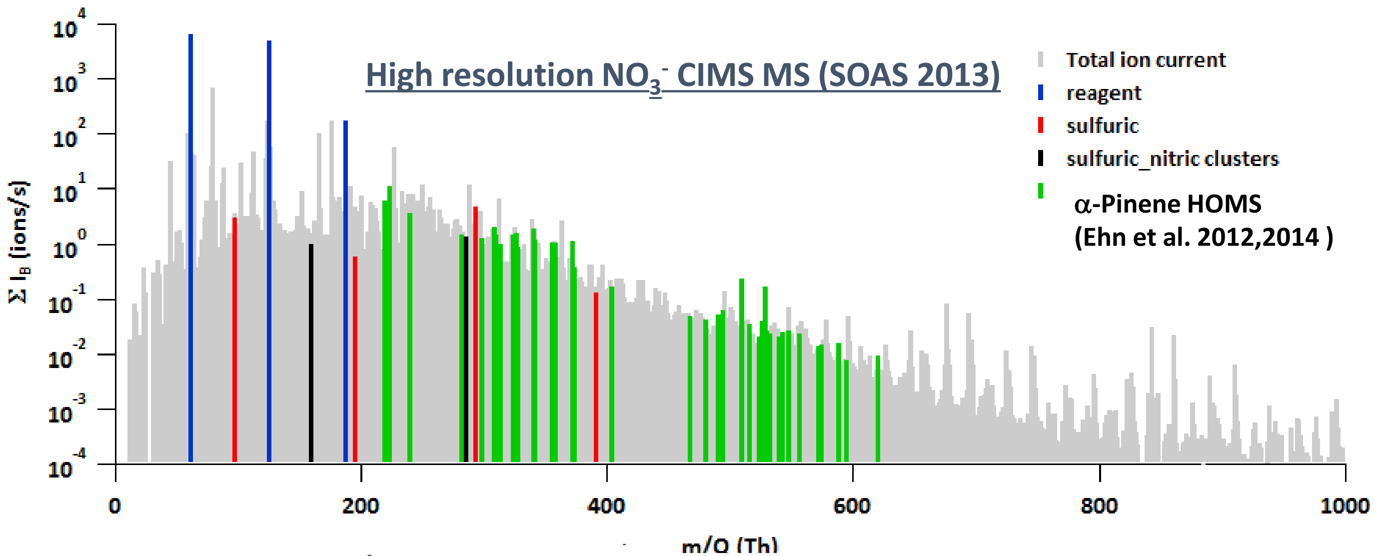


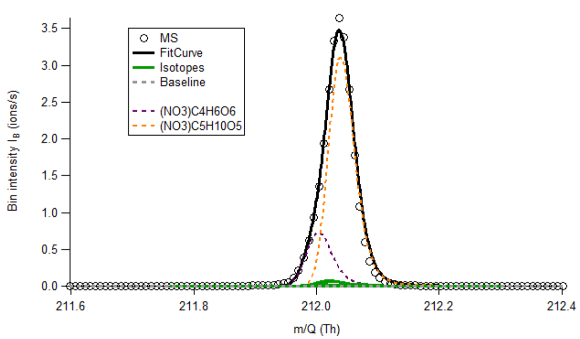


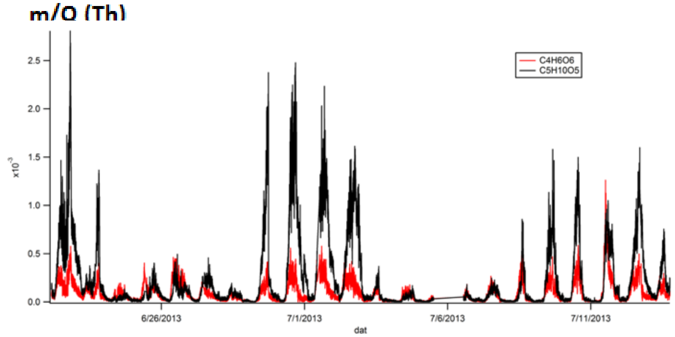
Different mass spectrometry options enable detection of different molecular signals



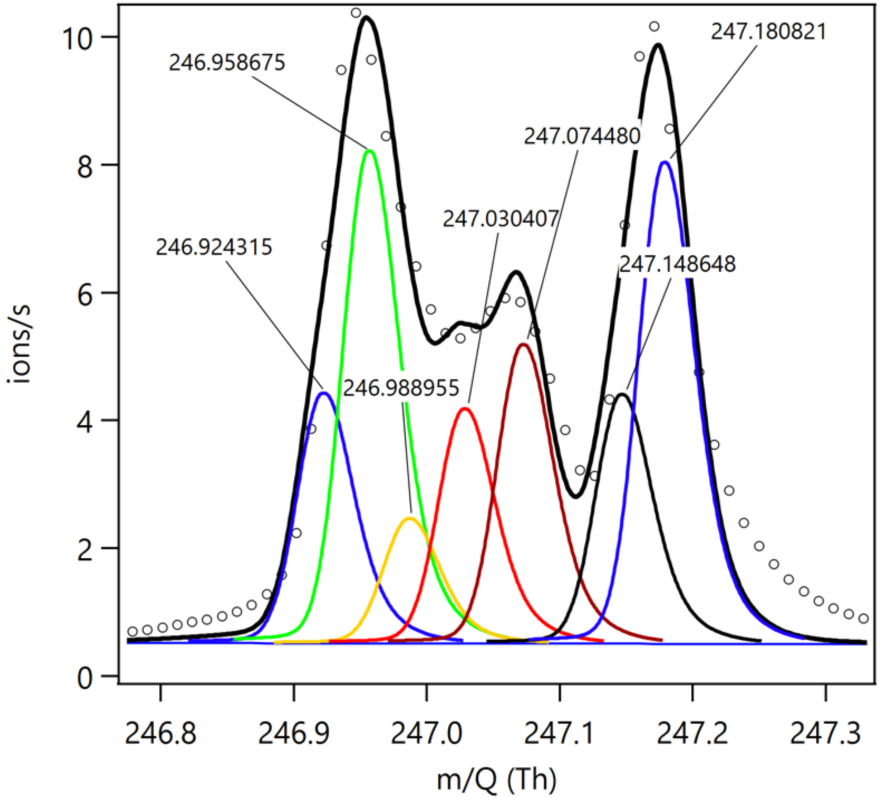
Vast Amounts of Data







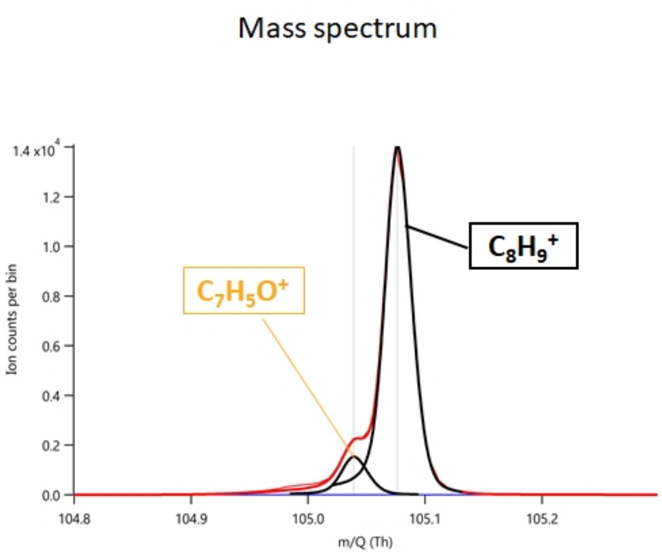
High-Resolution Analysis

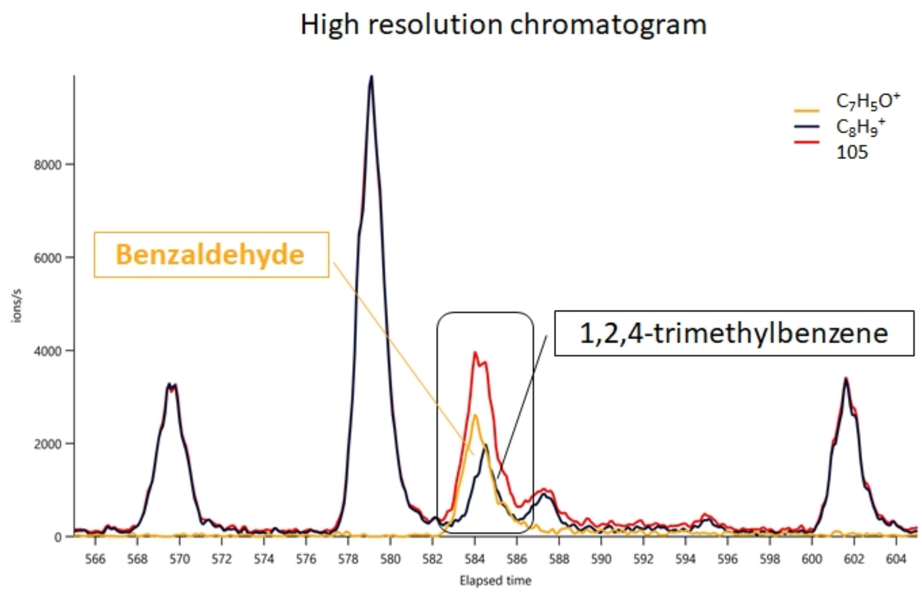


Averaged mass spectrum from the I⁻CIMS at the San Antonio measurement site during the SAFS. This example is relevant to all mass-spectral methods deployed at the SAFS.

- Extract multiple individual ion signatures from a single mass window

HR Fitting Example



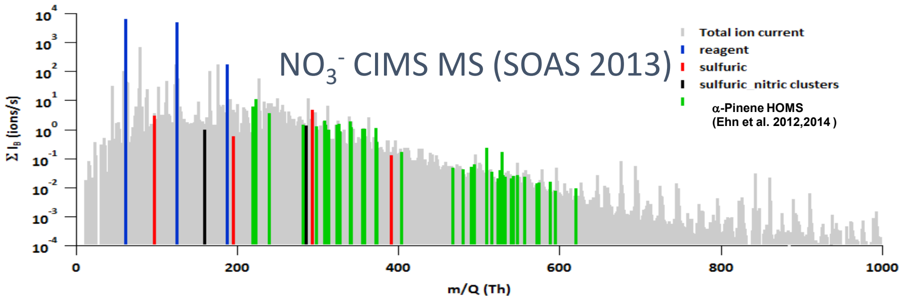


Left panel: contributions from individual ions to total UMR signal at m/z = 105. Right panel: Example chromatogram during pre-campaign testing showing UMR and individual ion chromatographic peaks at retention time = 584 sec.

Data Volume Problem

Problem

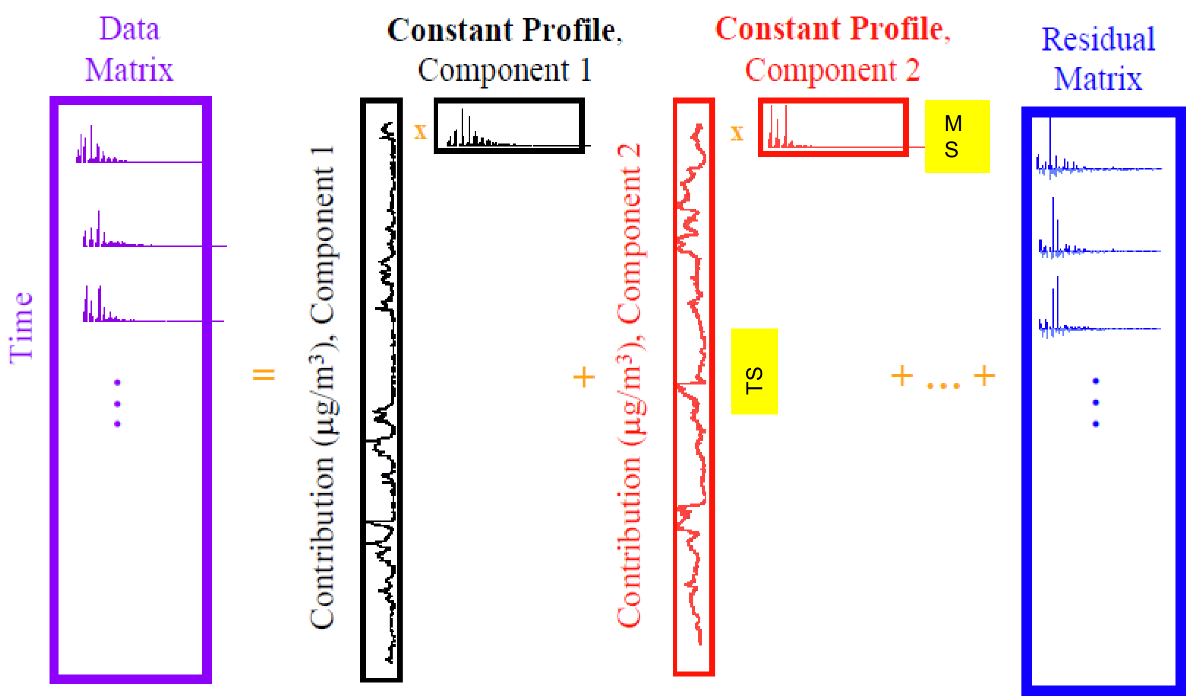
- Hundreds and hundreds of individual signals
  - Some known
  - Some with known



Solution

- Positive Matrix Factorization
  - Mathematical technique groups co-varying signals into “factors”
  - Each factor has numerous contributing masses

Generic Receptor Model Schematic



A data matrix is decomposed into an **arbitrary number** of factors, each of which is represented by a **constant mass spectrum** and a contribution **time series**. There is usually some *residual* of fit.

PMF: Use linear least squares in multiple dimension to solve this problem

Fit Details

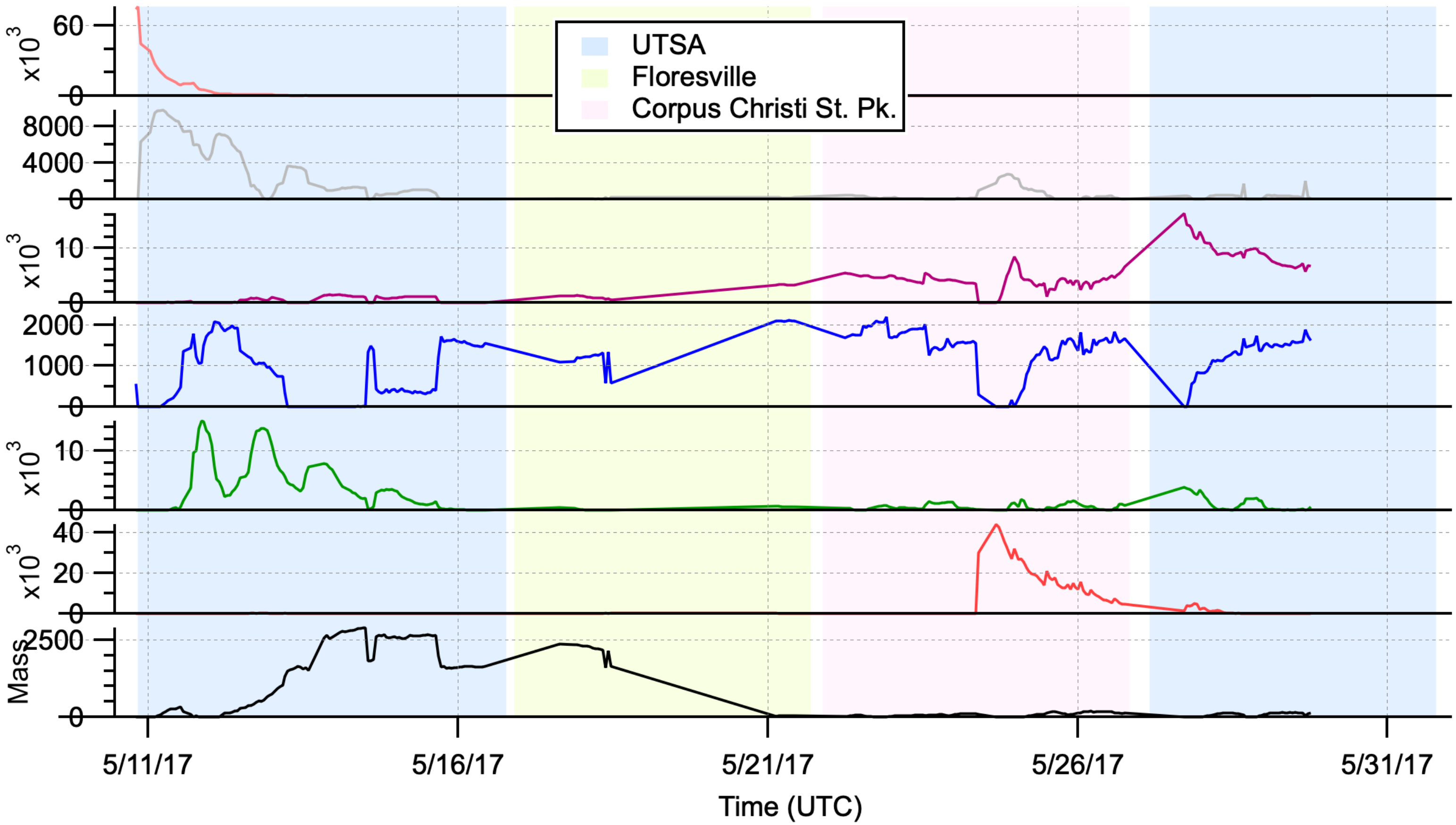
- Each point in the data matrix is weighted by its uncertainty
- Time Series and Mass Spectra have positive elements

PMF:
Paatero, P. ,1997

Slide adapted from I. Ulbrich

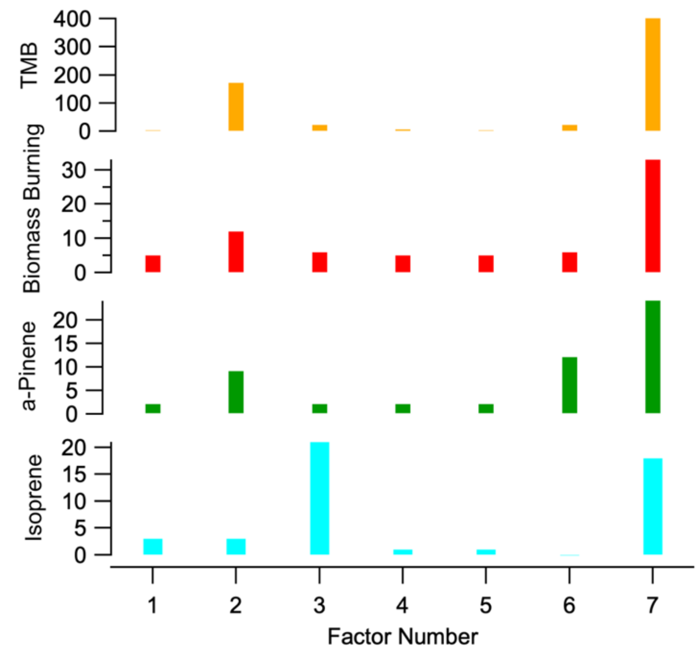
Species of Atmospheric Interest

I-CIMS: Oxygenates and other Intermediates



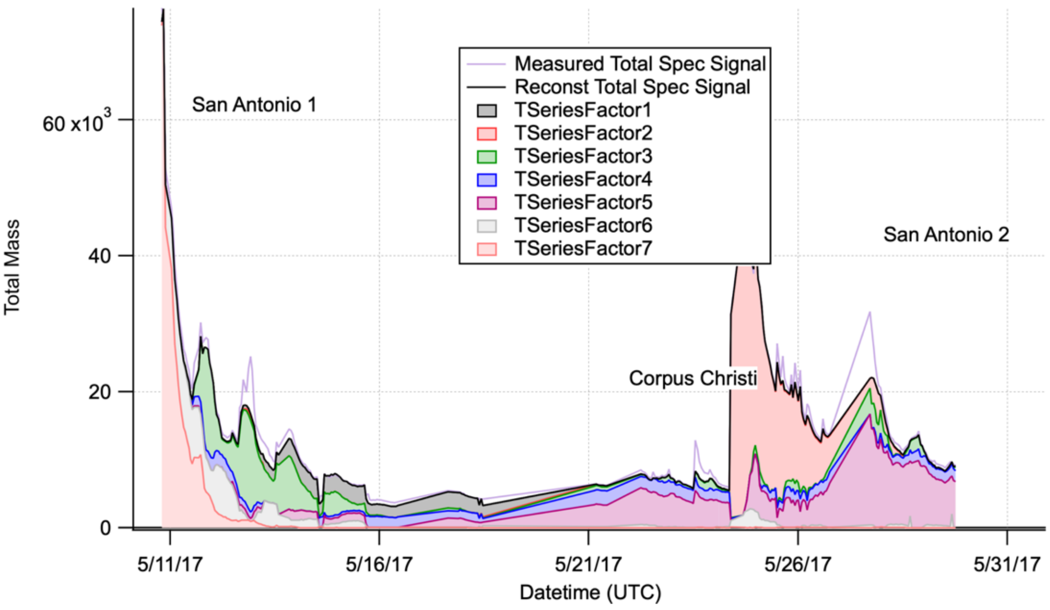
Identifying Factors

- Identify using
  - literature [*Mohr et al.*, 2013] and
  - laboratory experiments [Aerodyne, unpublished]
- Known signatures:
  - Isoprene oxidation
  - Alpha-pinene oxidation
  - Biomass burning
  - Trimethyl benzene oxidation (high-NOx conditions)



Signature ions of each factor categorized according to their match with known source-specific ions.

I-CIMS Species of Interest

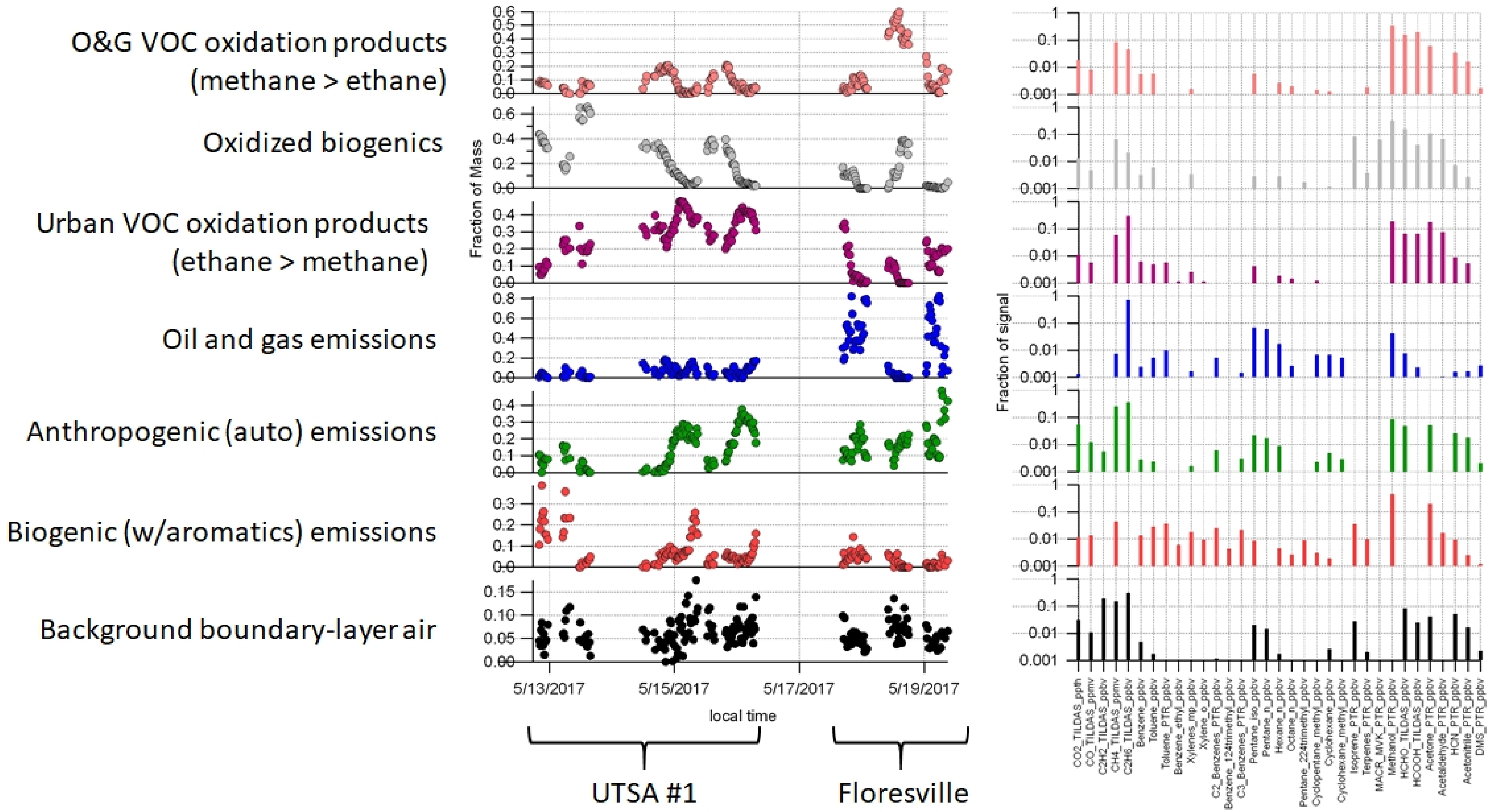


	Source Influences
Factor 1	Mixed Source
Factor 2	Instrument Artifact
Factor 3	Isoprene signature
Factor 4	Mixed Source
Factor 5	Mixed Source
Factor 6	a-pinene signatures
Factor 7	Instrument Artifact

PMF: VOCs and Direct Tracers

TILDAS Species	**GC-EI-TOFMS Species**	**PTR-TOFMS Species**
CO [ppm]	Benzene	Isoprene
Methane	Toluene	Monoterpenes*
Ethane	Ethylbenzene	Methyl vinyl ketone & methacrolein*
Ethyne	m&p-Xylenes*	Methanol
Formaldehyde	o-Xylene	Acetone
Formic acid	1,2,4-trimethylbenzene	Acetaldehyde
	i-Pentane	Dimethyl sulfide
NDIR Species	n-Pentane	Acetonitrile
CO_2 [ppth]	n-Hexane	
Hydrogen cyanide	n-Octane	
	2,2,4-trimethylpentane	
	Methylcyclopentane	
	Cyclohexane	
	Methylcyclohexane	

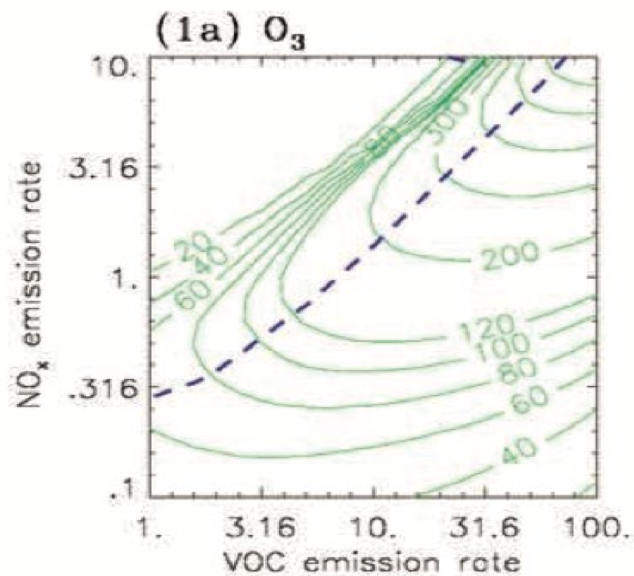
PMF: VOCs and Direct Tracers



PMF results, with nominal description of each factor. Left: Individual factor contribution to total chemical burden. Right: chemical signature for each factor.

Apportioning the Sources of Ozone Formation

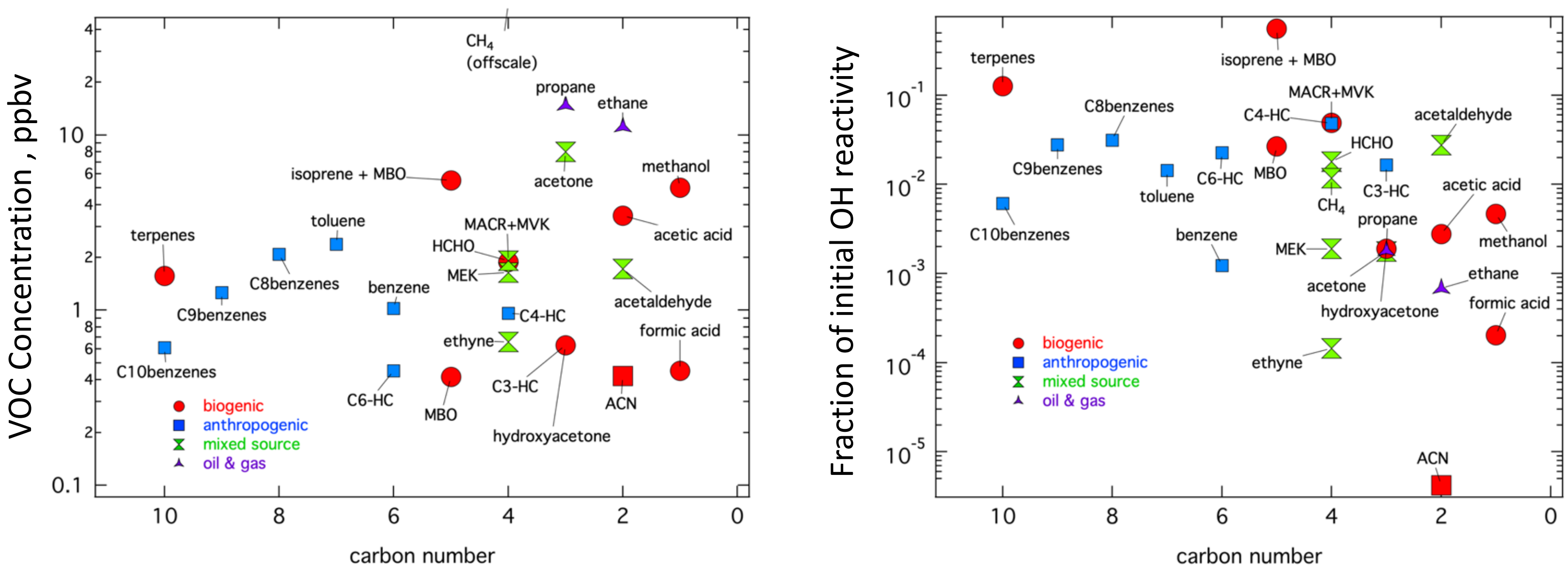
OH Reactivity to Apportion Ozone Formation



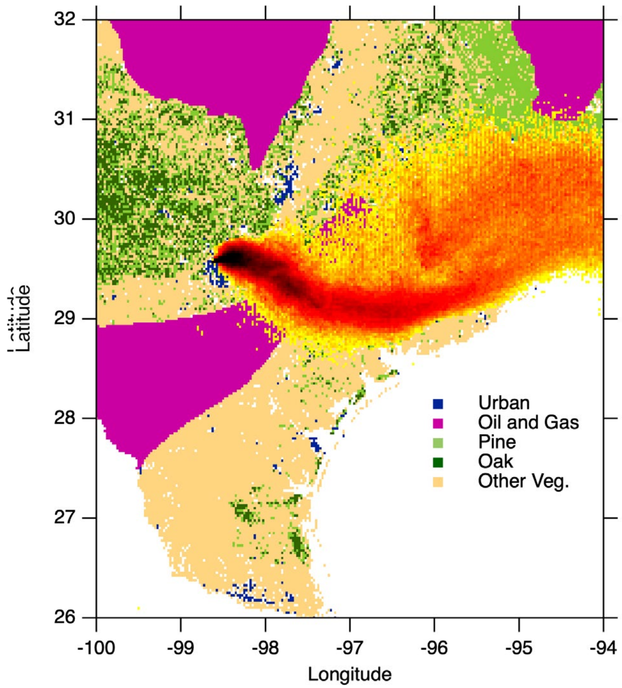
- Ozone depends on the interplay between NOx and VOCs
- VOCs reacting with OH kick off ozone chemistry.
- Aim to apportion OH reactivity to understand ozone formation

Silman and He, 2002

Relative impact of VOCs during Campaign



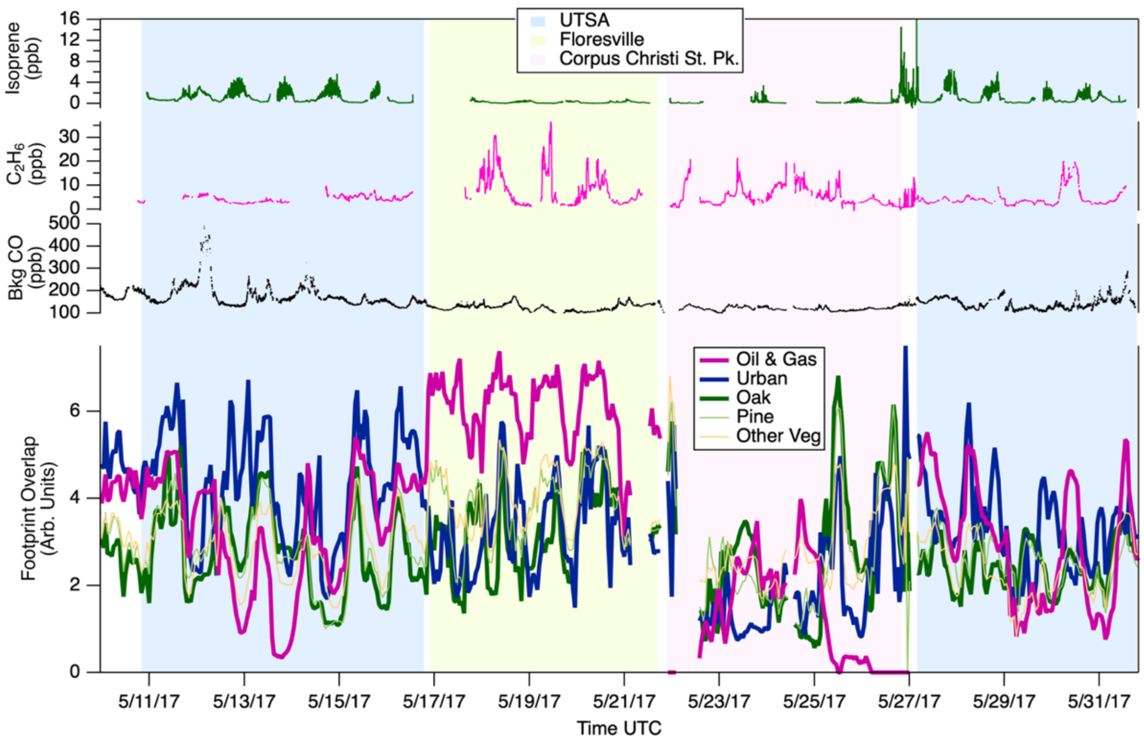
Where does the measured airmass originate?



- Previously:
  - Wind direction analysis
- Now:
  - Full Hysplit trajectory analysis
  - Land cover broadly categorized

Ecological and oil and gas mapping information is shown gridded onto a 0.025 x 0.025 decimal degree grid. The city bounds of San Antonio (center left) are outlined in black.

Where does the measured airmass originate?



Hysplit footprint overlap with 5 different land cover types. Measured isoprene, ethane and background carbon monoxide time traces are also shown. Shaded areas represent time spent at UTSA (blue), Floresville (green) and Corpus Christi State Park (pink).

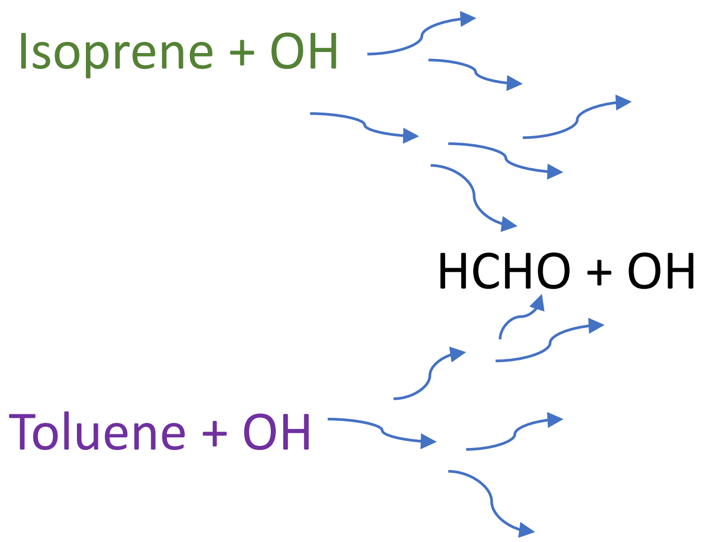
Do Intermediates Matter?

Problem

- Hard to find unique intermediate
- Many measured oxygenated intermediates can have multiple sources

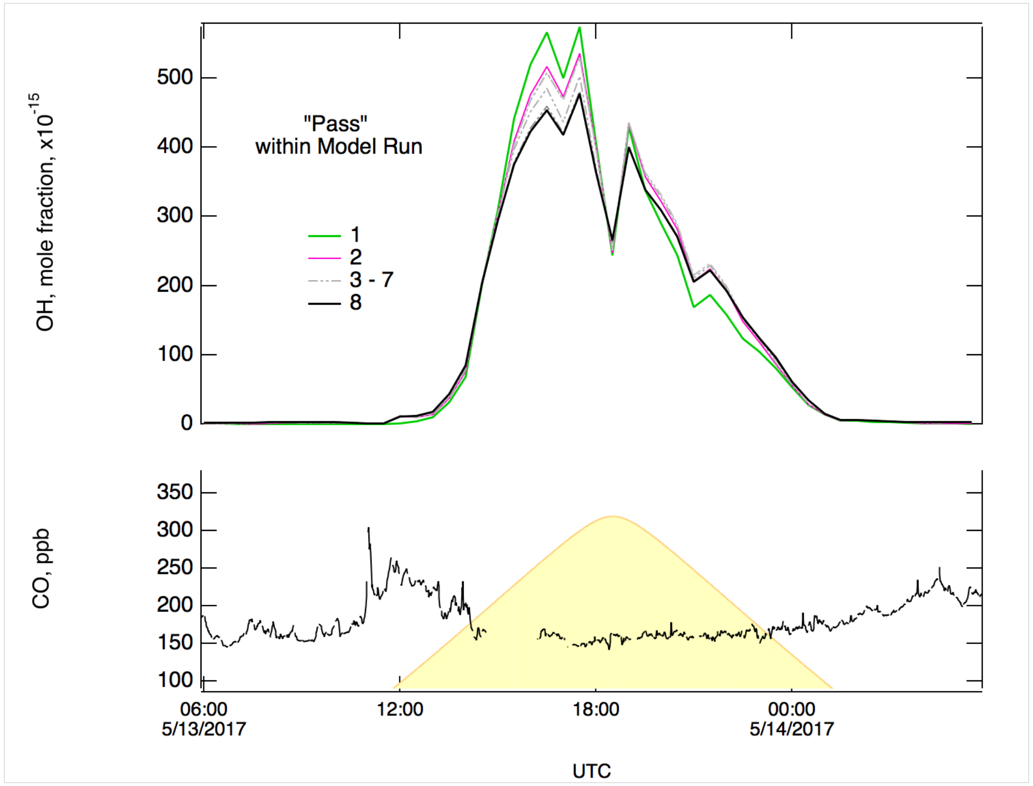
Solution

- Use a chemical model to keep score
- Model can allows us to follow each individual branching point

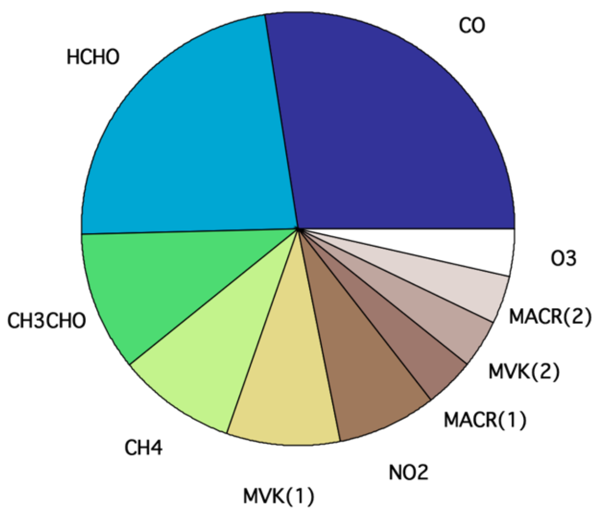


Significant Effort Required to Configure Model

- Igor Pro
- Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) [Emmerson and Evans, 2009]
- Master Chemical Mechanism (MCM) version 3.3



Apportioning OH reactivity

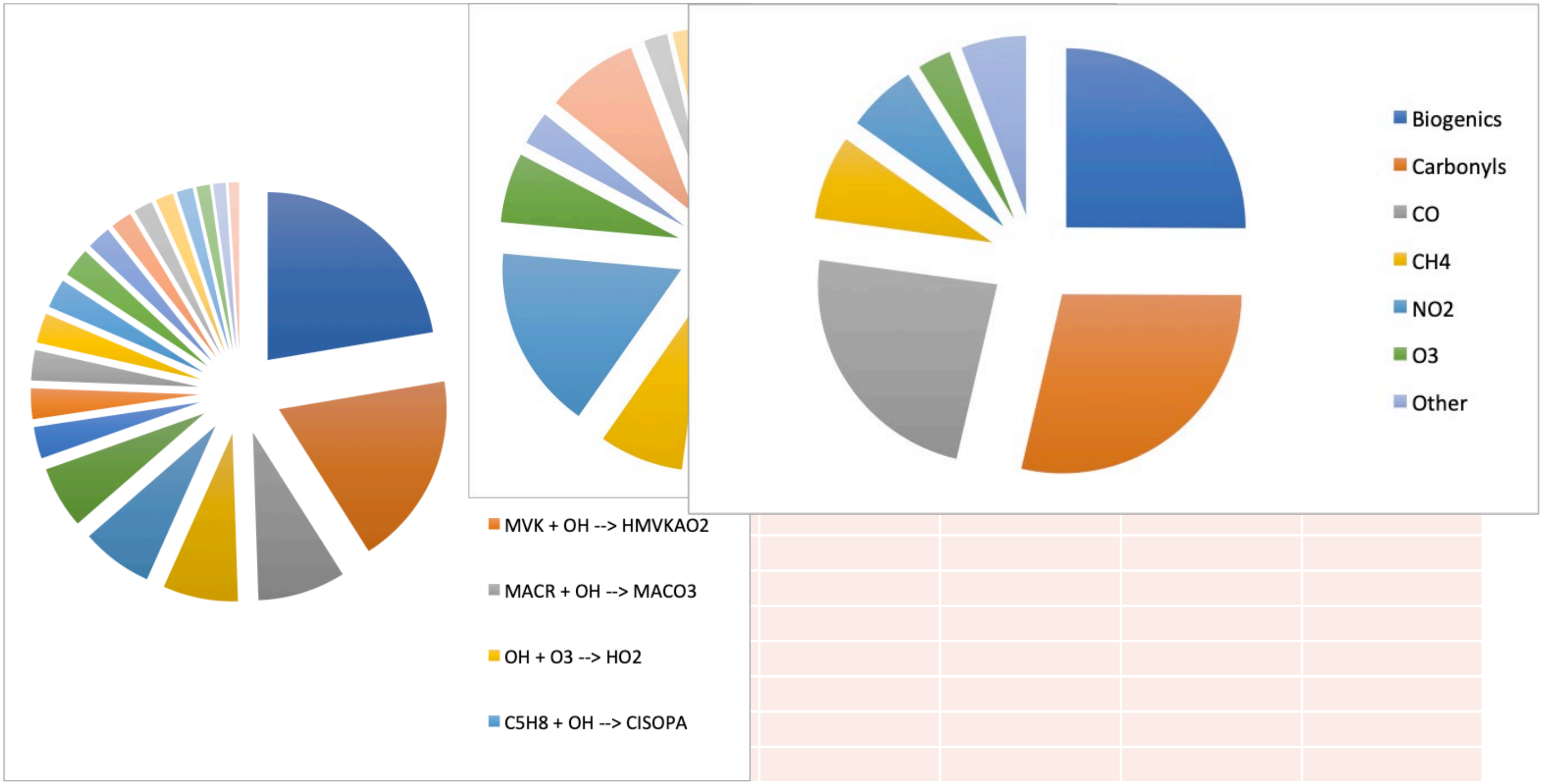


Initial Igor/DSMACC model result
Photostationary local noon on 5/13

- The intermediates are critical
- Dominant primary contributor is isoprene in San Antonio 5/12-5/14 2017
- Some species have both direct and indirect sources (e.g. HCHO)
- Model running now to account for HCHO from isoprene vs aromatics

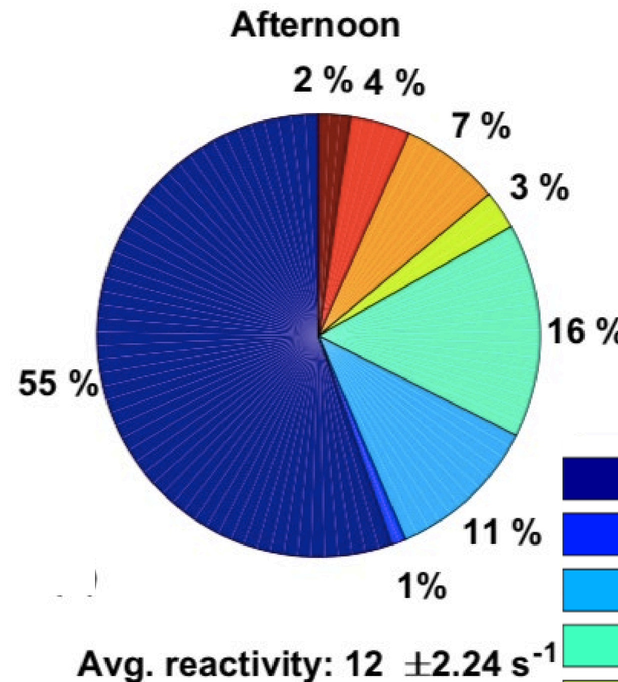
[MACR+MVK] - Modeled ~ ½ Measured

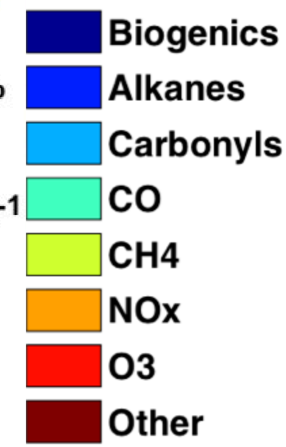
Model incorporates isoprene, small alkane and simple aromatics, but need more long chain alkanes are needed


MVK + OH --> HMVKAO2
MACR + OH --> MACO3
OH + O3 --> HO2
C5H8 + OH --> CISOPA
Biogenics
Carbonyls
CO
CH4
NO2
O3
Other

Prelim. Result
Igor/DSMACC

Anderson et al, ACP, 2019

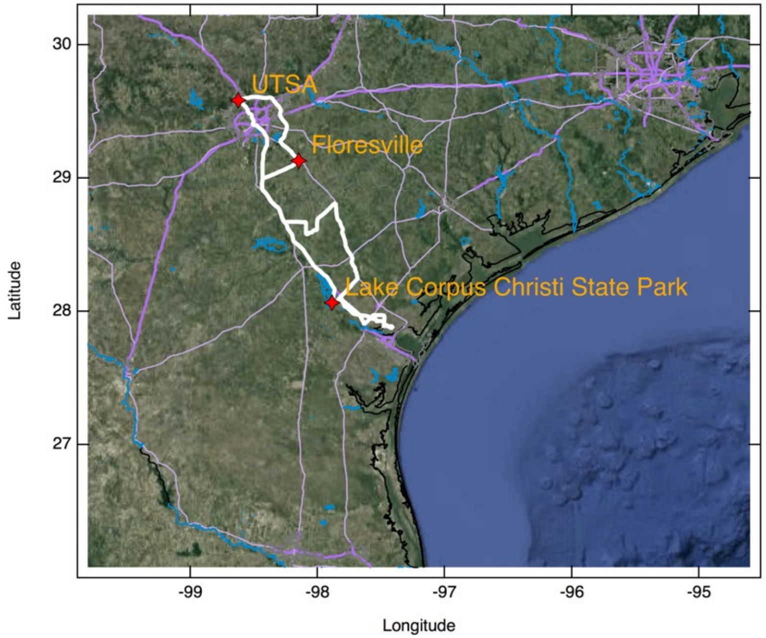




The distribution of the various contributors to the overall OH reactivity for the UTSA (13–16 May) […] is shown for […] the afternoon, for times between 13:00 and 20:00. The average OH reactivity (±1σ) is also shown.

Conclusions

- Composition of the atmosphere differs greatly between UTSA, Floresville
- Biogenic VOCs (e.g. isoprene from oak trees) contribute significantly to OH radical formation in the SAFS study area



Recommendations for Future Work: AQRP 19-025

Outstanding Questions

- More sophisticated model runs
  - Carbonyl sensitivity analysis, e.g.
- Biogenic precursors in SAFS area
  - Emissions inventories & spatial distributions
- Analysis of ozone mitigation strategies

Measurement Successes and Lessons-Learned

- Campaign Design:
  - 3 different locations
  - CAMS co-location
- Early strategies to manage volume of data/analysis produced by HR instruments
- Minimize gaps in measurements