Deciphering the origins and transformations of atmospheric organics: CalNex2010 Bakersfield

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CalNex Pasadena Science Team

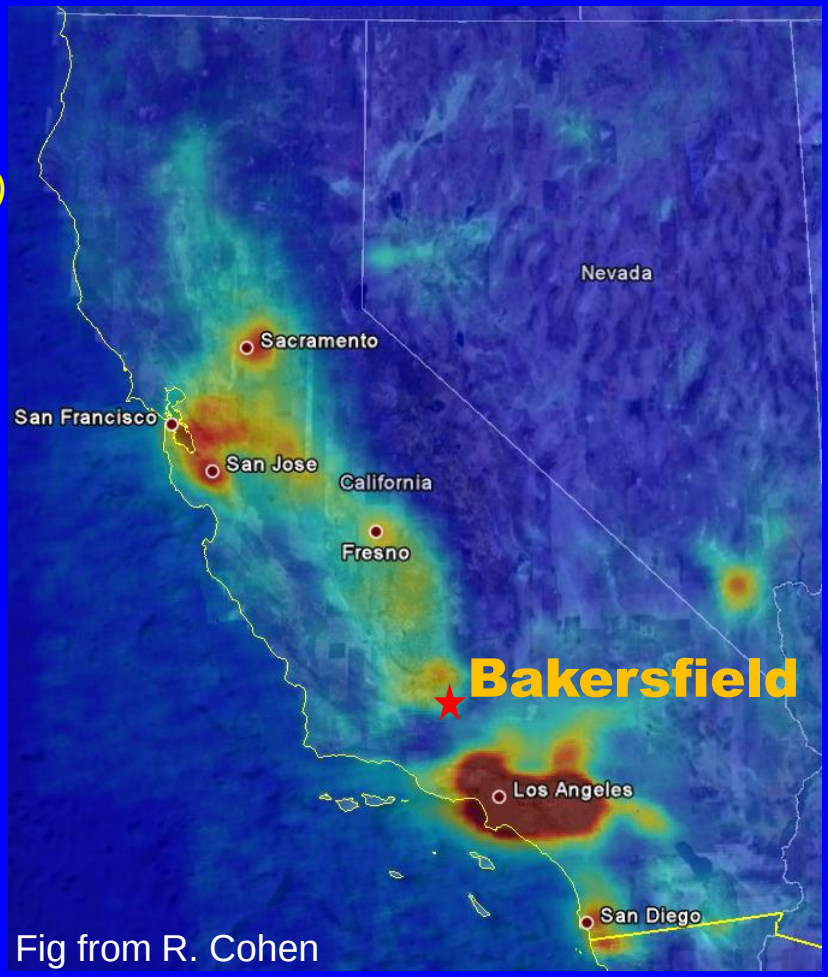

Fig from R. Cohen

SPECIAL THANKS TO:
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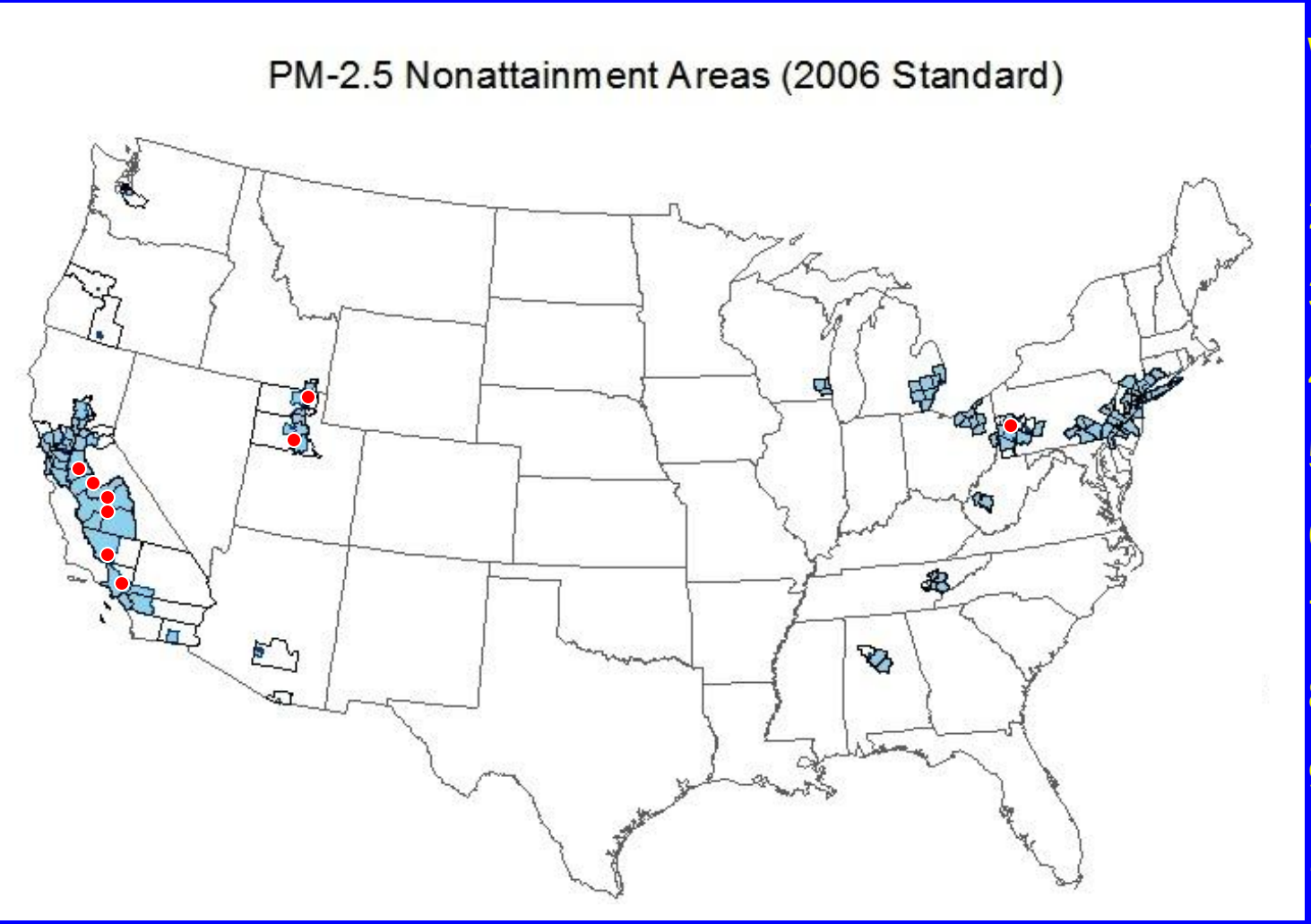
R. Cohen, S. Pusede UC Berkeley (PI and site organization)

California Environmental Protection Agency AIR RESOURCES BOARD

Funding: Contracts #08-316 and #09-316

PM2.5 Nonattainment Areas in U.S.

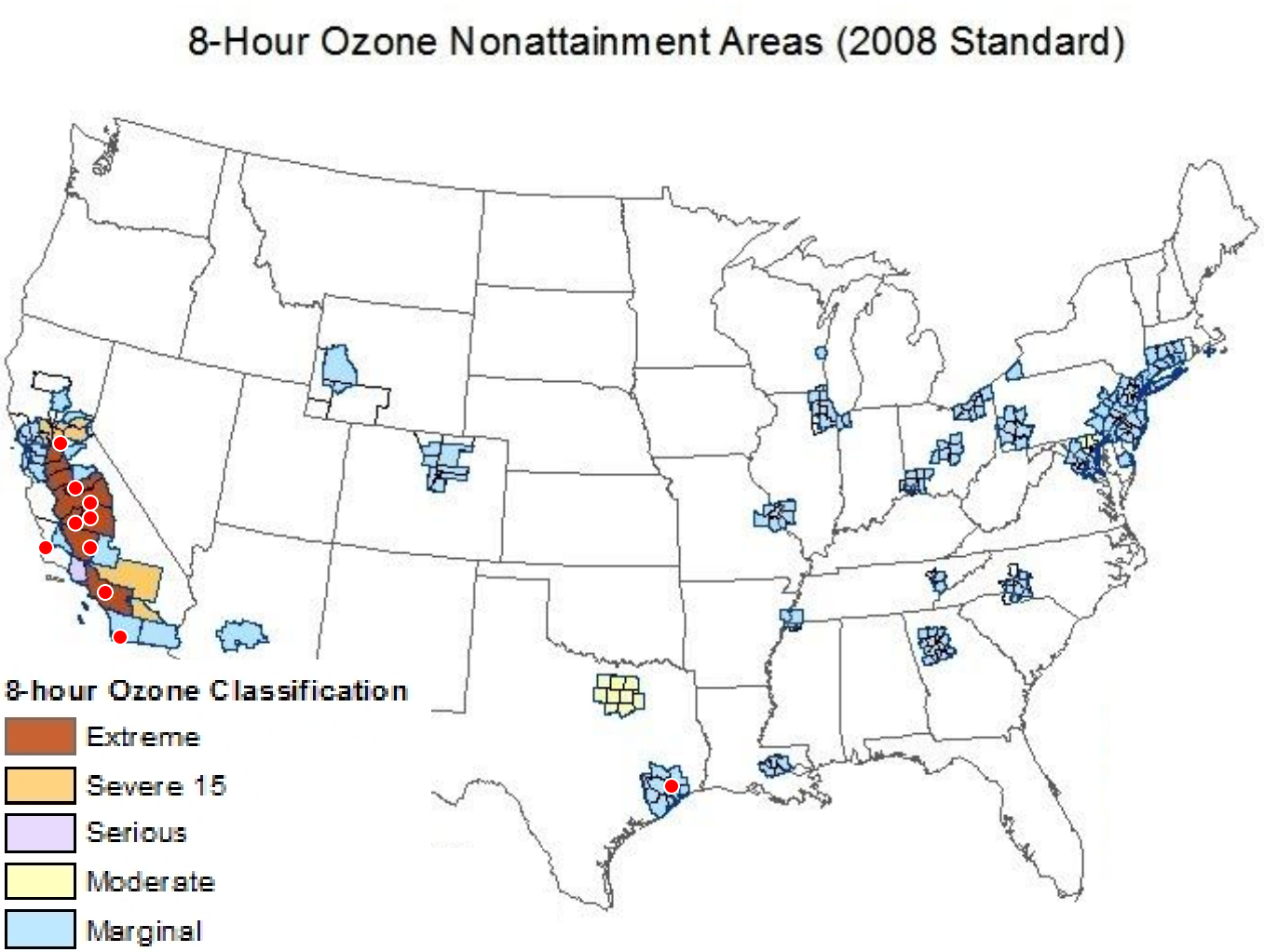


Worst Cities ($PM_{2.5}$)

1) Bakersfield, CA
2) Fresno, CA
3) Hanford, CA
4) Los Angeles, CA
5) Modesto, CA
6) Pittsburgh, PA
7) Salt Lake City, UT
8) Logan, UT
9) Fairbanks, AK
10) Merced, CA

U.S. EPA & American Lung Assoc. (2012)

Ozone Nonattainment Areas in U.S.

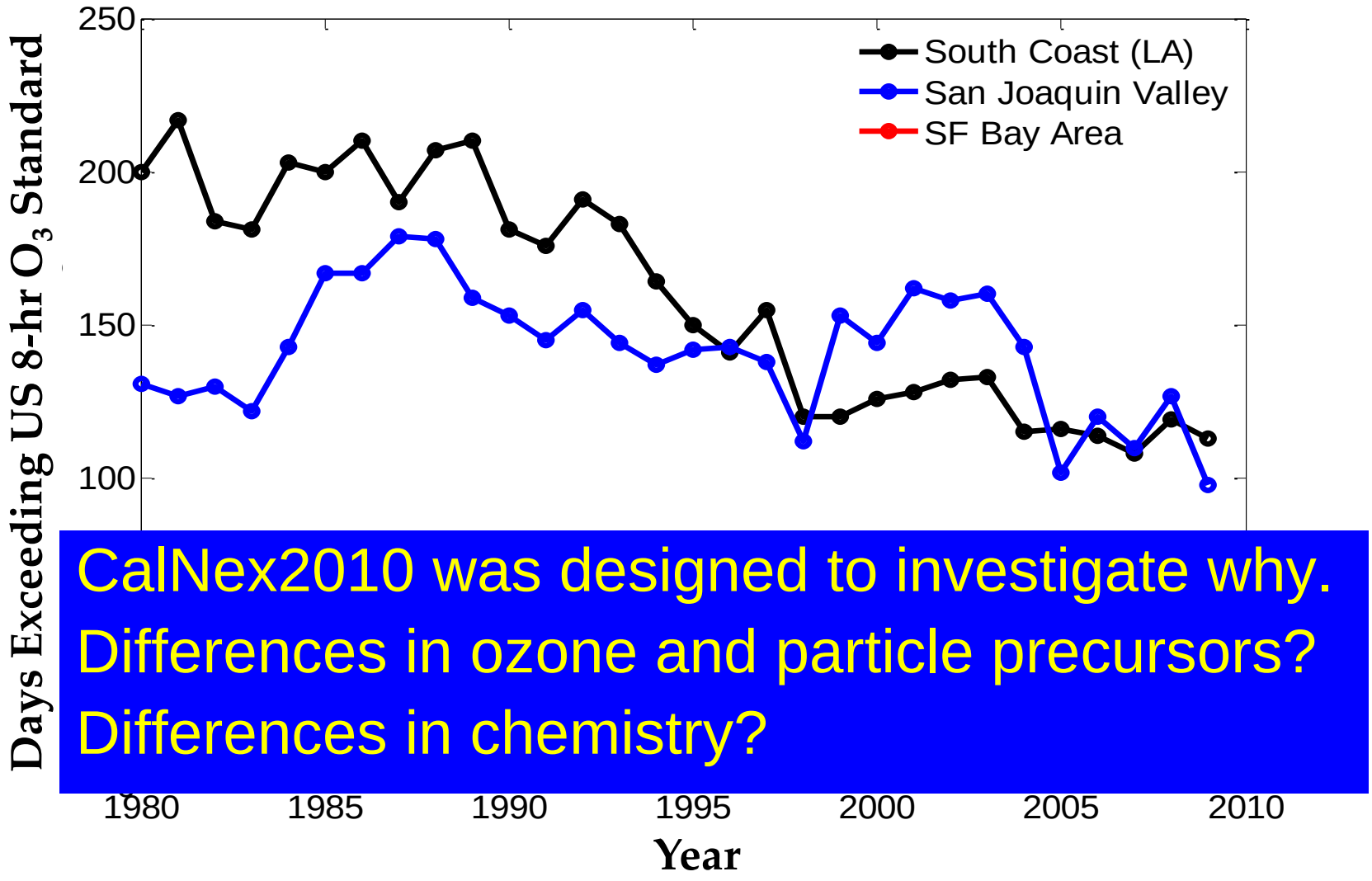


Worst Cities (O_3)

1) Los Angeles, CA
2) Visalia, CA
3) Bakersfield, CA
4) Fresno, CA
5) Hanford, CA
6) Sacramento, CA
7) San Diego, CA
8) Houston, TX
9) San Luis Obispo, CA
10) Merced, CA

U.S. EPA & American Lung Assoc. (2012)

Air Quality Control Has Been More Effective in LA than San Joaquin Valley



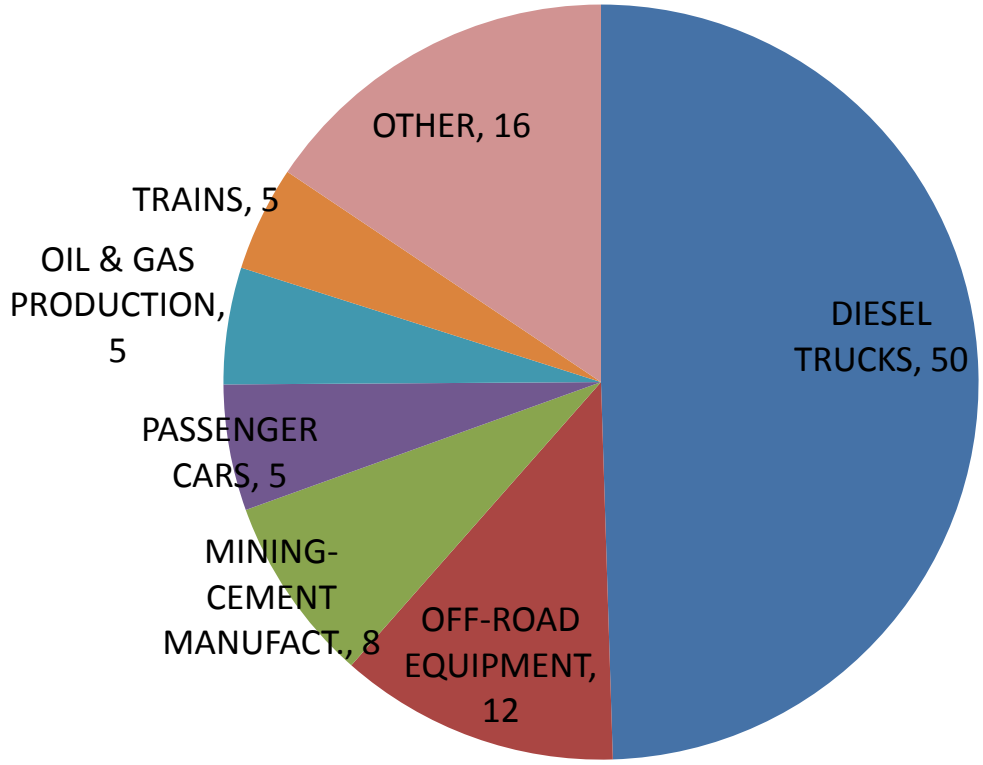
CalNex2010 was designed to investigate why.
Differences in ozone and particle precursors?
Differences in chemistry?

Data from www.arb.ca.gov

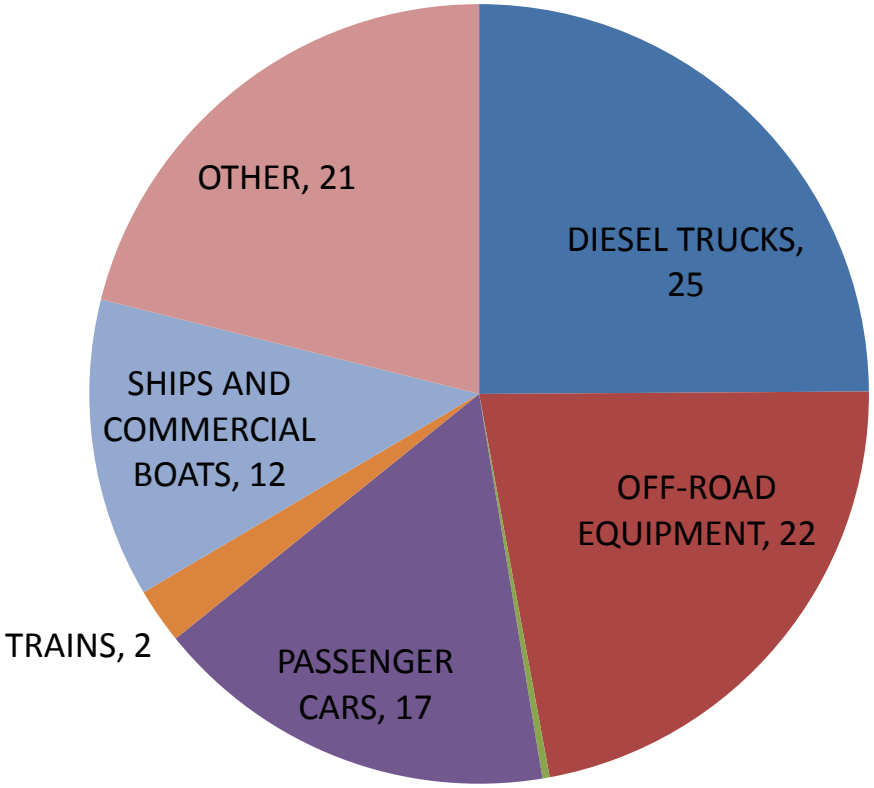
NO_x 2010 CARB Emission Inventory Anthropogenic Emission Projections (%)

(Bakersfield is in Kern County)

Kern County



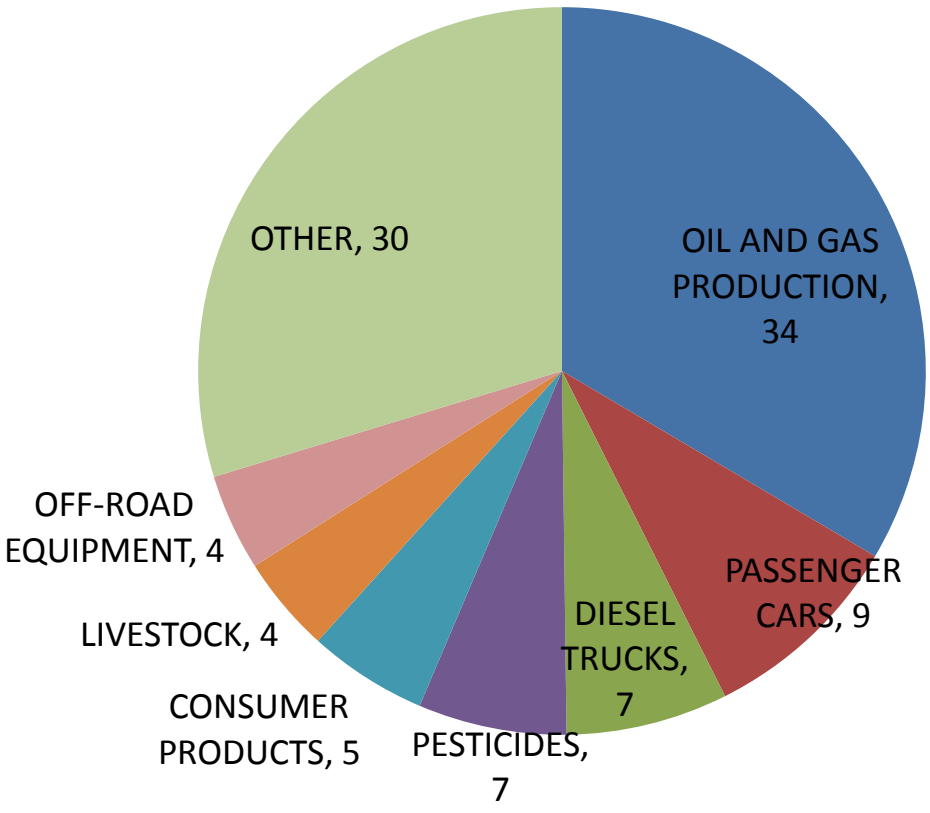
Los Angeles County



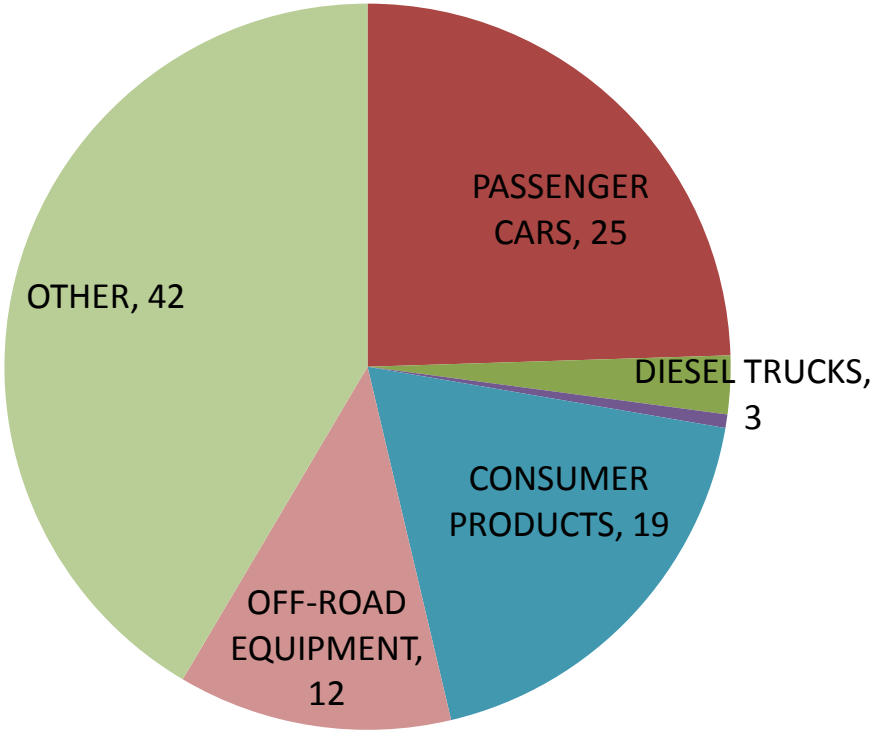
Data from www.arb.ca.gov

Reactive Organic Gas (ROG)
2010 CARB Emission Inventory
Anthropogenic Emission Projections (%)
EXTREMELY DIFFERENT

Kern County



Los Angeles County



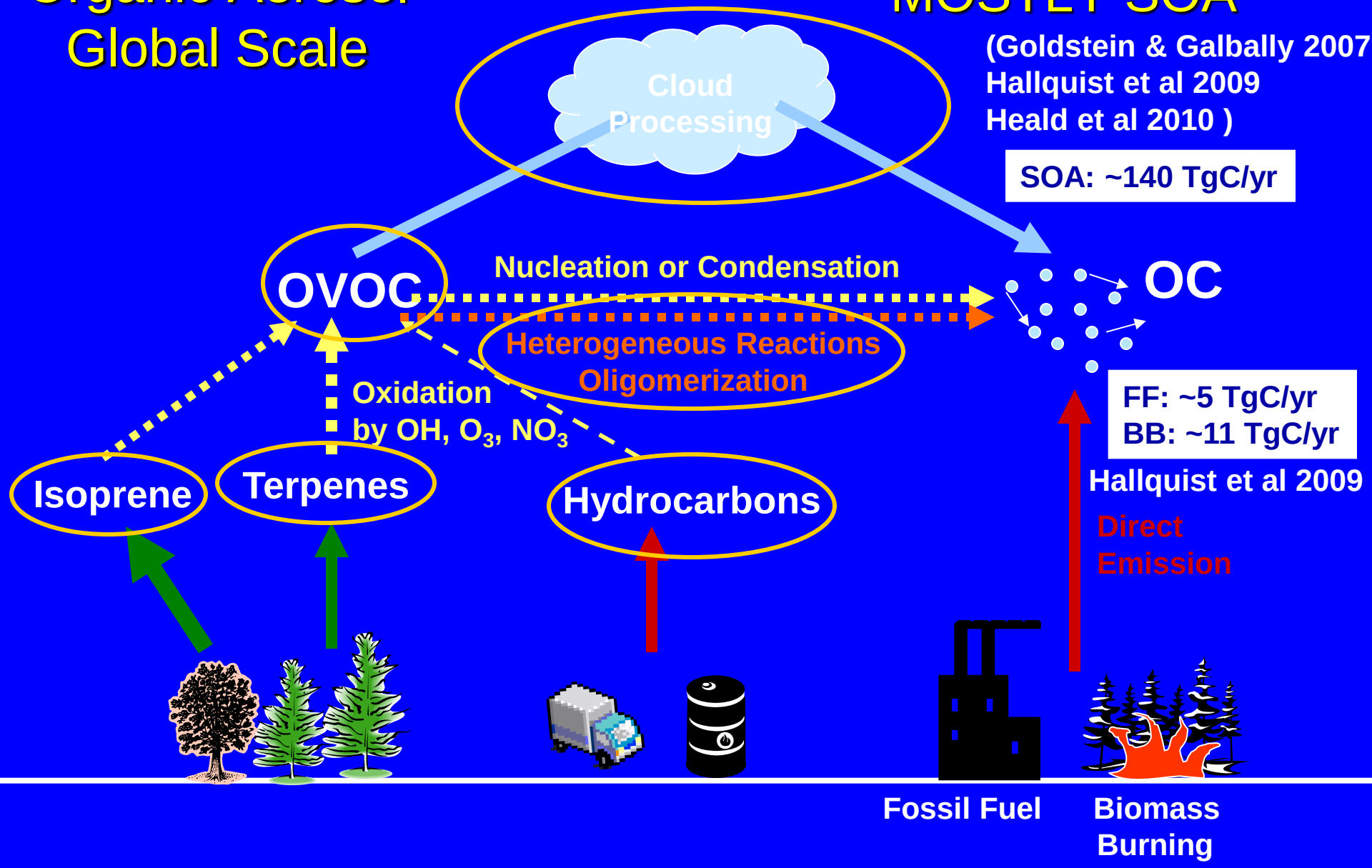
Data from www.arb.ca.gov

Organic Aerosol Global Scale

MOSTLY SOA

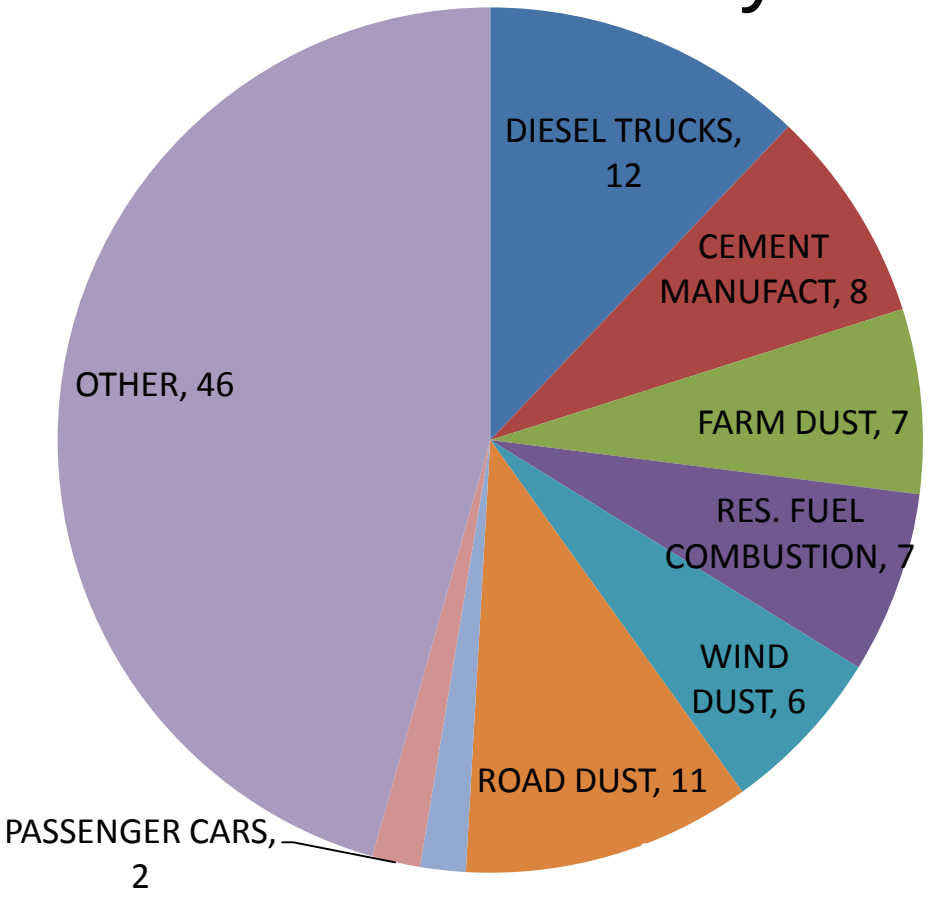
(Goldstein & Galbally 2007
Hallquist et al 2009
Heald et al 2010)

SOA: ~140 TgC/yr

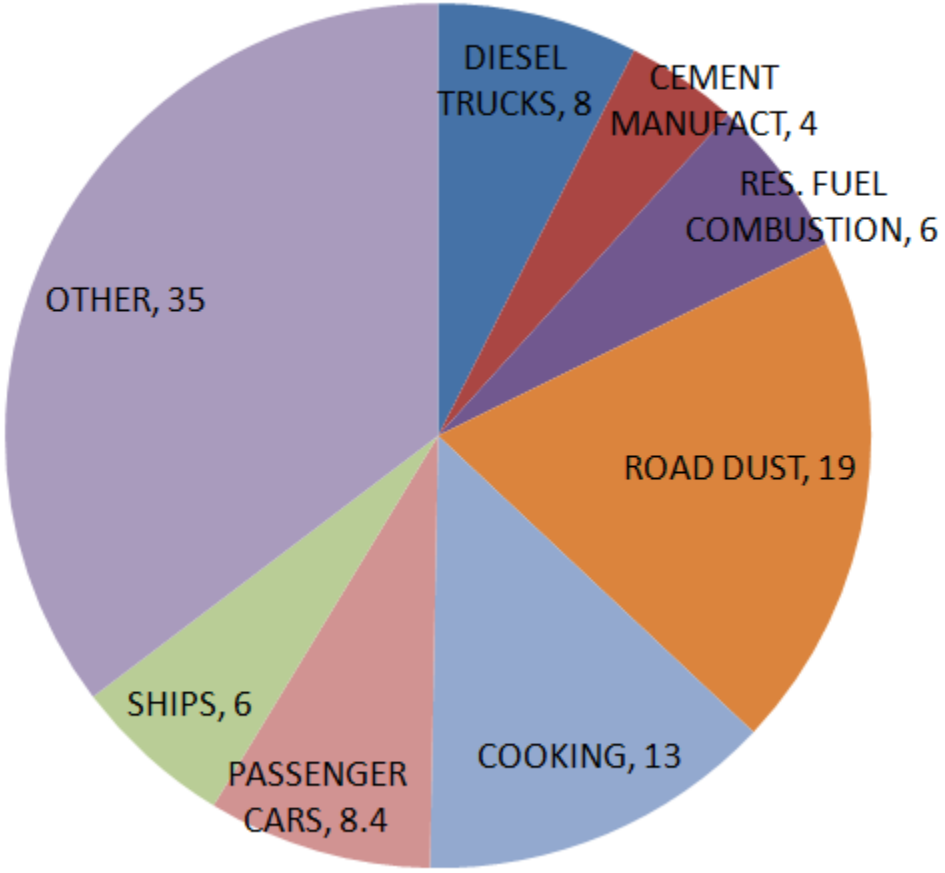


Primary PM2.5
2010 CARB Emission Inventory
Anthropogenic Emission Projections (%)

Kern County



Los Angeles County



Data from www.arb.ca.gov

Primary versus Secondary PM

SOAR 2005 Aerosol in Riverside:
Organic is dominant component of submicron aerosol.
Organic aerosol is ~70% secondary in summer.
(Williams et al., 2010 ACP; Docherty et al, 2008 ES&T)

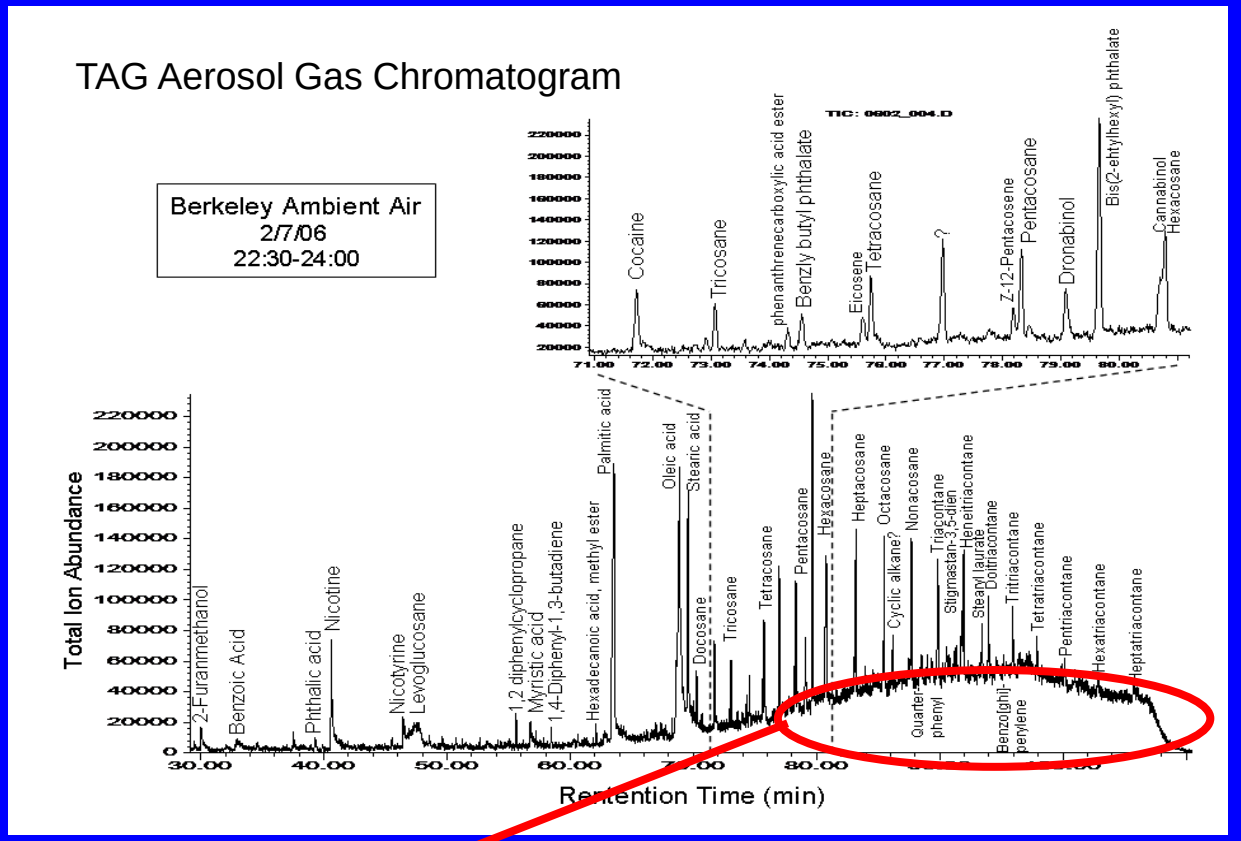
Questions for CalNex 2010 Bakersfield and LA:
Primary versus secondary PM?
Sources of Primary and Secondary Precursors?

Current Major Issues & Questions

- Why are models under-predicting organic aerosol (missing precursors or formation pathways)?
  [Hodzic et al. ACP (2010), de Gouw et al. JGR (2008), Dzepina et al. (2011)]
- Importance of diesel vs. gasoline vehicles in urban areas (hotly debated issue)?
  [Bahreini et al. GRL (2012), Robinson et al. Science (2007), Weitkamp et al. ES&T (2008)]
- Importance of non-traditional SOA precursors that have not been measured (e.g. intermediate volatility organic compounds)?
  [Robinson et al. Science (2007), Kroll & Seinfeld Atmos. Env. (2008), Jimenez et al. Science (2009)]

Key Challenge: Atmospheric Organics

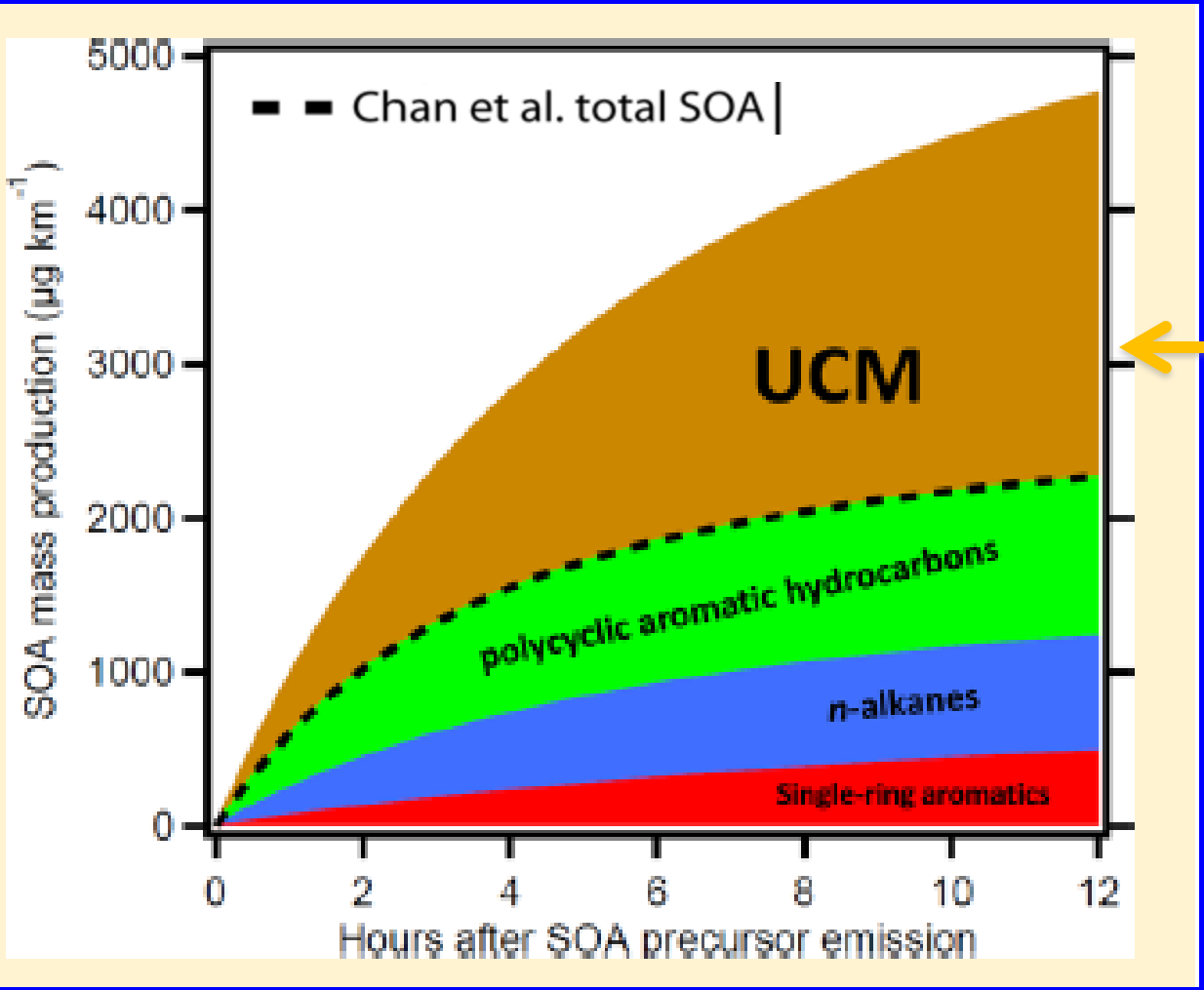
How do we <u>measure</u> and <u>model</u> (represent) emission, oxidation and fate of 1000's of individual compounds?



Williams et al 2006

"Unresolved Complex Mixture" (UCM)
50-80% of mass (e.g. Diesel)
Schauer et al 1999

SOA production from diesel exhaust



UCM characterization must be improved

Tkacik et al (Robinson group) 2012

Field Measurements of Organic Carbon

Urban (Bakersfield & LA) and on-road tunnel measurements

Gasoline and Diesel fuel samples (52 across CA)

In-Situ GCMS C1-C17 VOCs

In-Situ TAG speciated PM2.5 organics & I/SVOCs

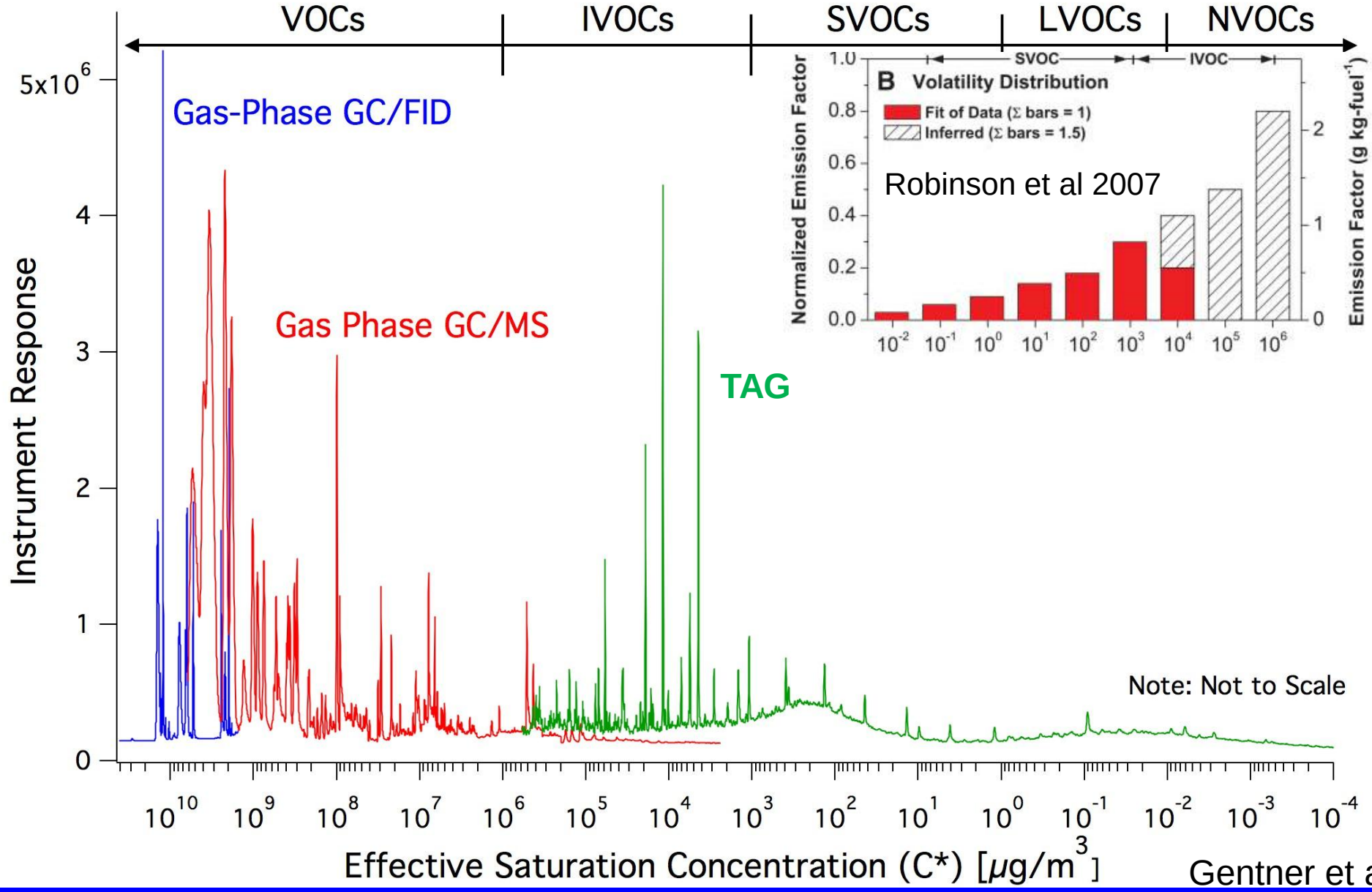
Offline Filter Analysis using novel techniques

(GCxGC-VUV-HRTOFMS)

Caldecott Tunnel, Oakland, CA

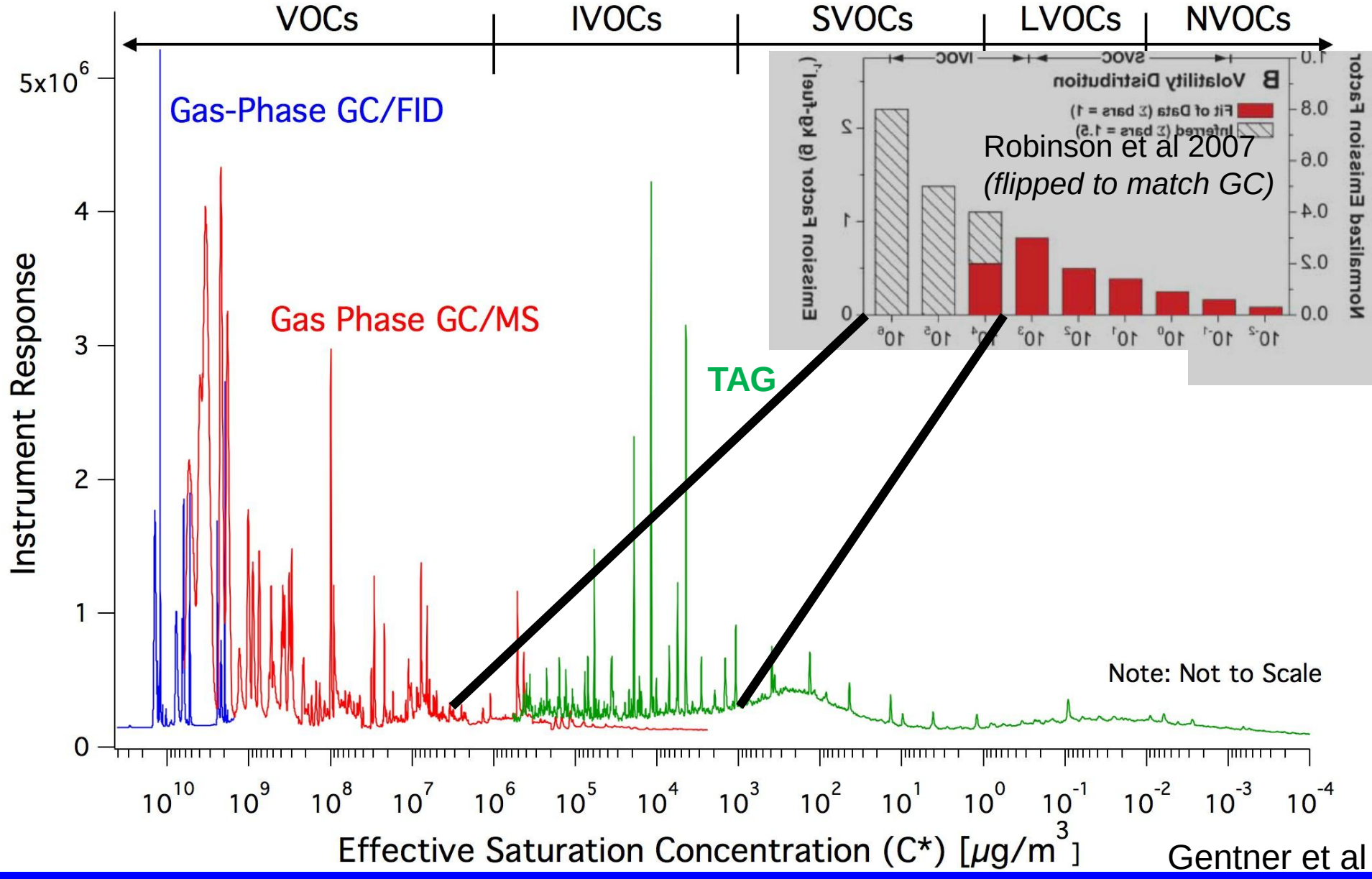
Bakersfield, CA

Speciated Organics Observed
Spans 15 orders of Magnitude in Volatility!



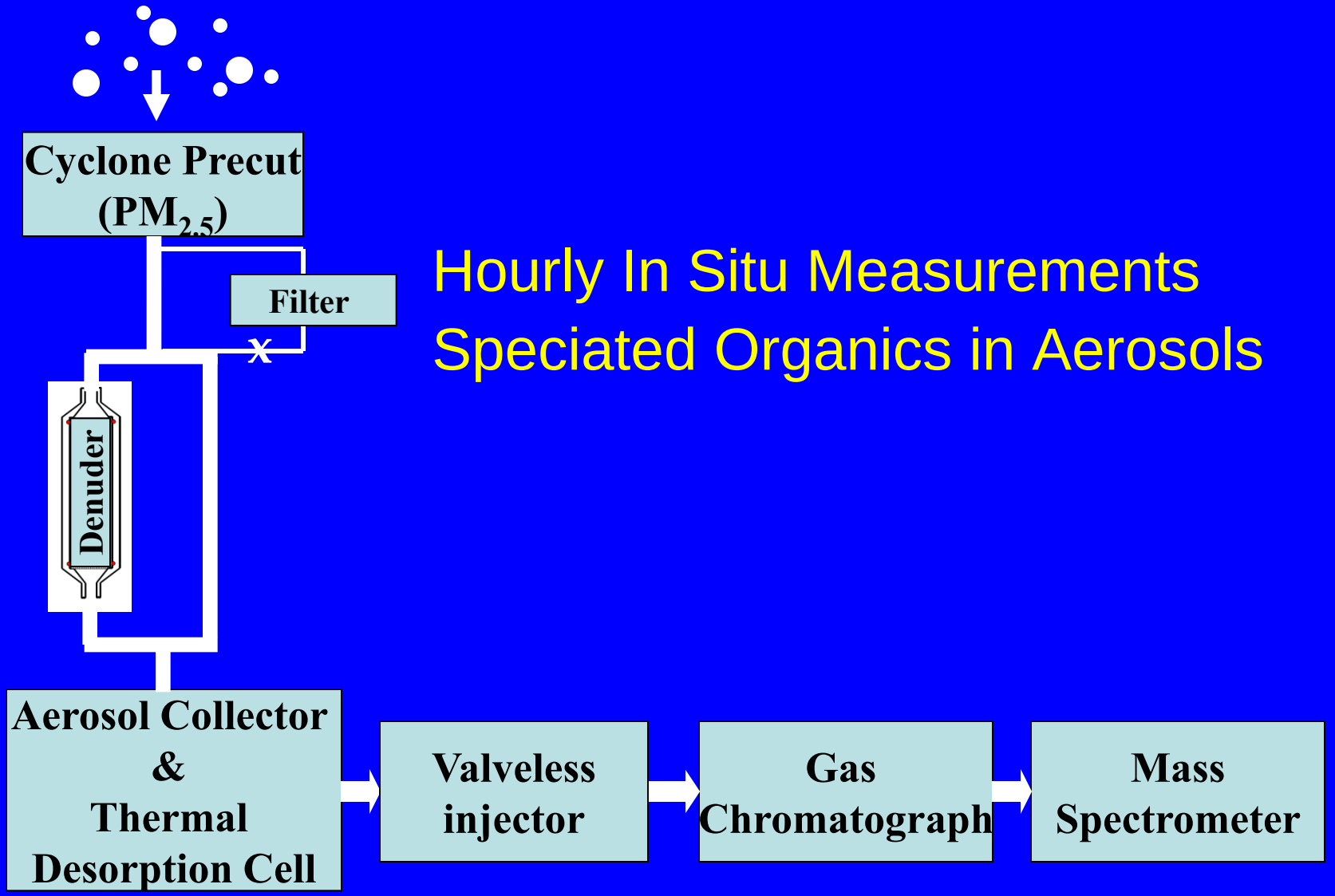
Gentner et al

Focus on quantifying “inferred” IVOCs/SVOCs



TAG

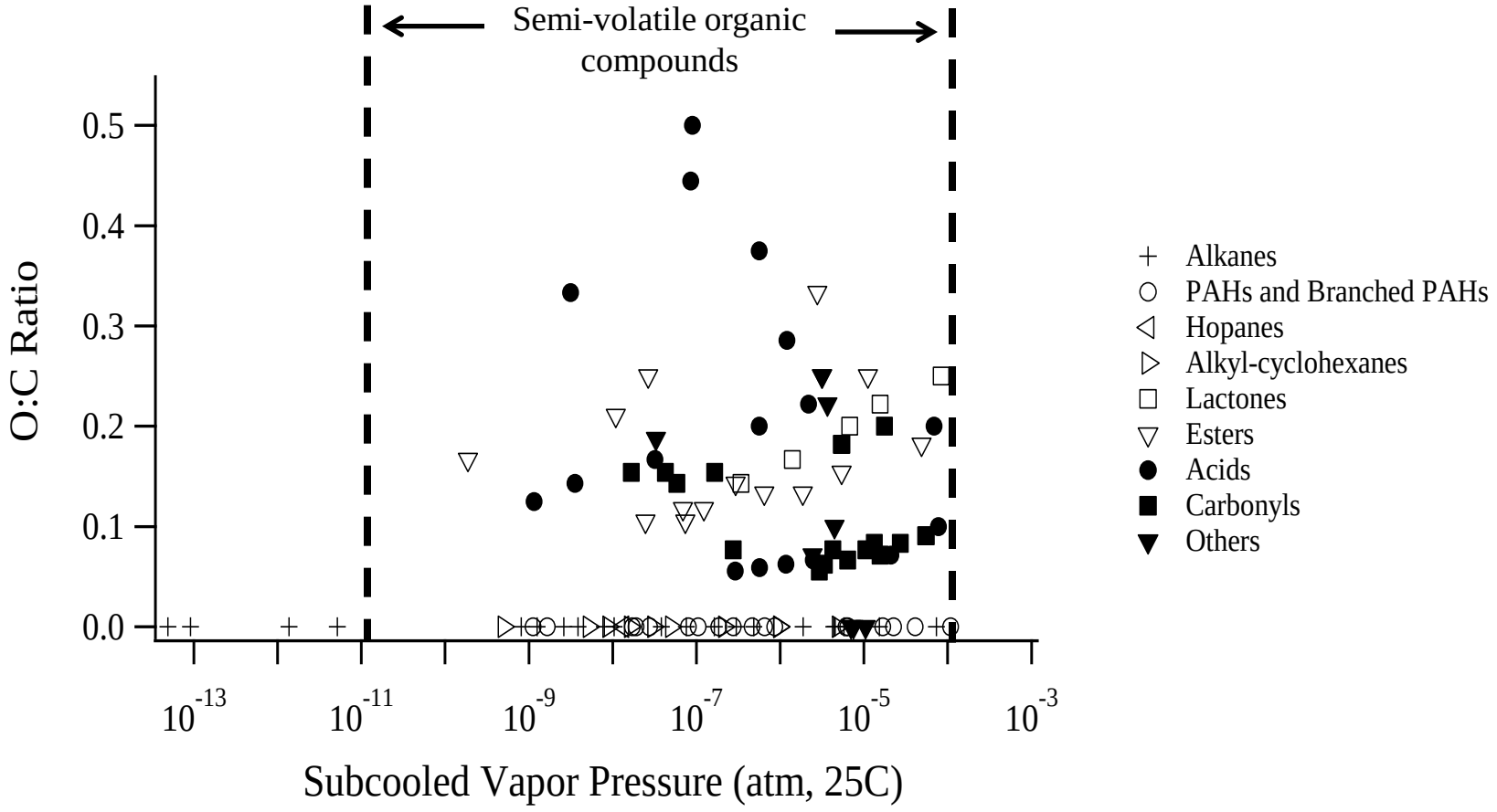
= Thermal desorption Aerosol Gas chromatograph



Hourly In Situ Measurements
Speciated Organics in Aerosols

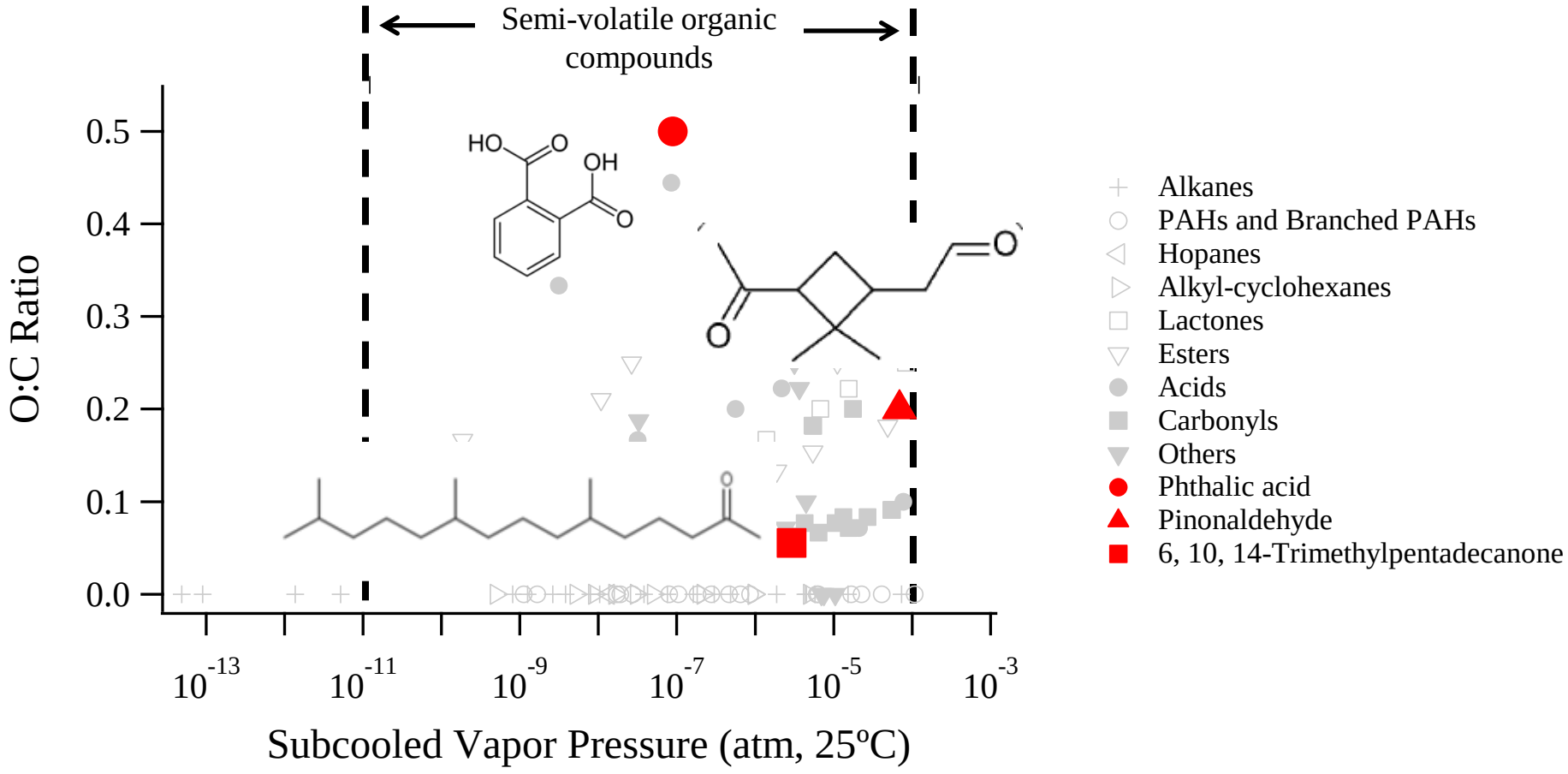
Williams et al AS&T 2006, Goldstein et al J Chrom A 2009, Zhao et al AS&T 2013

CalNex Bakersfield:160 compounds measured hourly by TAG



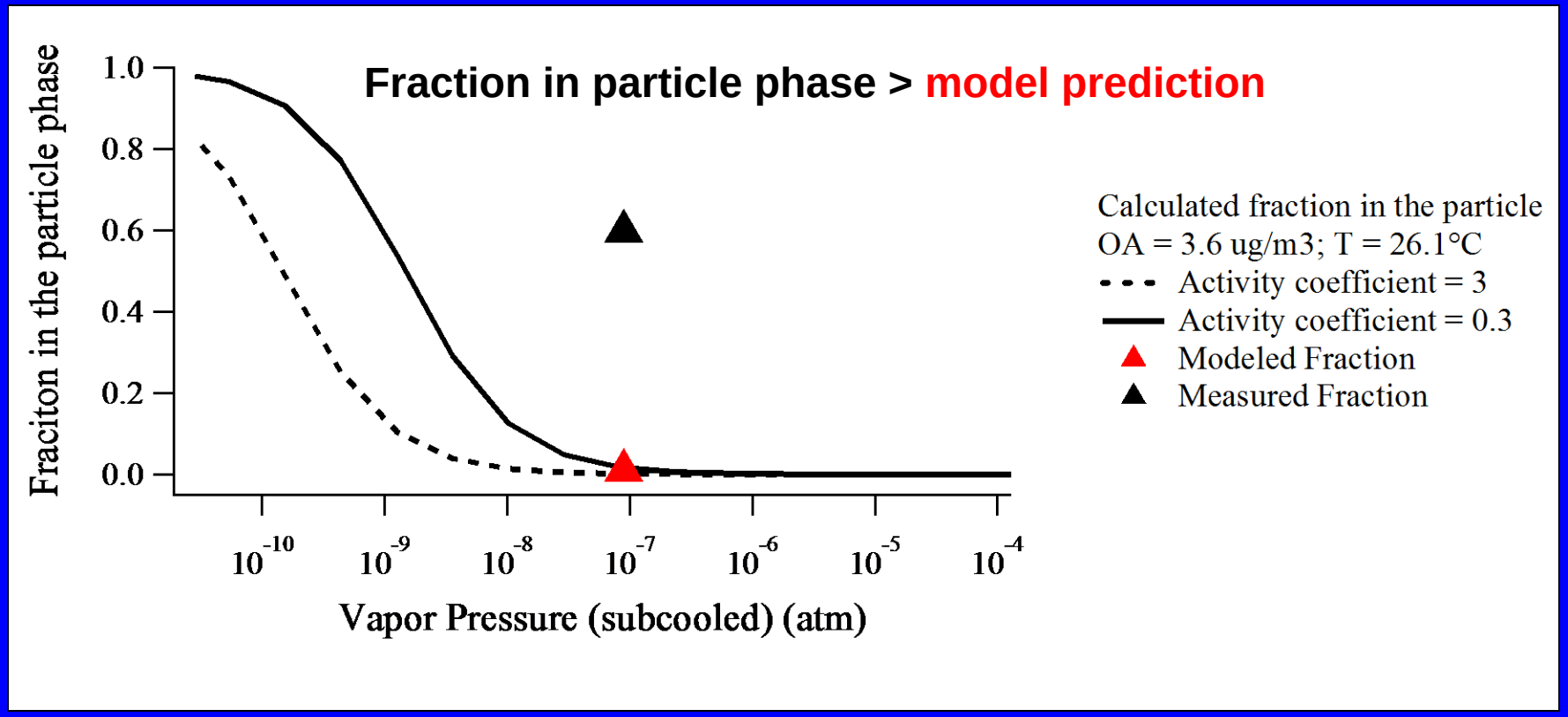
Zhao et al ES&T In Press

Examine Partitioning of Typical Compounds



Zhao et al ES&T In Press

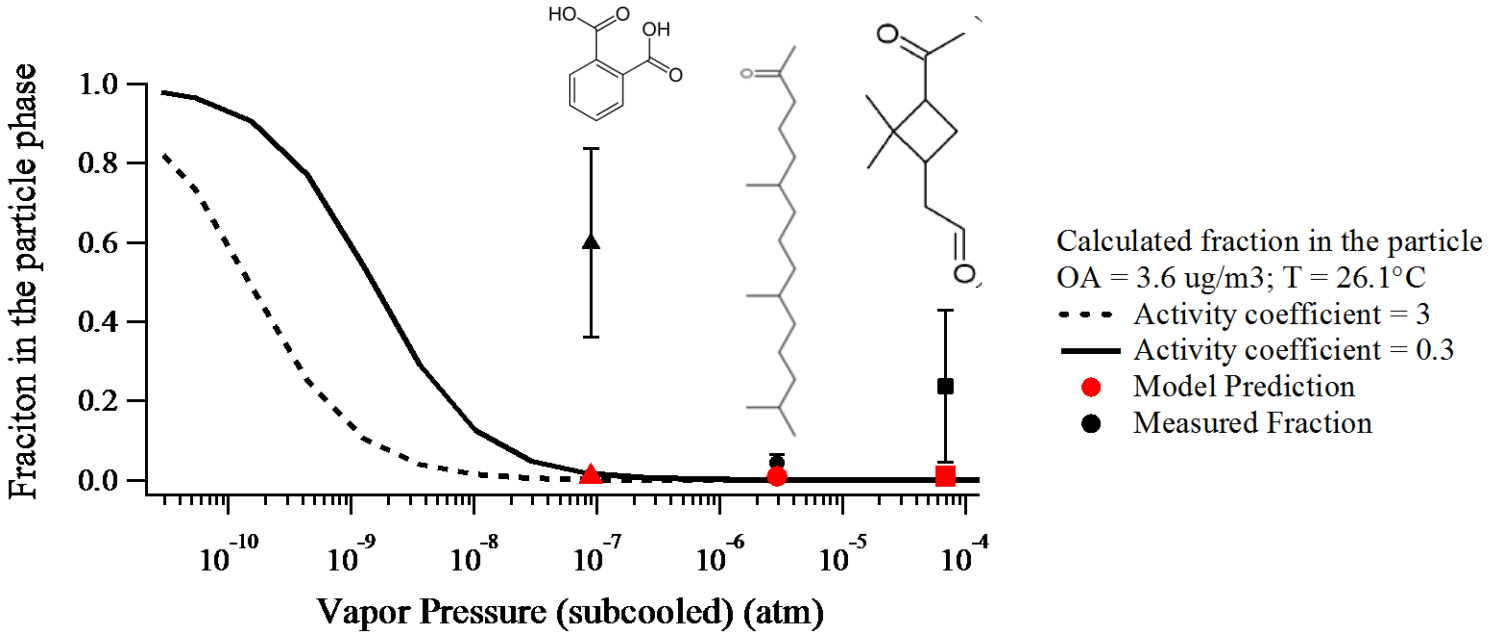
Are additional gas-to-particle partitioning pathways important beyond traditional partitioning theory?



Pankow, 1994; Jang et al., 2002; Tillmann et al., 2010

Zhao et al ES&T In Press

Evidence for additional formation pathways: Fraction in particle higher than model prediction



Phthalic acid

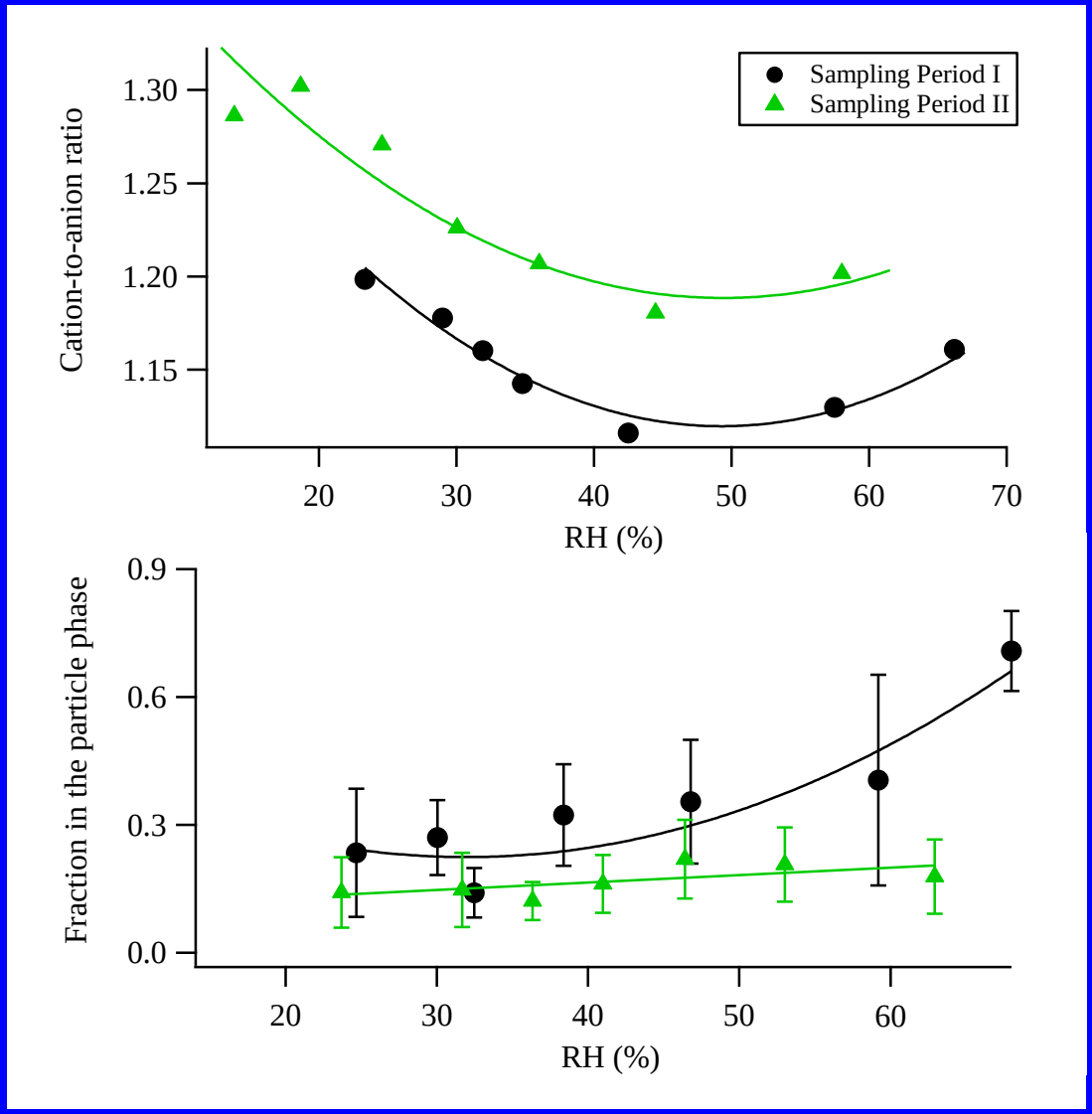
1) Organic acids can react with ammonia (Na et al., 2007)
2) Phthalic acid ammonium salts can be thermally desorbed back to phthalic acid and ammonia (Hajek et al.,1971)

Pinonaldehyde

1) Chamber studies have shown that dimers of pinonaldehyde can form in the presence of sulfuric acid (Liggio and Li, 2006)
2) Oligomerization increases with acidity (Liggio and Li, 2006)

Zhao et al ES&T In Press

What else does particle-phase pinonaldehyde depend on?

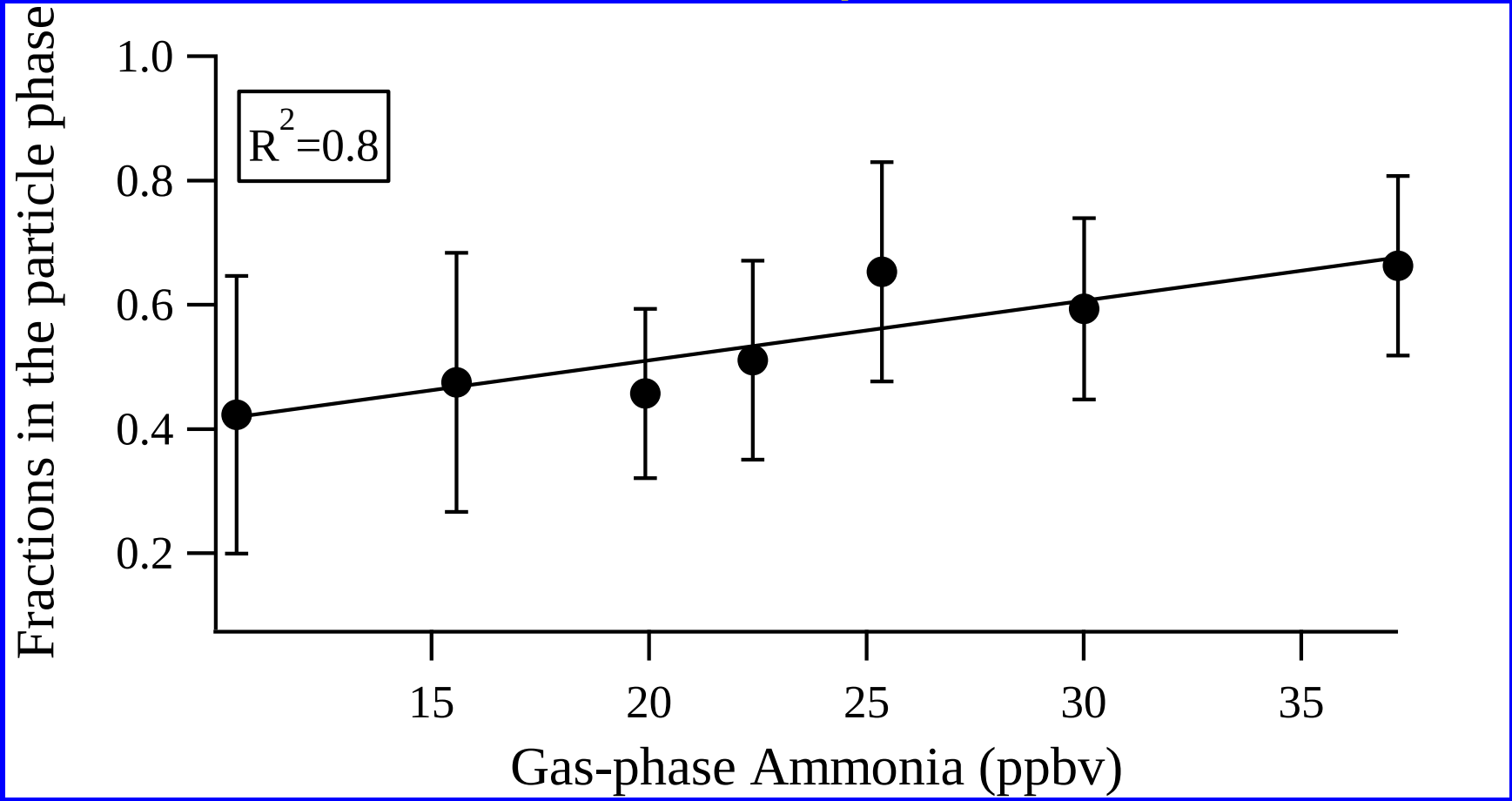


Acidity doesn't increase as RH increases

Fraction of Pinonaldehyde in particles increases as RH increases

Zhao et al ES&T In Press

Formation of particle-phase phthalic acid in the atmosphere



Phthalic acid ammonium salts thermally desorb to phthalic acid and ammonia *(Hajek et al.,1971)*
Some of the particle phase phthalic acid was actually an ammonium salt.

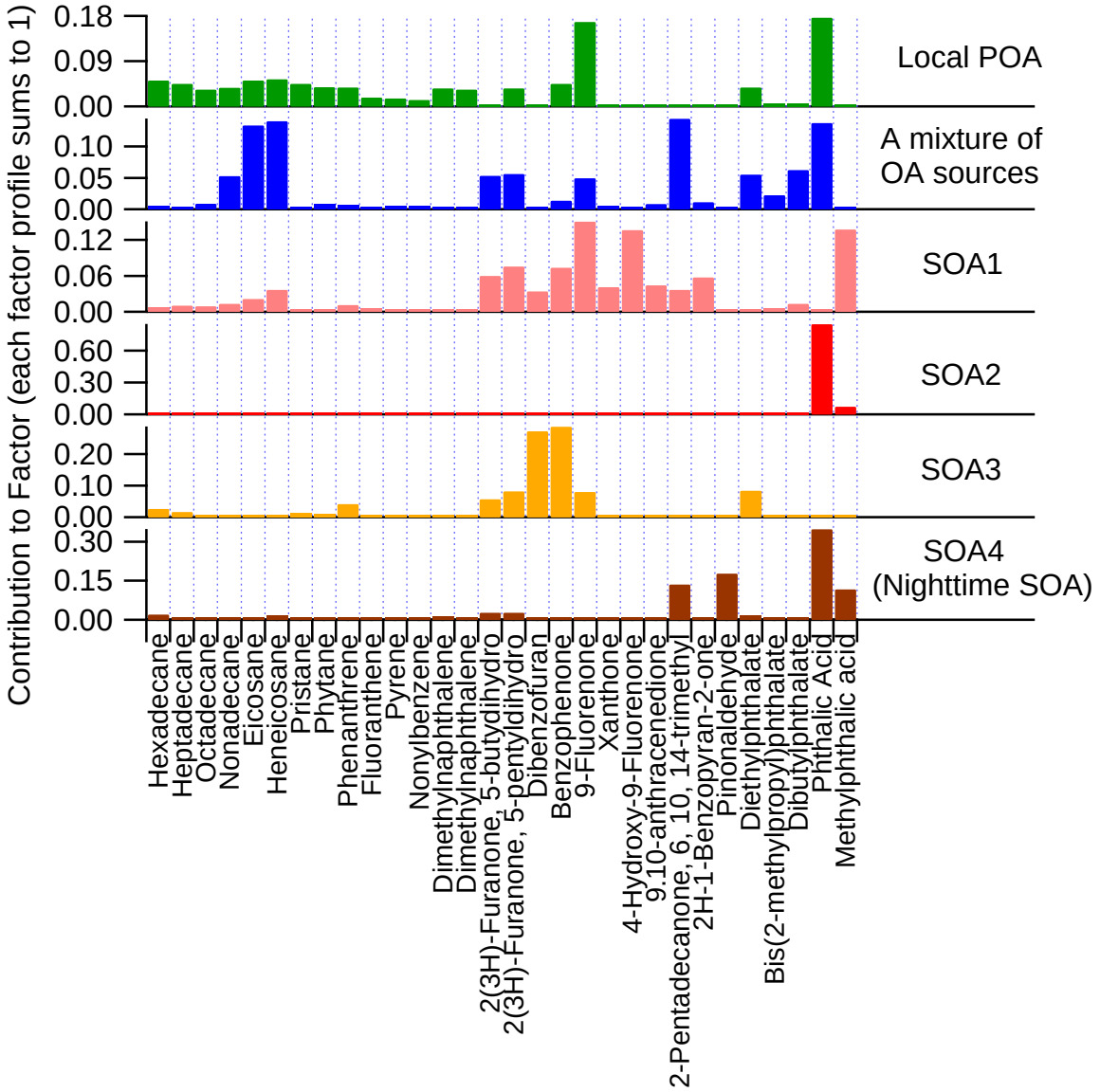
Particle phase uptake of phthalic acid enhanced by availability of ammonia in Bakersfield.
Zhao et al ES&T In Press

Partitioning
Take Home Messages

Additional pathways of gas-to-particle partitioning are important beyond absorptive partitioning in SJV:

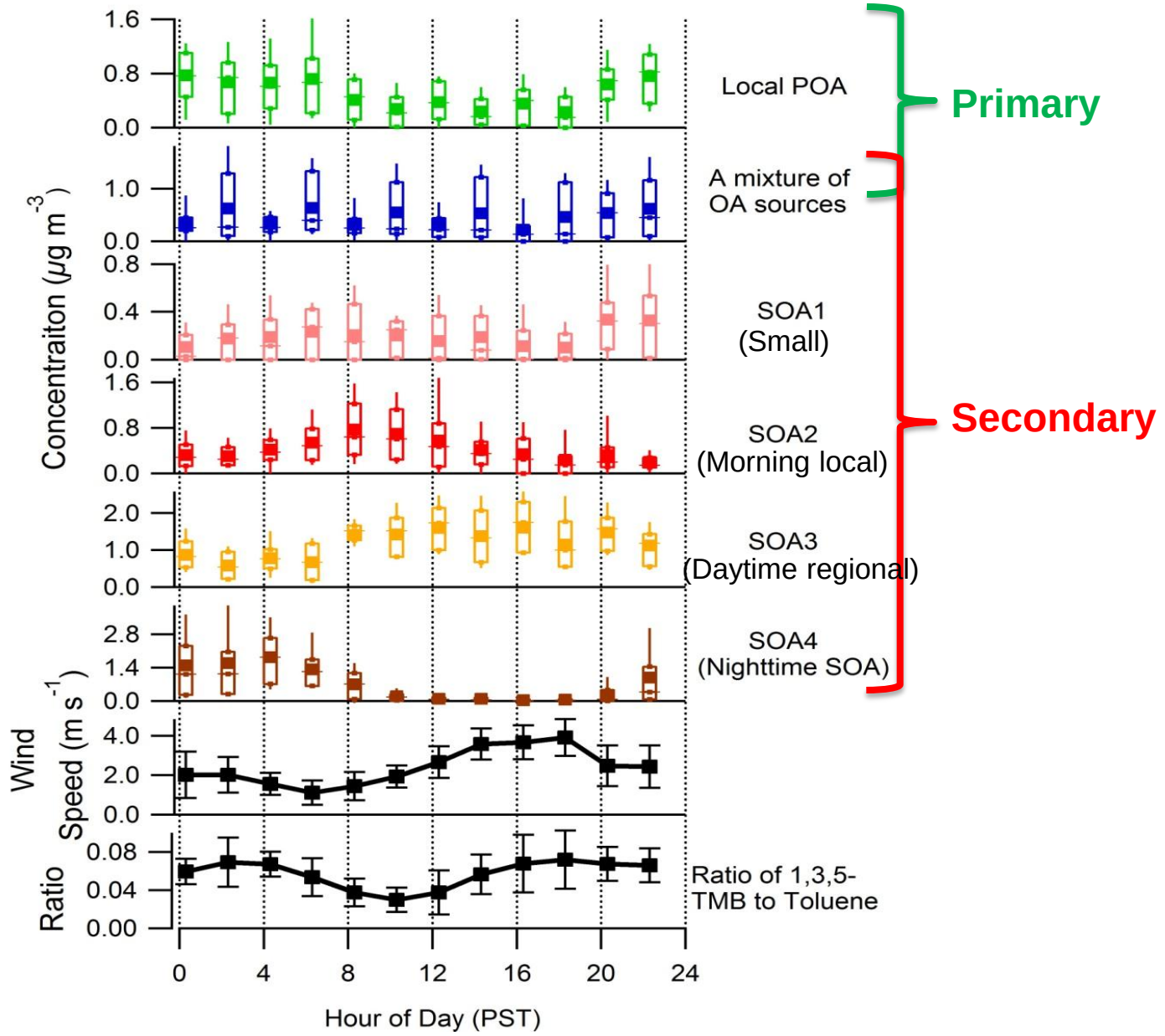
1) Reactions of phthalic acid with ammonia form SOA
2) Reactive uptake of pinonaldehyde into particles does not need the presence of inorganic acids.

Organic Aerosol (OA) PMF to Examine Sources
6 Contributing Factors Identified with TAG

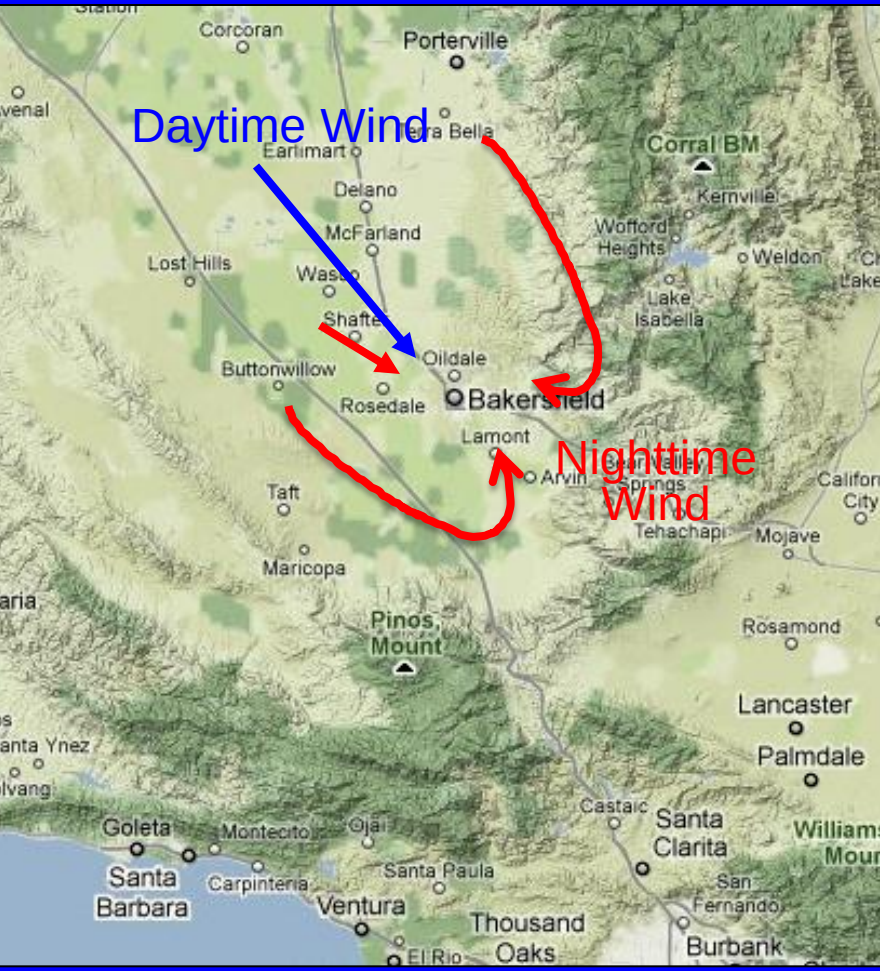


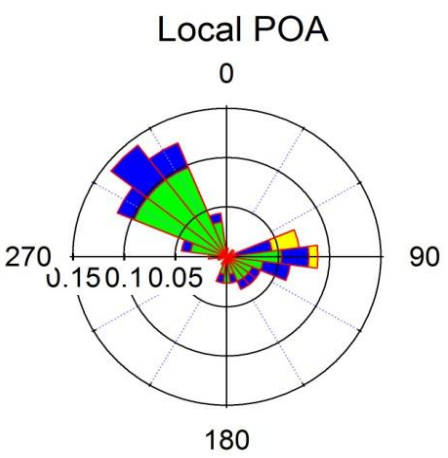
Zhao et al in review

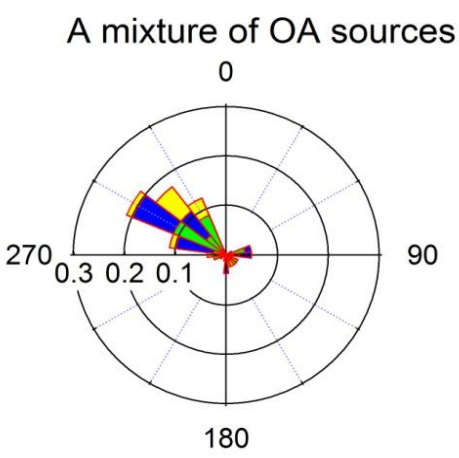
OA PMF factor Diurnal Cycles

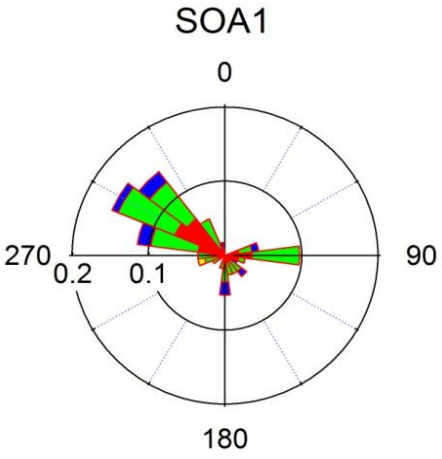


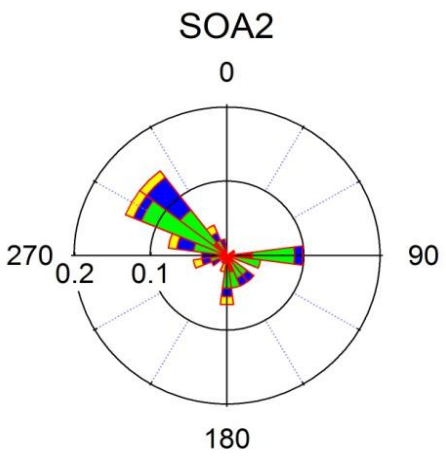
OA PMF Factor Wind Roses

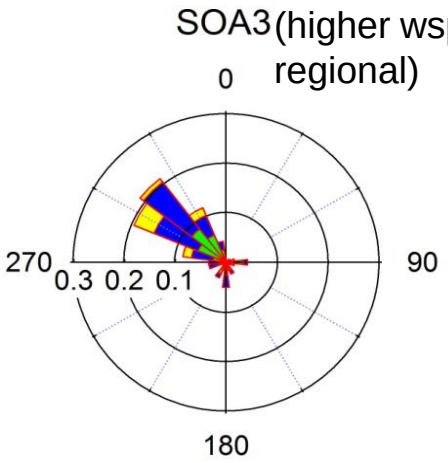


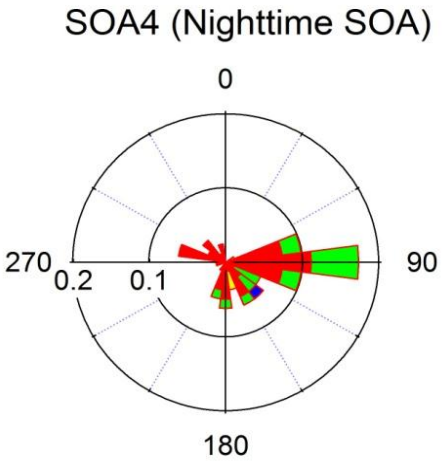




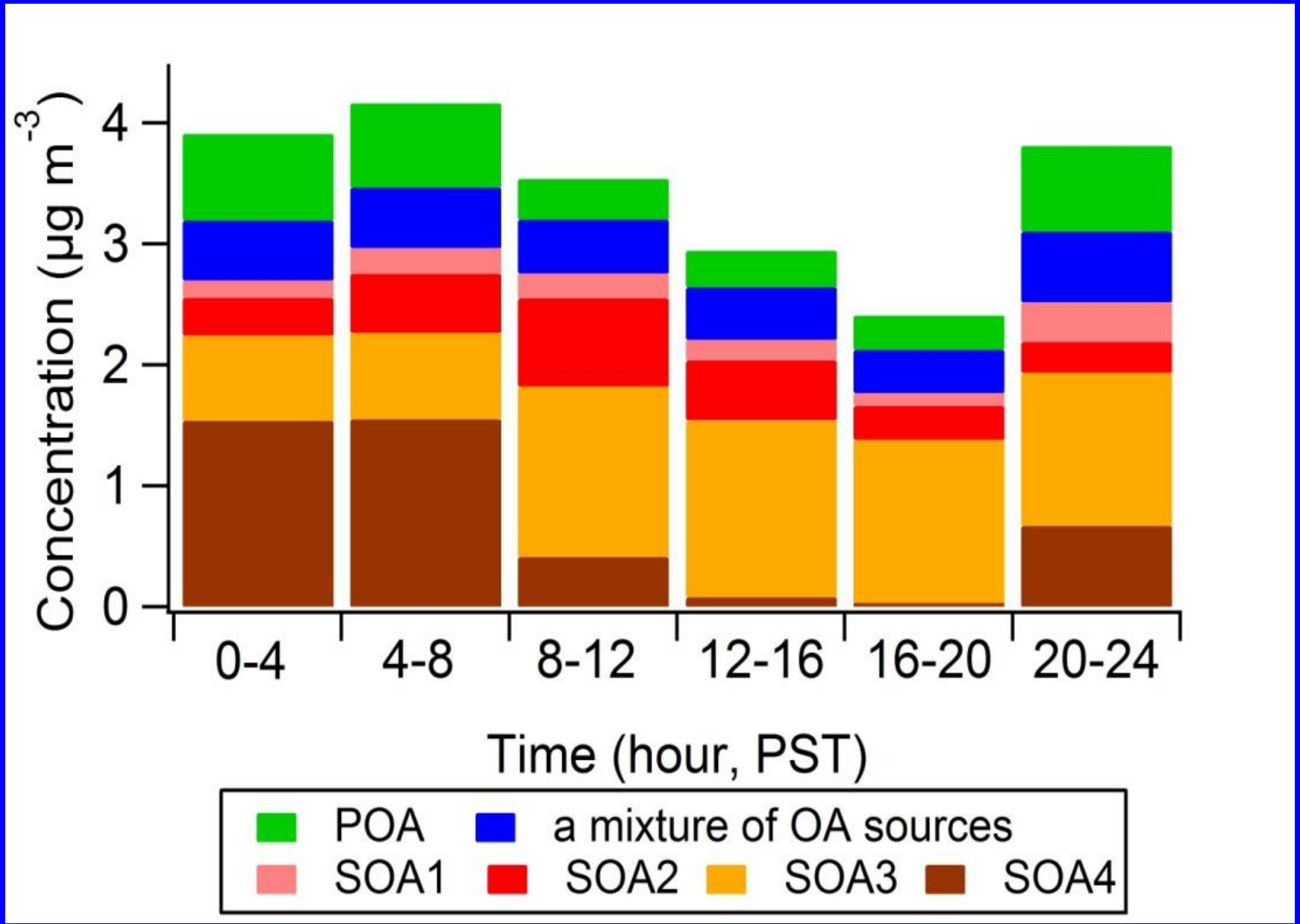




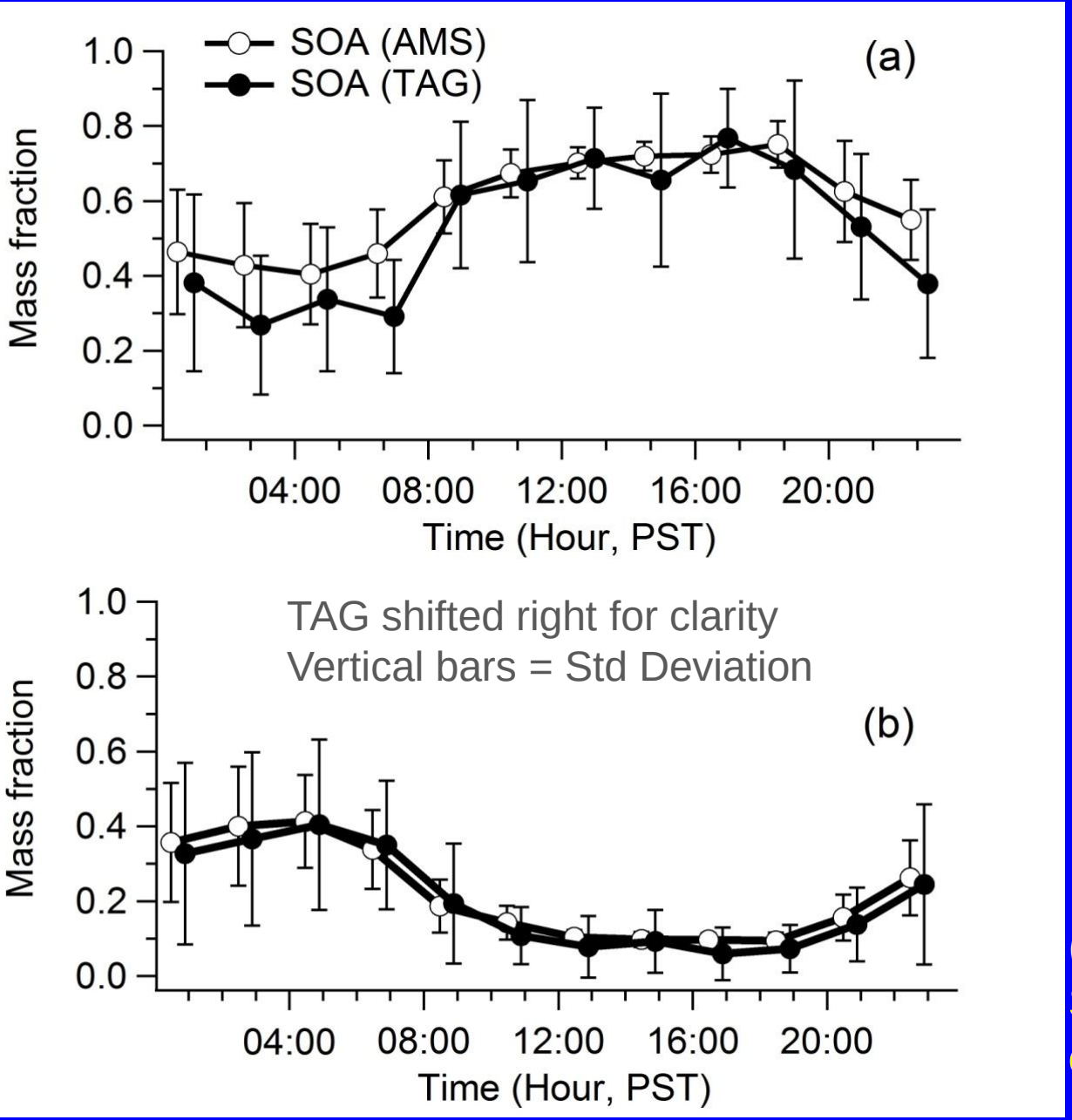




Diurnal Cycle of OA Source Contributions



SOA fractions agree for TAG and AMS PMF's



(a) Daytime SOA
TAG = SOA2 + SOA3
AMS = high O/C aromatic
+ high O/C alkane
+ petroleum SOA

(b) Nighttime SOA
TAG = SOA1 + SOA4
AMS = low O/C alkane +
nighttime OA.

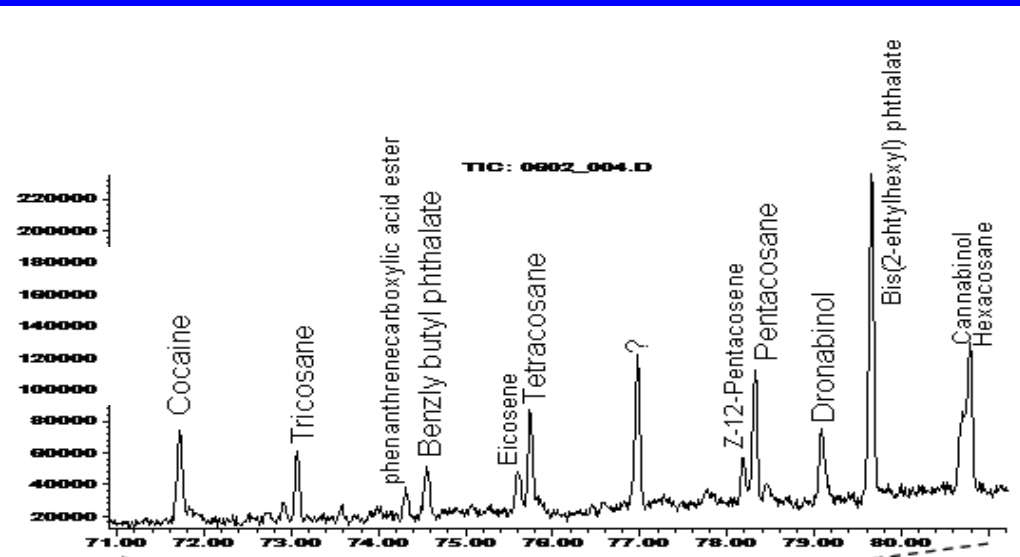
(Liu et al., JGR 2012,
SOA from fossil fuel sources
contributes majority of OA)

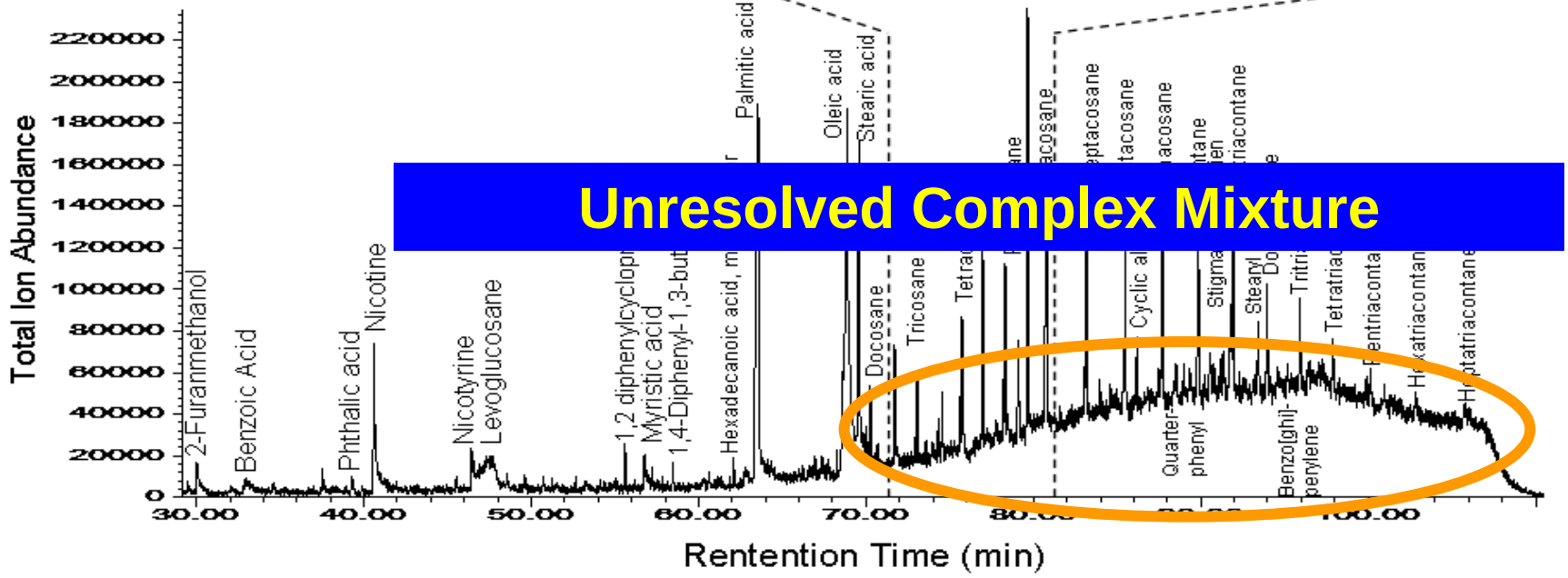
Organic Aerosol PMF Analysis Policy Relevant Messages

1) SOA accounts for approximately 75% of OA in Bakersfield (TAG and AMS PMFs agree)
2) SOA has multiple different sources, with daytime and nighttime SOA dominated by different primary precursor sources, chemical transformation, and partitioning processes.
3) Ammonia emission control could be important for SOA control in San Joaquin Valley due to formation of acid-ammonia salts.

TAG

Need Better Baseline Separation to Improve Identification and Quantification

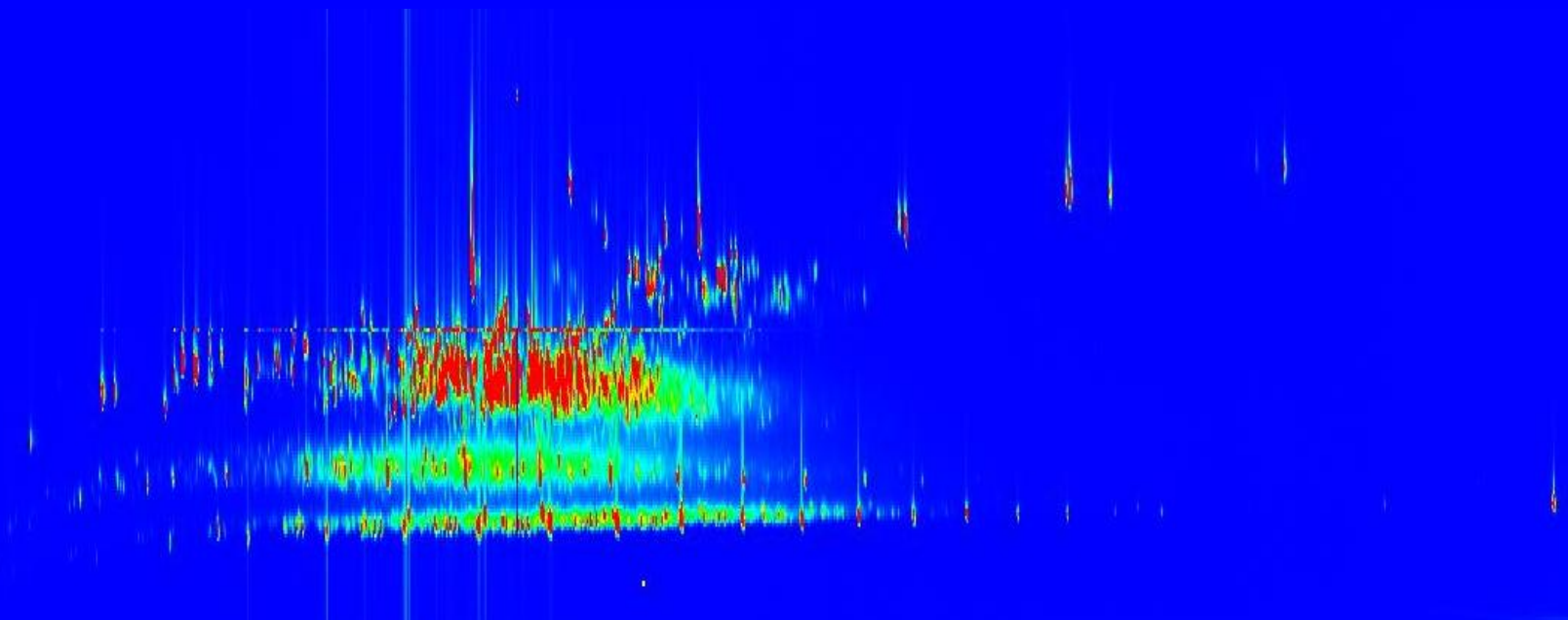




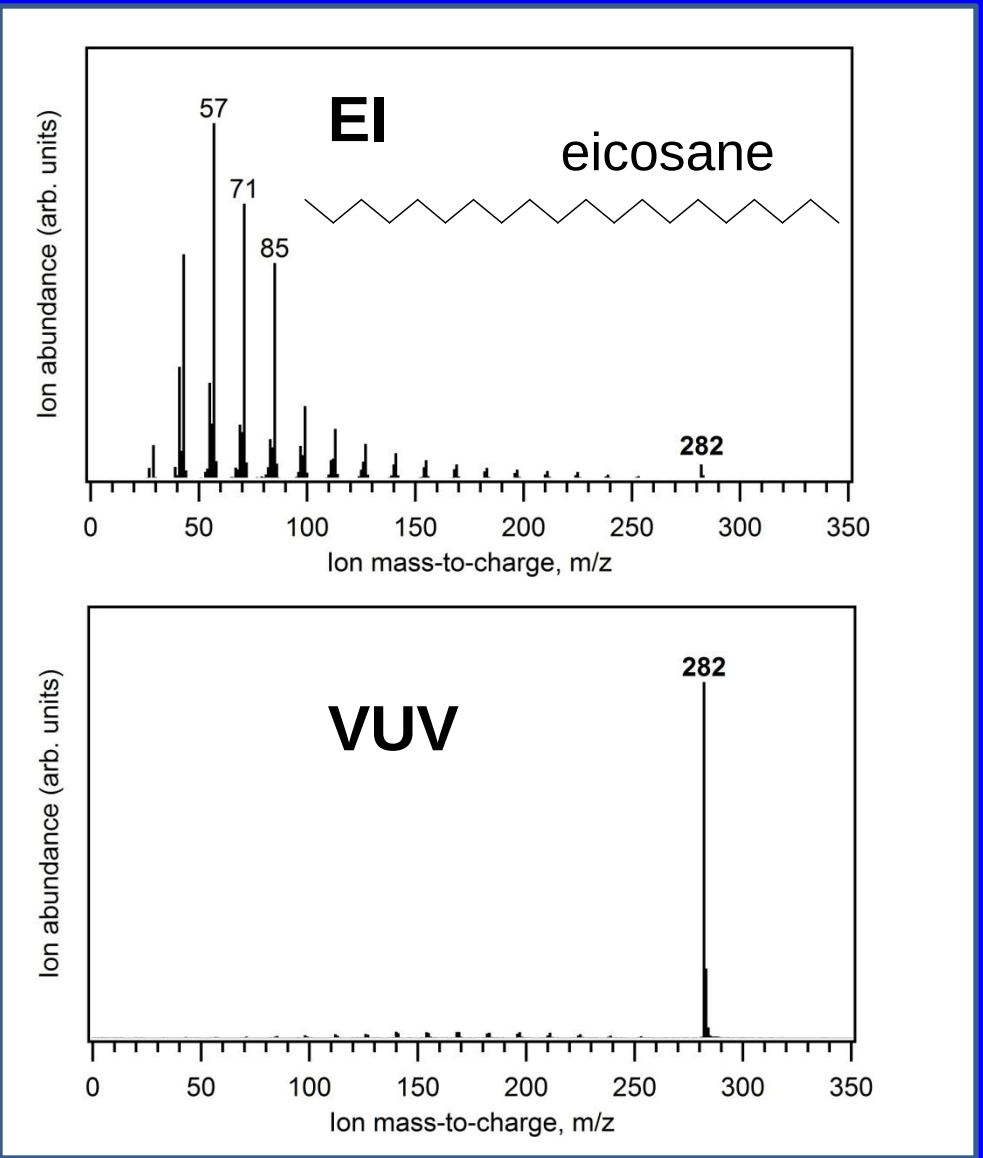
Unresolved Complex Mixture

Instrument Development to Enhance Exploration of Atmospheric Organics

Multi-dimensional Gas Chromatography with Vacuum Ultraviolet Ionization and High Resolution Time of Flight Mass Spectrometry (GCxGC-VUV-HRTOFMS)



Can Soft Ionization Improve Identifications? GC-Vacuum Ultraviolet Ionization-MS



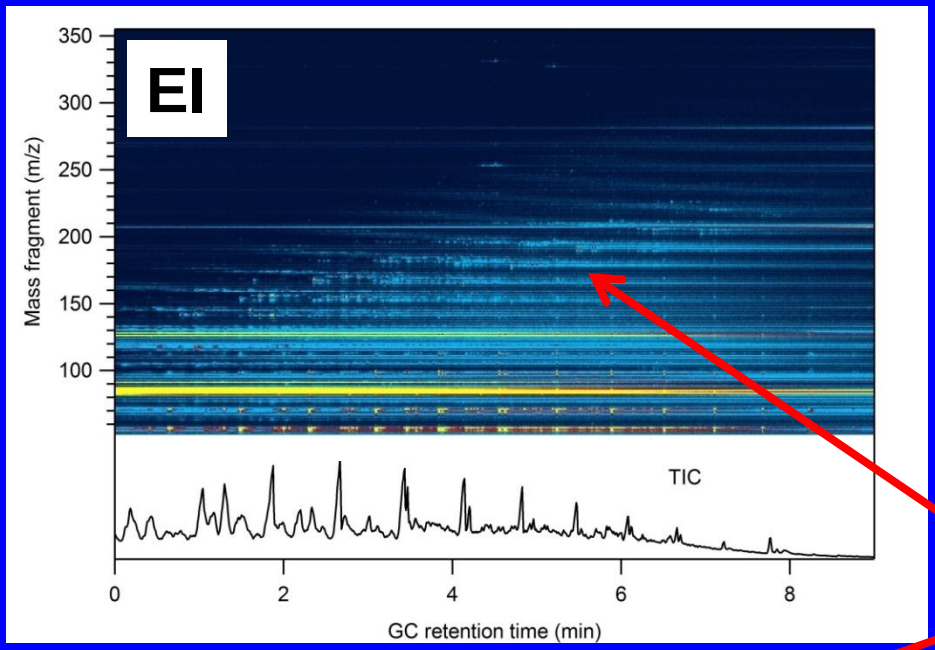
Electron Impact Ionization (70 eV, harder ionization)

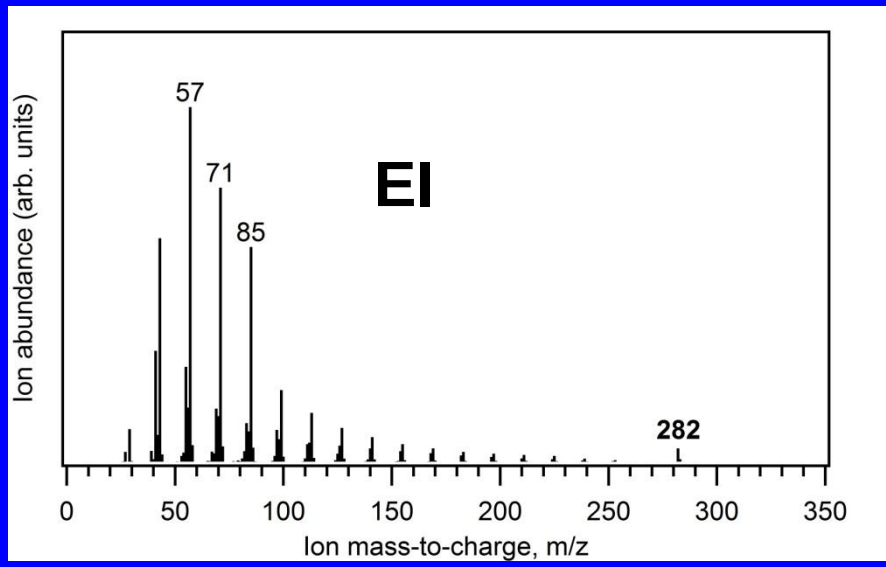
Lots of fragment ions
Hard to distinguish organic species

VUV Photoionization (10.5 eV, softer ionization) at Advanced Light Source

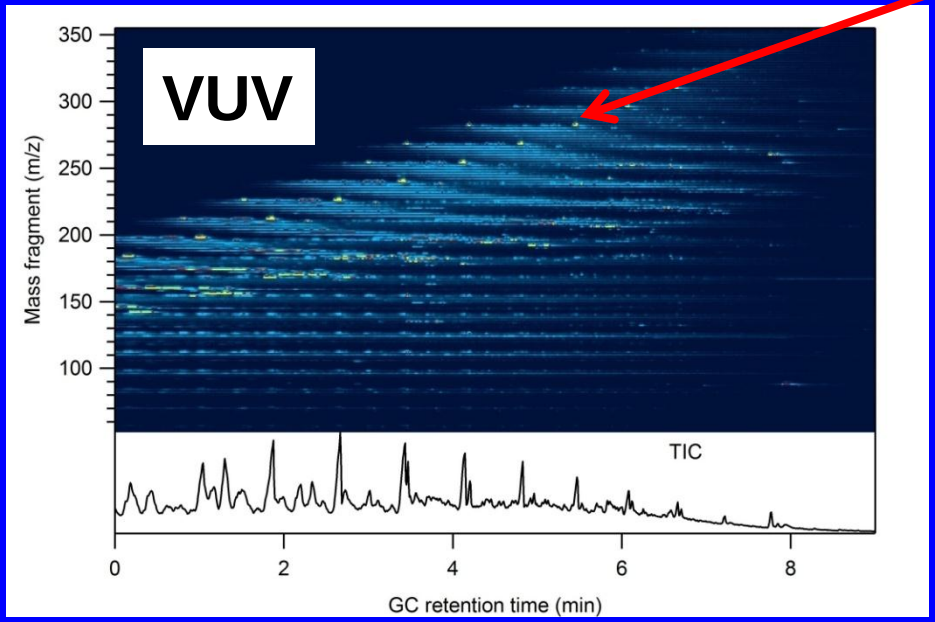
Very little fragmentation
Easy molecular identification of organic species

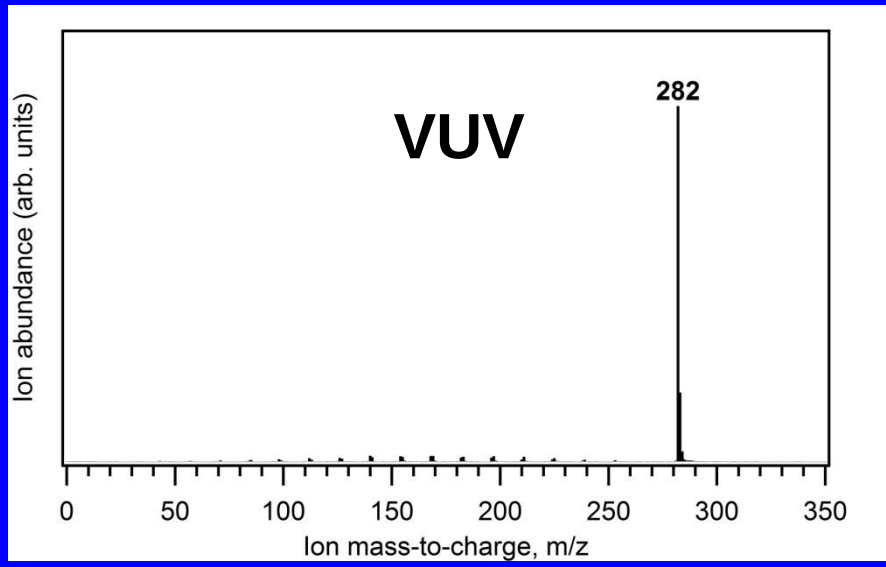
Diesel Fuel Mass Spectrum versus GC retention time



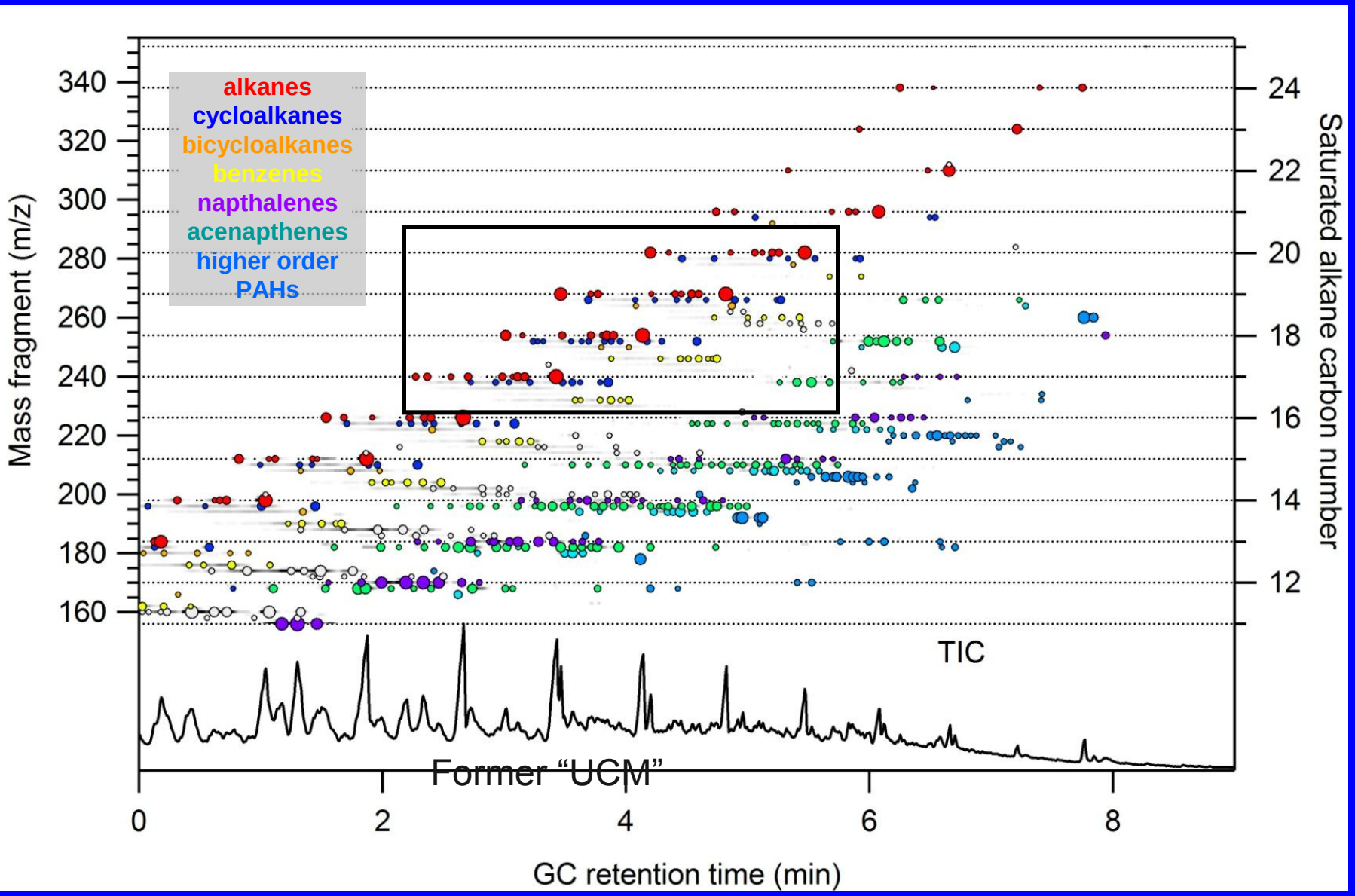


eicosane



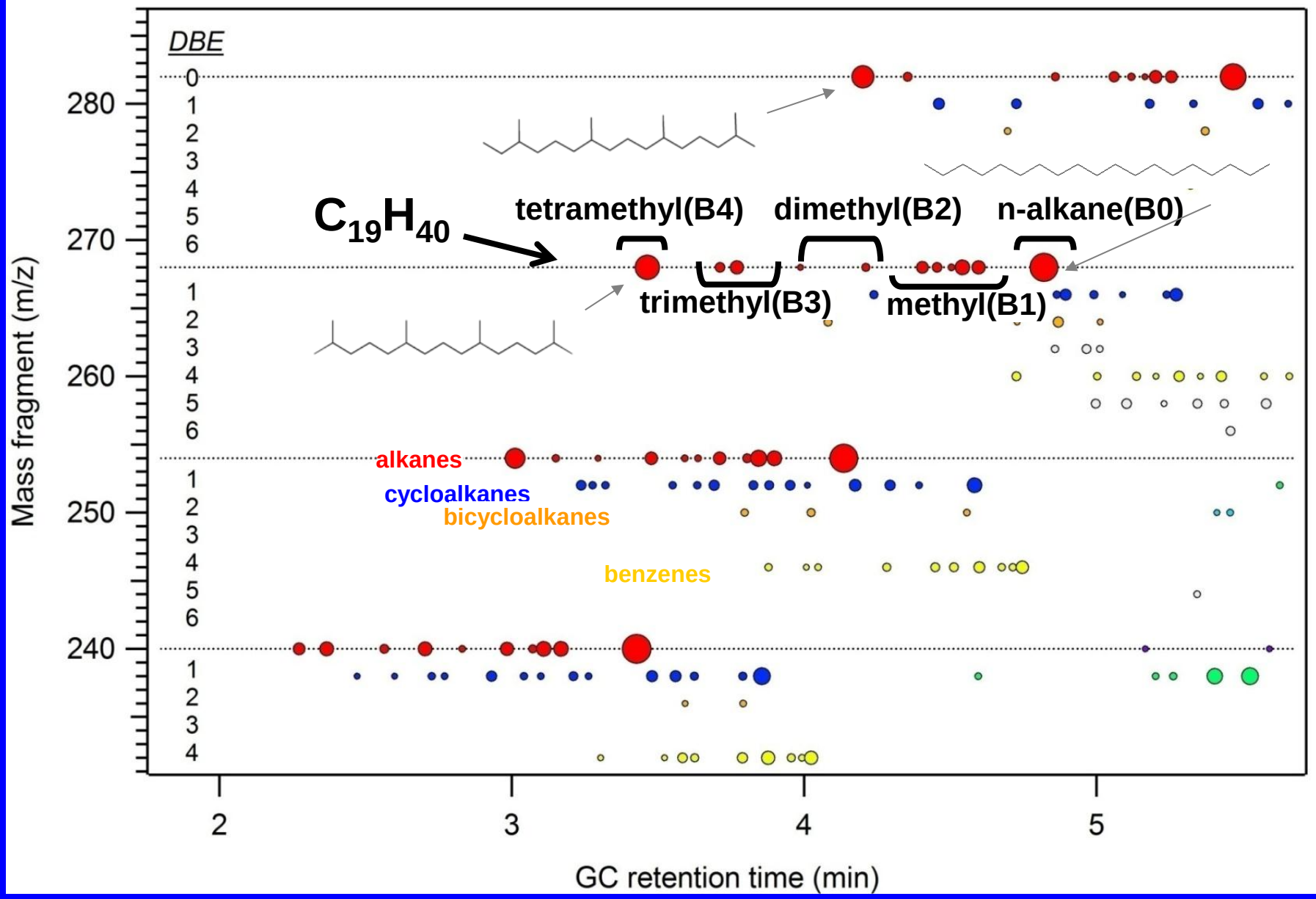


Diesel Fuel VUV Mass Spectrum versus GC retention time
"Classic Complex Hydrocarbon Mixture"



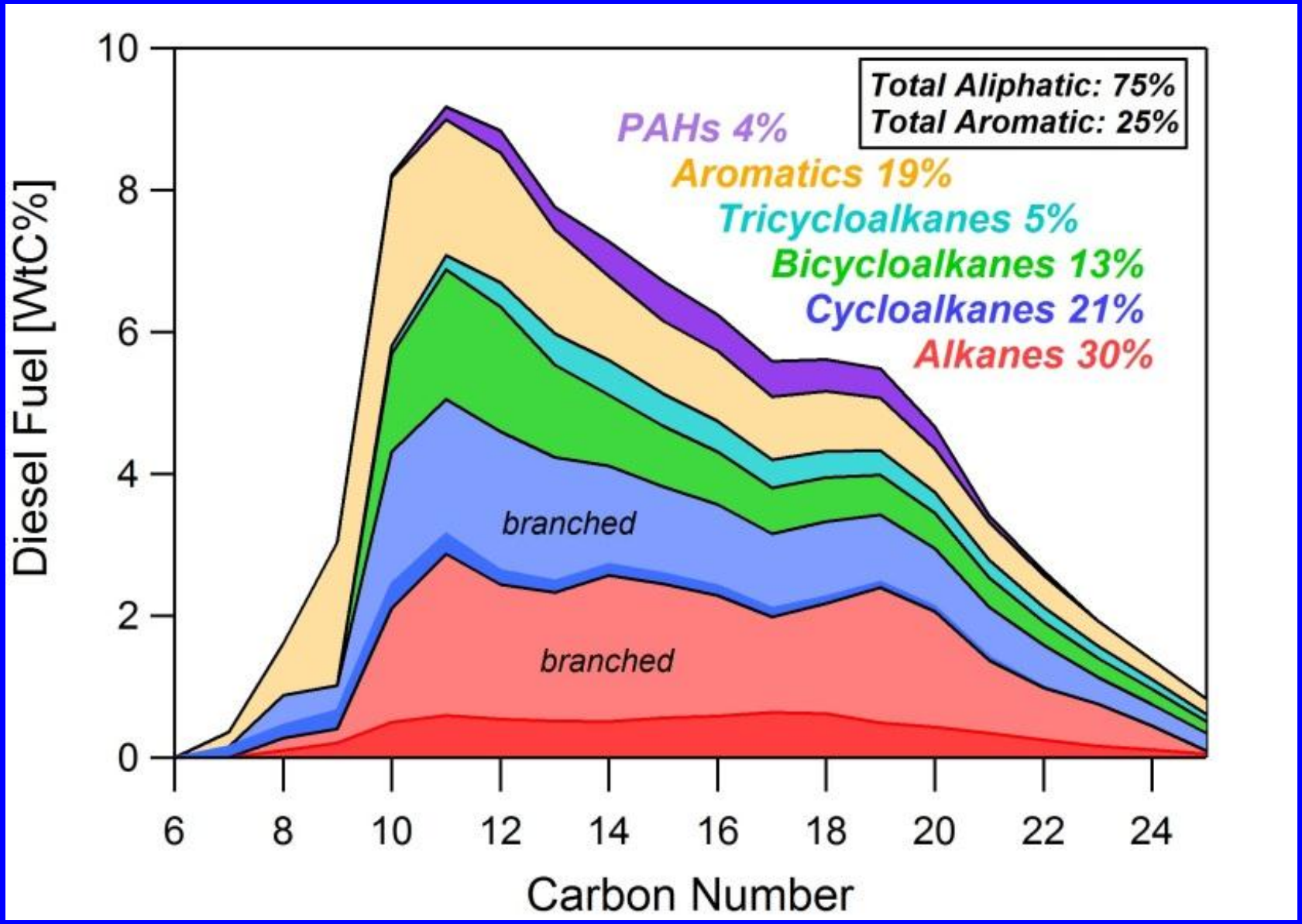
Isaacman et al Anal Chem 2012

Isomers Cleanly Separated



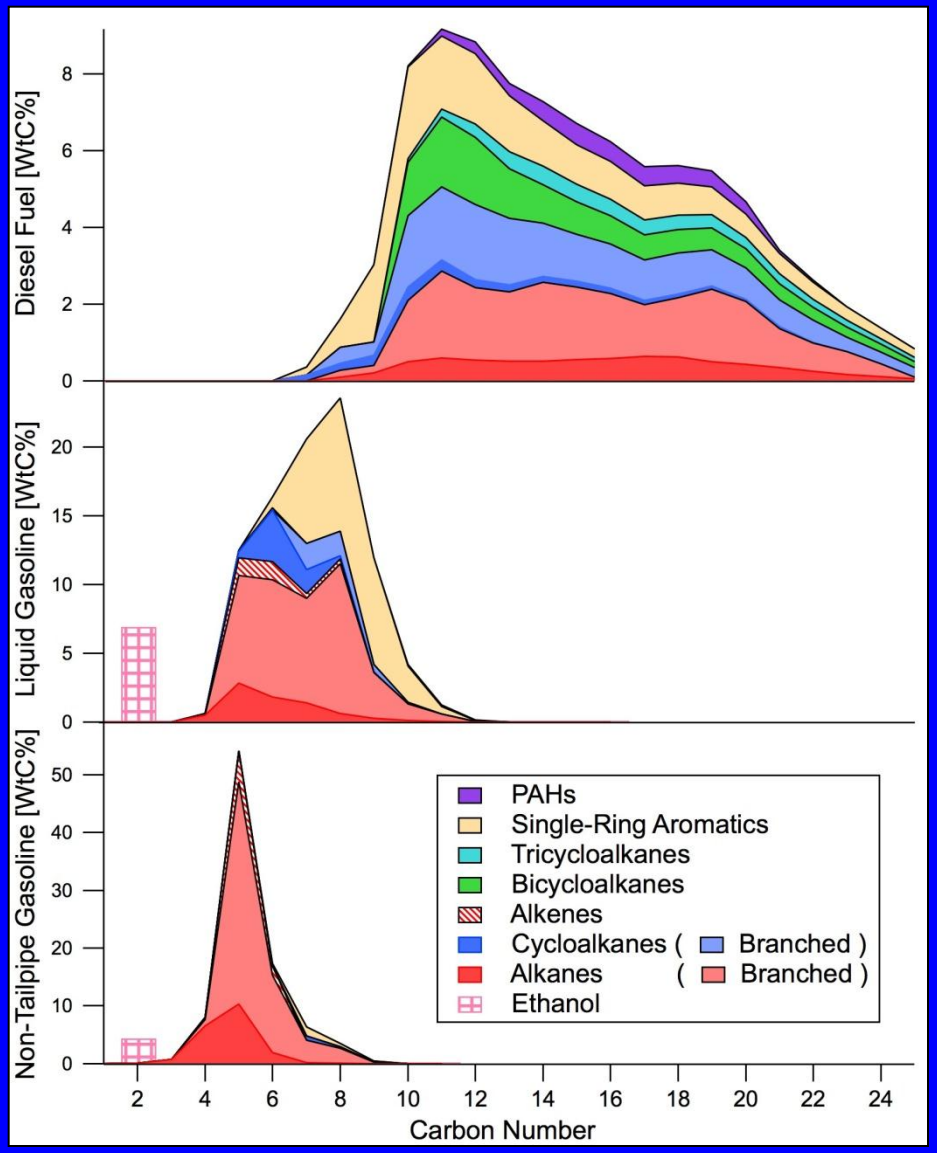
Isaacman et al Anal Chem 2012

Quantitatively Speciated Diesel Fuel (No More Unresolved Complex Mixture)



Isaacman et al Anal Chem 2012; Gentner et al PNAS 2012

Chemical Speciation of Motor Vehicle Sources

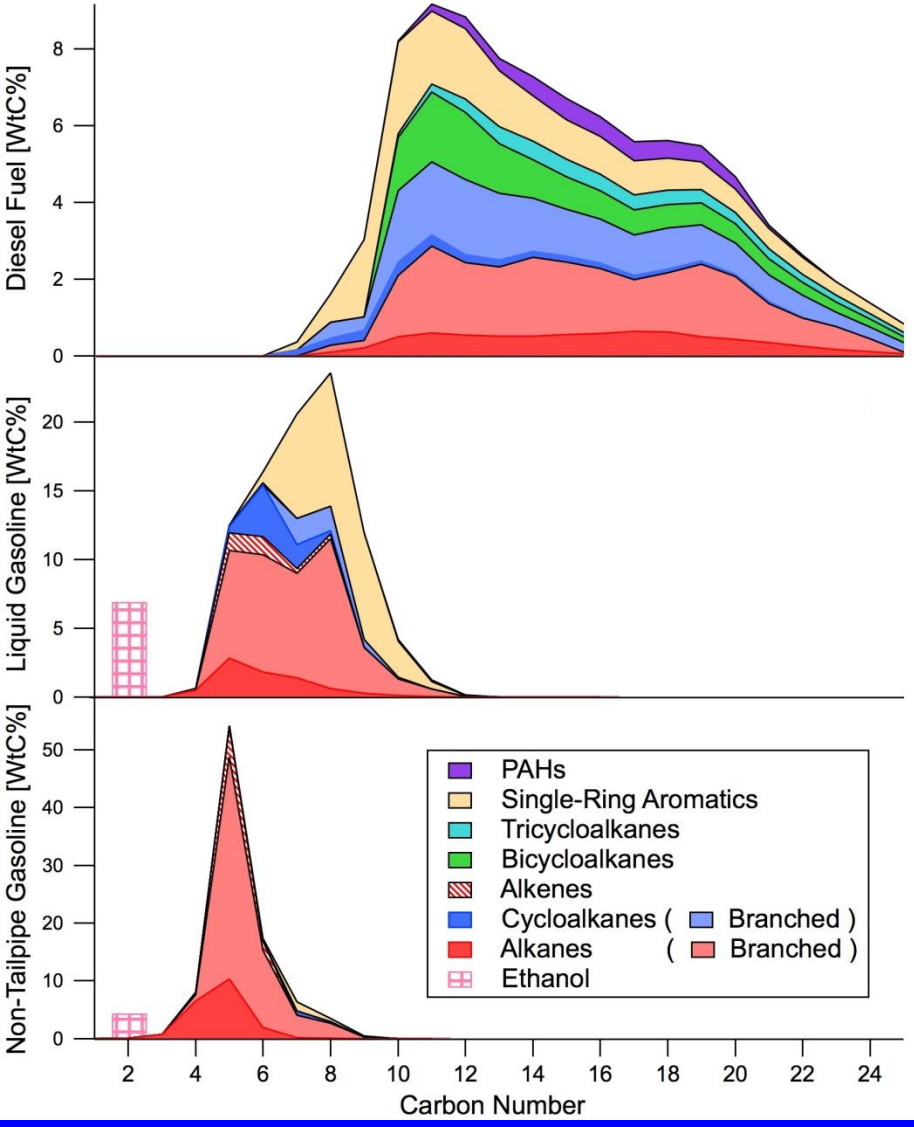


- Diesel fuel fully characterized via VUV soft ionization
  mostly C10-C20, branched and cyclic
  former “UCM” SOA yields largely unstudied
- Gasoline 30% aromatics
  mostly C4-C10
- Non-tailpipe gasoline almost all light alkanes
  mostly C4-C8

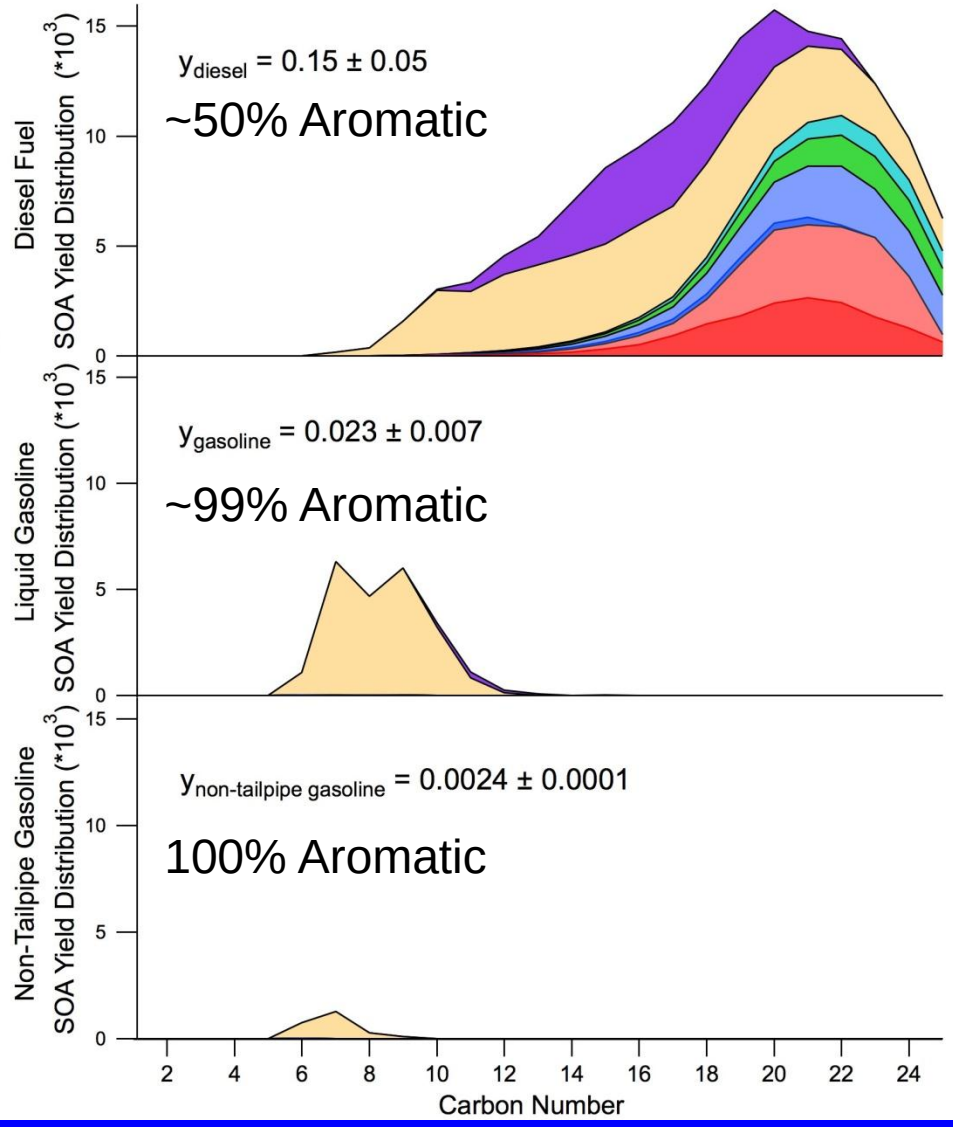
Gentner et al., PNAS 2012

Motor Vehicles

Precursor Emissions

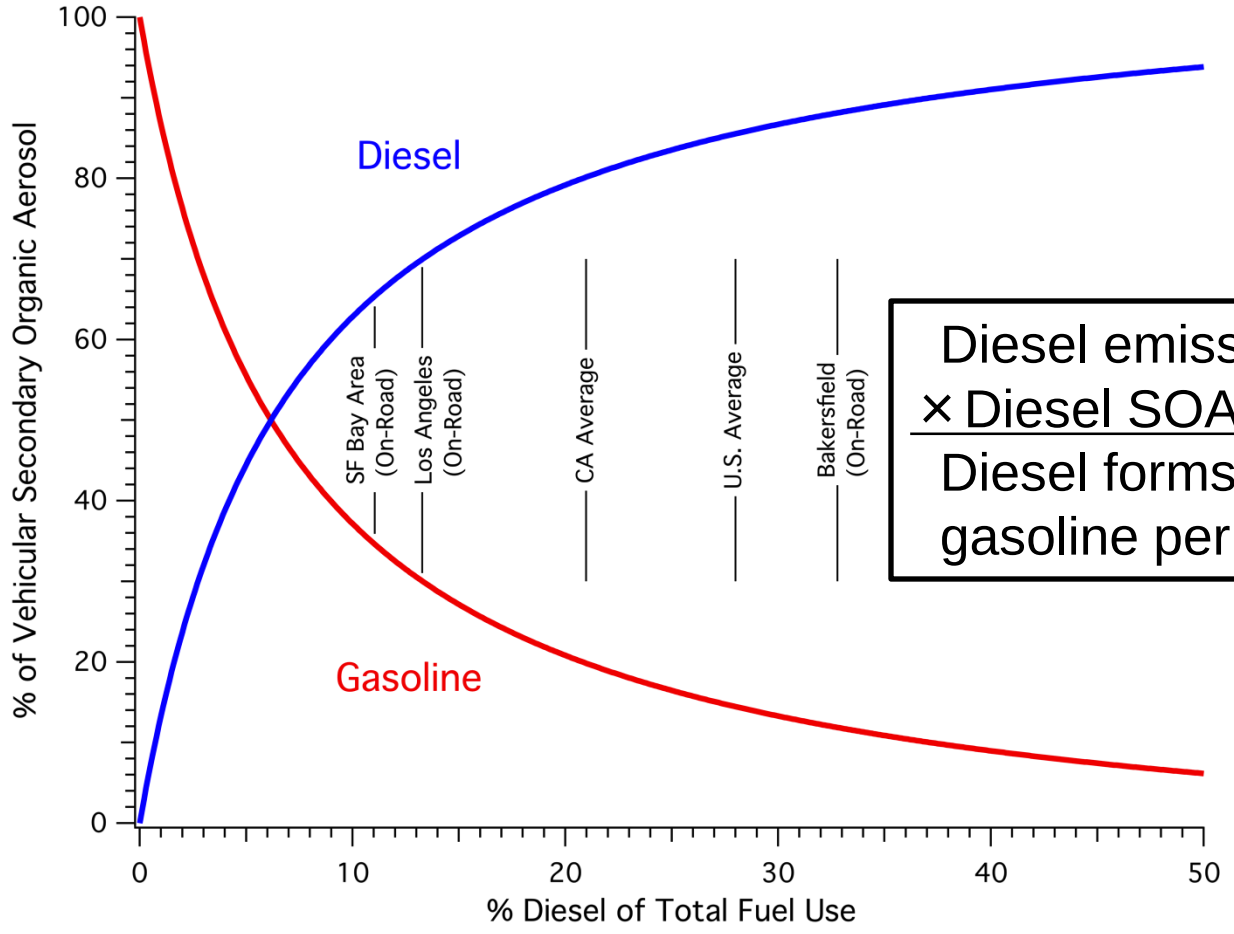


SOA Yields



Gentner et al., PNAS 2012

How Much SOA from Gasoline vs. Diesel? (In the United States Diesel = Large Trucks)



Diesel emission factor ~2x gasoline
× Diesel SOA yield ~7x gasoline
Diesel forms 15x more SOA than gasoline per liter of fuel burned

Diesel Forms 56-90% of Vehicular SOA (90% in Bakersfield)

Gentner et al., PNAS 2012

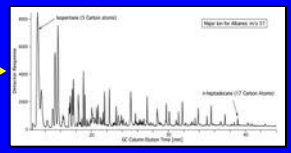
Deciphering a Complex Mixture of Sources

- Profile of compounds emitted from each source is unique
- Source contributions calculated using source profiles and atmospheric measurements
- Over-constrained source receptor model

Mix of 1000's of compounds in the atmosphere

Transport

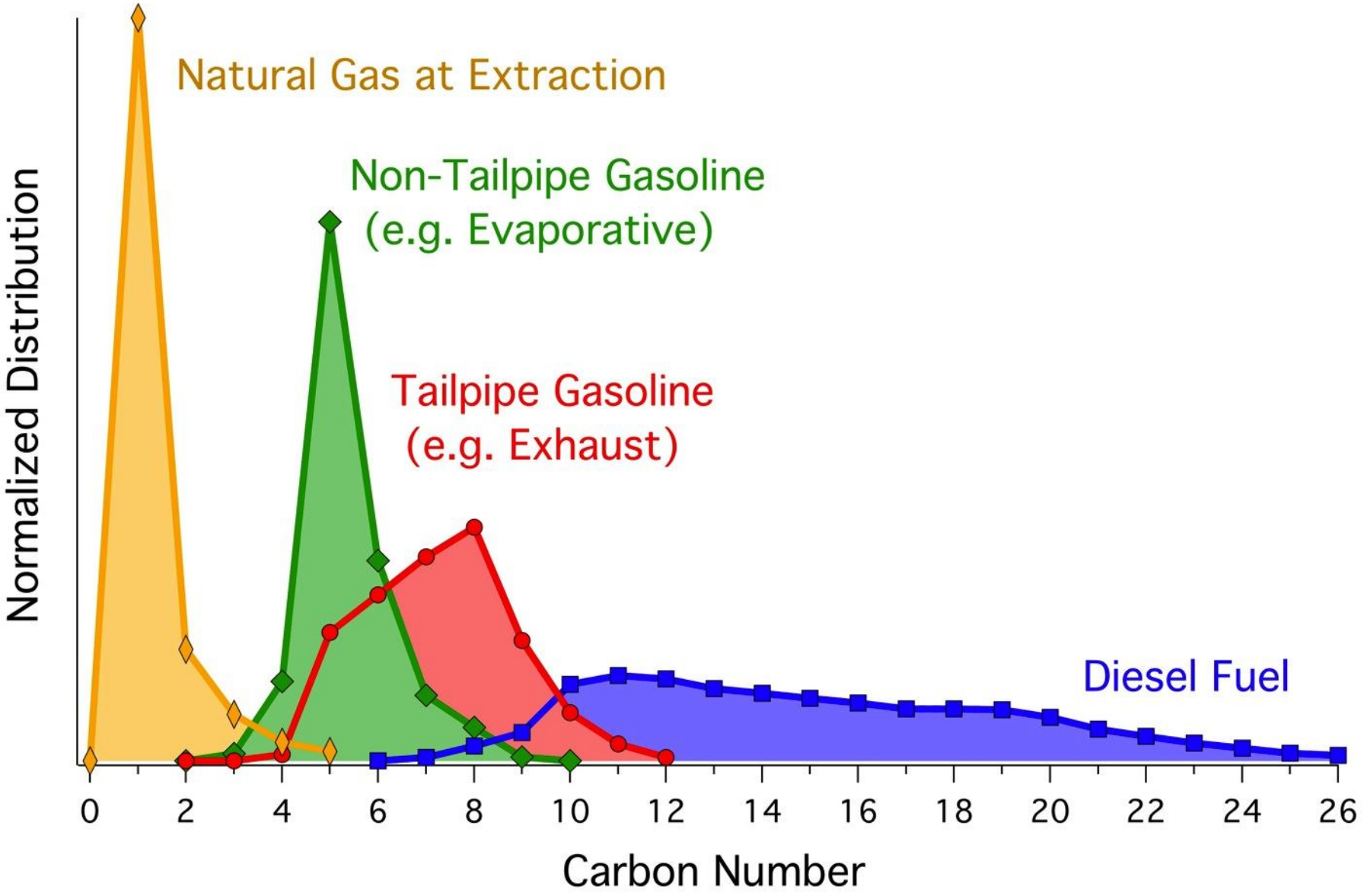
Data!



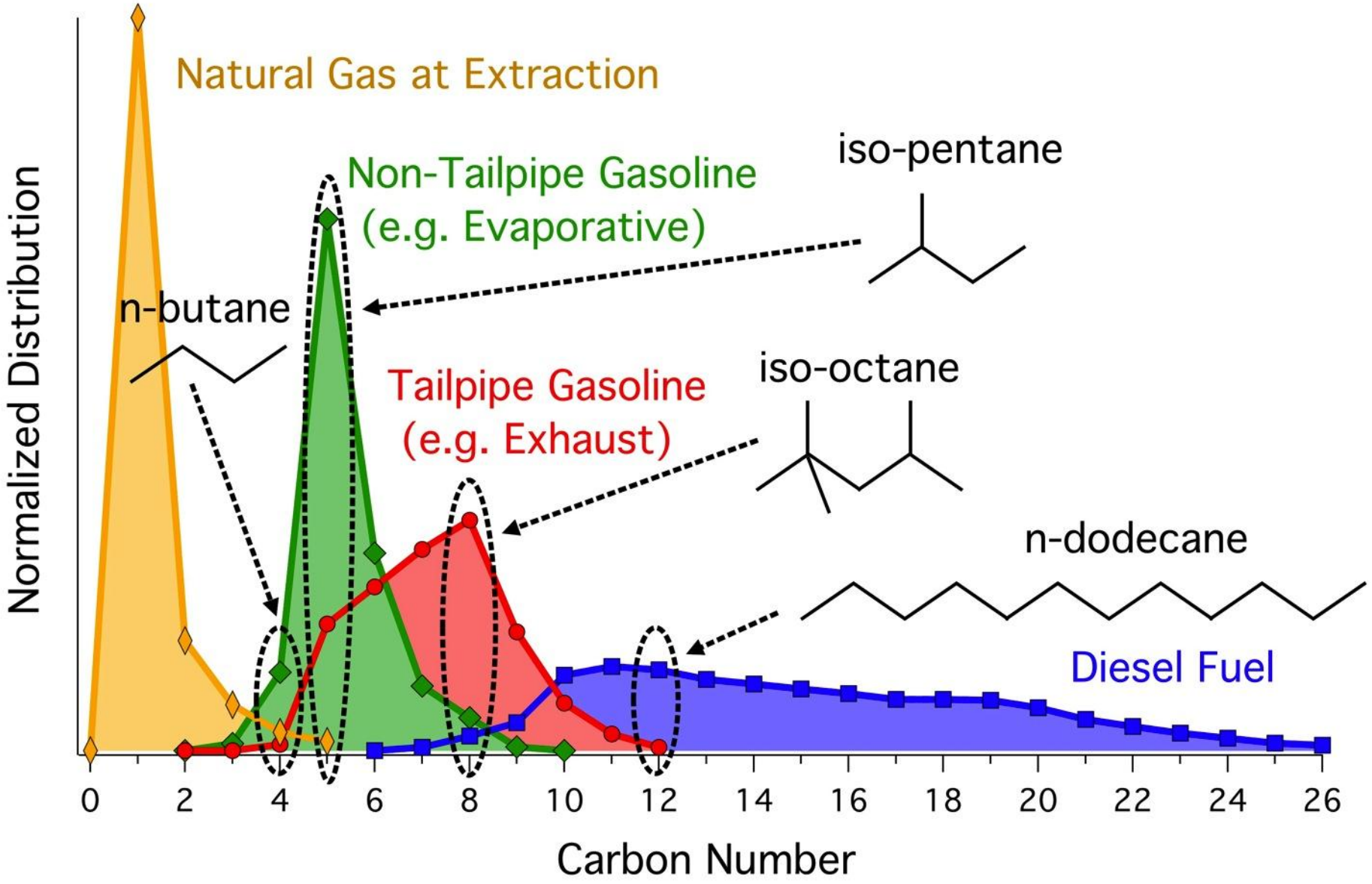
(on 100's of compounds…)

Emissions

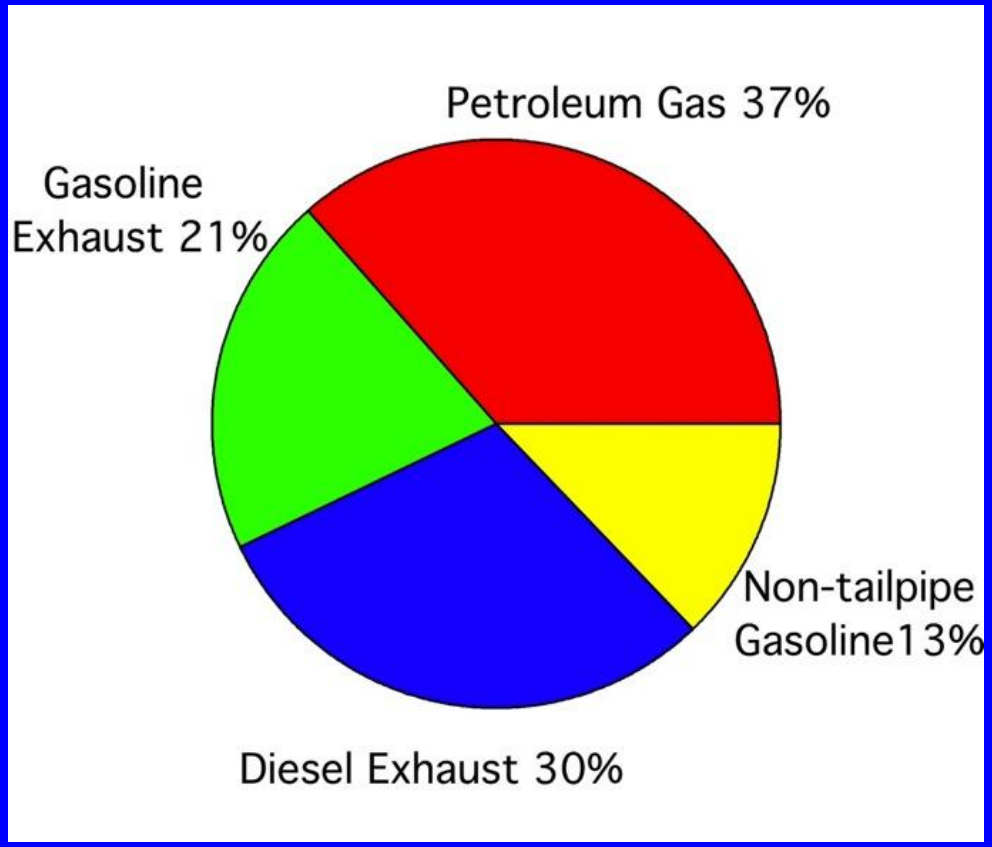
Fossil Fuel Source Apportionment



Fossil Fuel Source Apportionment



Bakersfield Reactive Organic Gas (ROG) Fossil Fuel Sources Receptor Model



- Petroleum associated gas major source of ROG emissions

  → Contributions to SOA are negligible since it's comprised of small hydrocarbons with very low SOA yields

Gentner et al., in prep

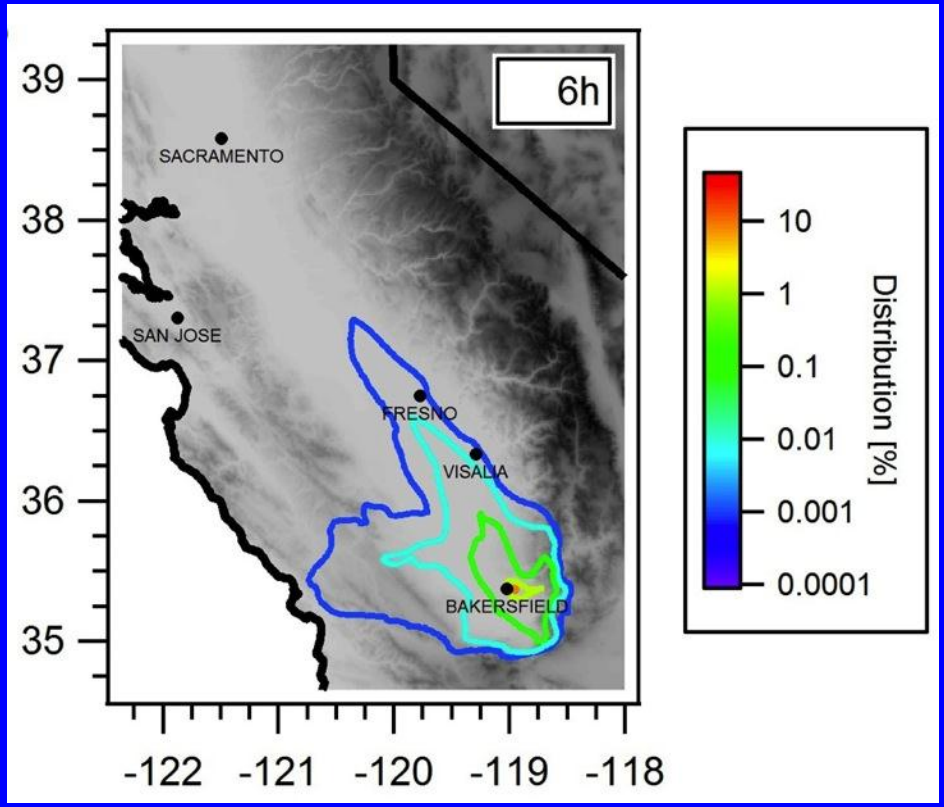
Locating Petroleum Gas Emissions

Use concentration data & meteorological modeling to locate emissions

Meteorological data is used to calculate “footprint” (aka back-trajectory) for each data time point

Met footprints are weighted by ground site concentration data to construct map of emissions for a region

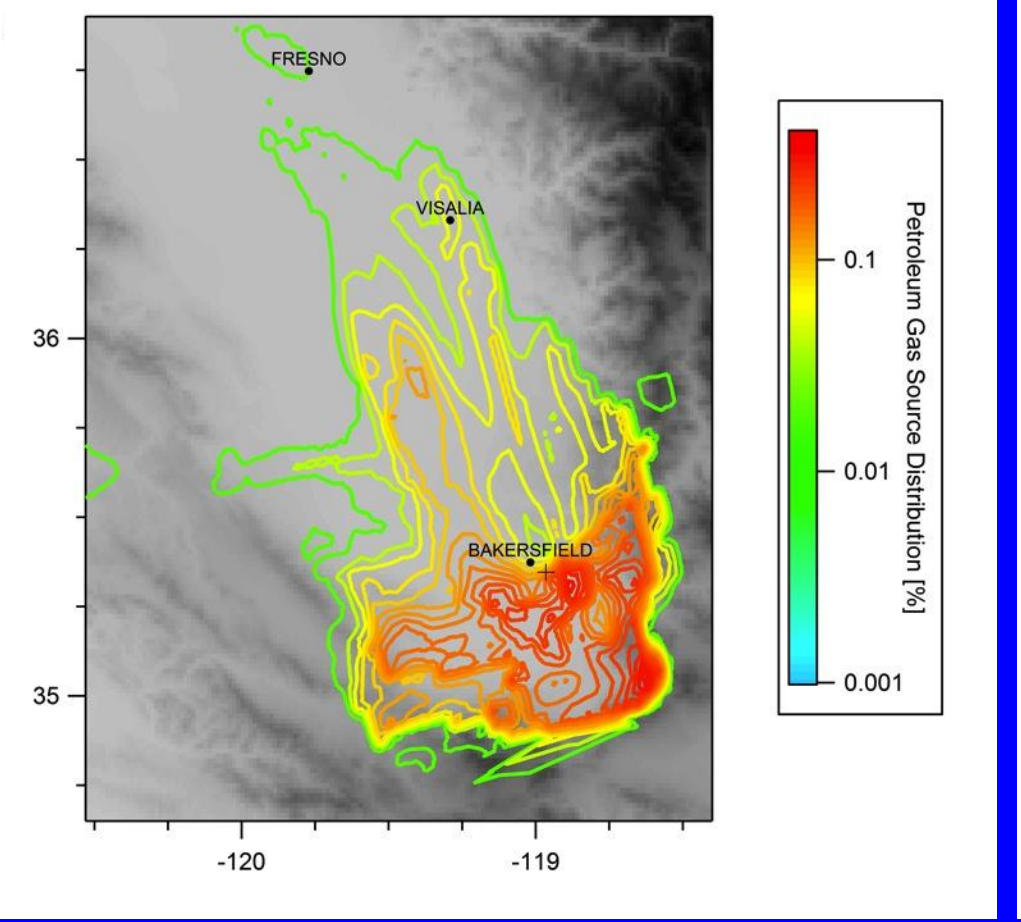
Average 6 hr Footprint



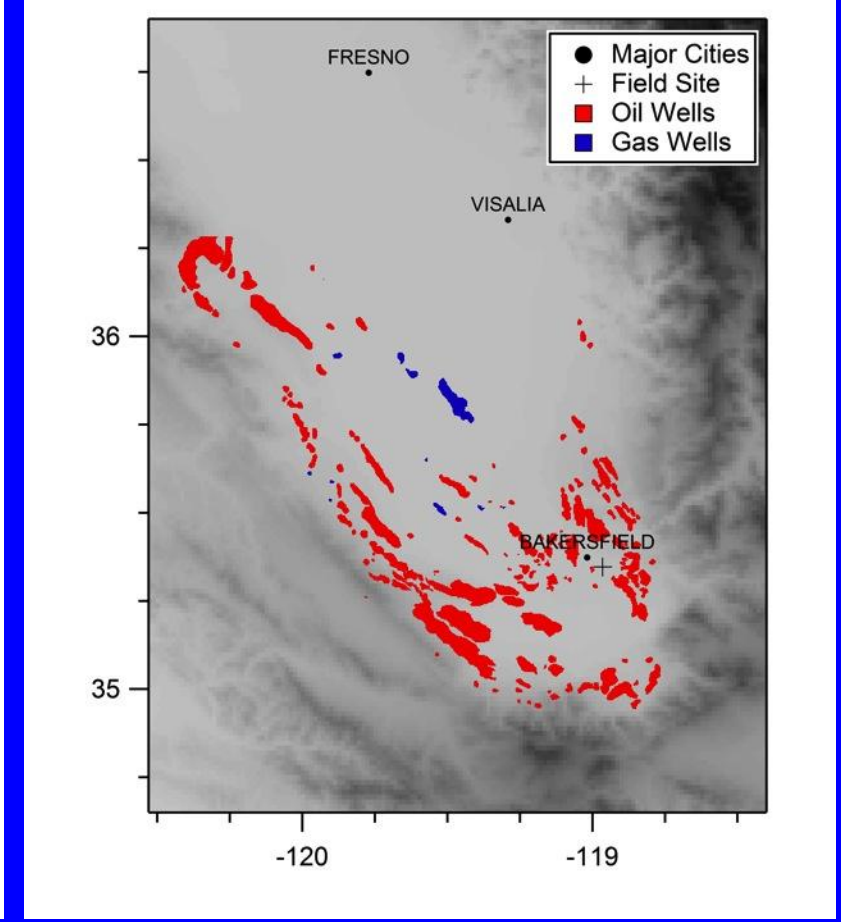
Average footprint (or area of influence) for 6 hrs before transport to Bakersfield site

Locating Petroleum Gas Emissions

Statistical Distribution of Petroleum Gas Source



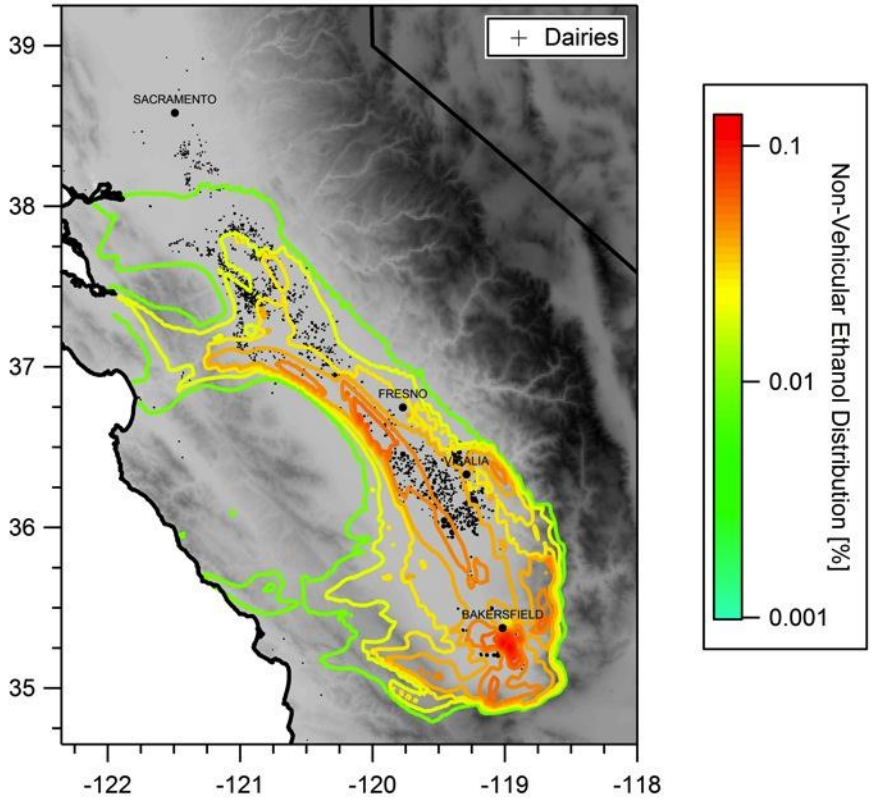
Location of Oil/Gas Wells



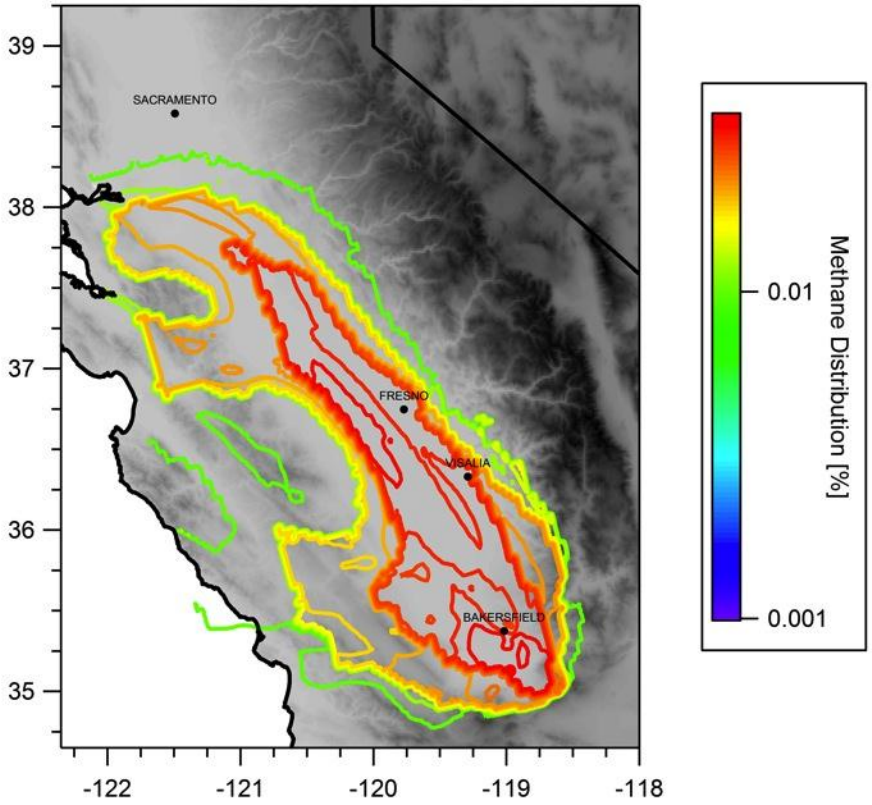
Gentner et al., in prep

Locating Dairy Emissions

Non-Vehicular Ethanol



Methane



Policy Implications
Fossil Fuel VOC sources

- Both gasoline & diesel vehicles are important urban sources of fossil fuel SOA precursors, but diesel dominates (65-90%), particularly in Bakersfield (90%)
- Further research on understudied SOA yields is necessary
- Fuel composition and potential SOA formation should be considered in SOA control policies
- Gasoline dominates over diesel for emissions of organic precursors to ozone [Gentner et al. ES&T, in review]
- Petroleum operations are a major source of ROG emissions in Bakersfield (potentially important for ozone, but not SOA)

Gentner et al., PNAS (2012)

Thank you for listening!

Deciphering the origins and transformations of atmospheric organics