Estimating Secondary Organic Aerosols for Regulatory Applications

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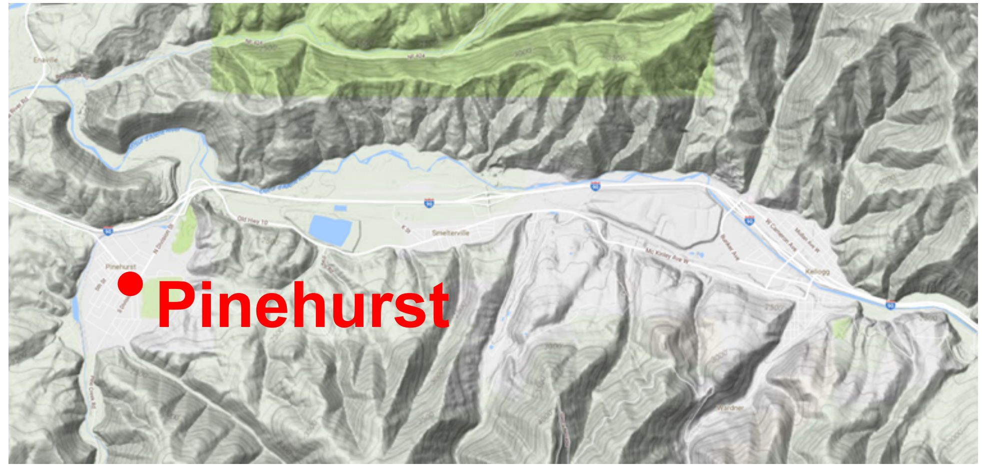
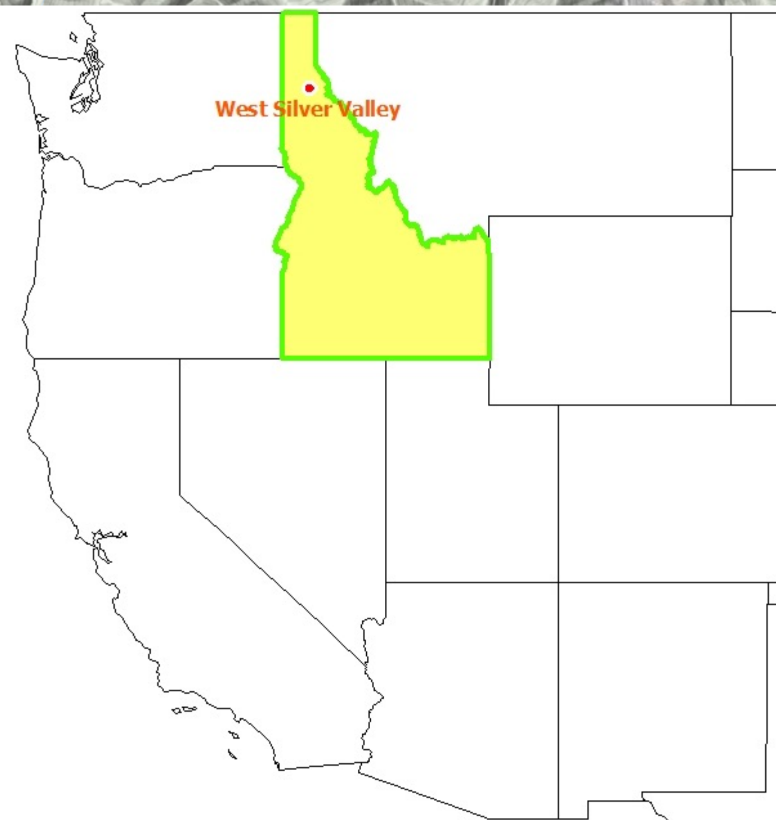
Background and Motivation

- $PM_{2.5}$ (<2.5 μm)
- Western Silver Valley
- $PM_{2.5}$ exceeded the annual National Ambient Air Quality Standard (NAAQS)
- Non-attainment area
- State Implementation Plan (SIP) Attainment Demonstration





Background and Motivation

- Most recent rule and guidance:
  - July 29, 2016: "Fine Particulate Matter National Ambient Air Quality Standards: State Implementation Plan Requirements; **Final Rule**" (40 CFR 50, 51, and 93)
  - November 17, 2016: "**Draft $PM_{2.5}$ Precursor Demonstration Guidance**"; Comment period ended March 31, 2017
  - Both SIP and Precursor Demonstrations: **SOA**
  - **Estimating SOA** for regulatory applications in the context of the new rule and guidance
  - **Challenges**

Chemical and Physical Processes

VOCs react with OH, O_3, and NO_3

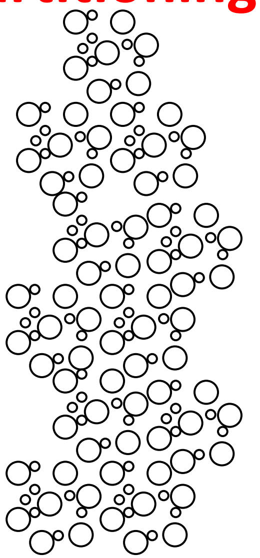
Produce bigger products

- Produce smaller products
- Decrease carbon number and the number of functional groups
- May not contribute to SOA formation and growth
- Reduce SOA

- Multi-generation and multi-phase reactions of VOCs: Toluene, Xylene, Benzene, Alkanes, Terpenes
- Measured: 10,000 to 100,000 different organic compounds
- Unmeasured: even more VOC species

- Increase carbon number and the number of functional groups
- May contribute to SOA formation and growth

partitioning



Fragmentation process

Scientific Challenges

- **Developing technologies** to measure such a big range of organic compounds
- Each VOC can participate in **a number of atmospheric chemical processes** to generate many products, which may or may not contribute to SOA formation and growth.
- **Understanding the chemical and physical processes of so many compounds** that lead to SOA production
- A**ir quality modeling systems** lags further behind scientific knowledge and understanding.

Parameterizations and Modeling of SOA

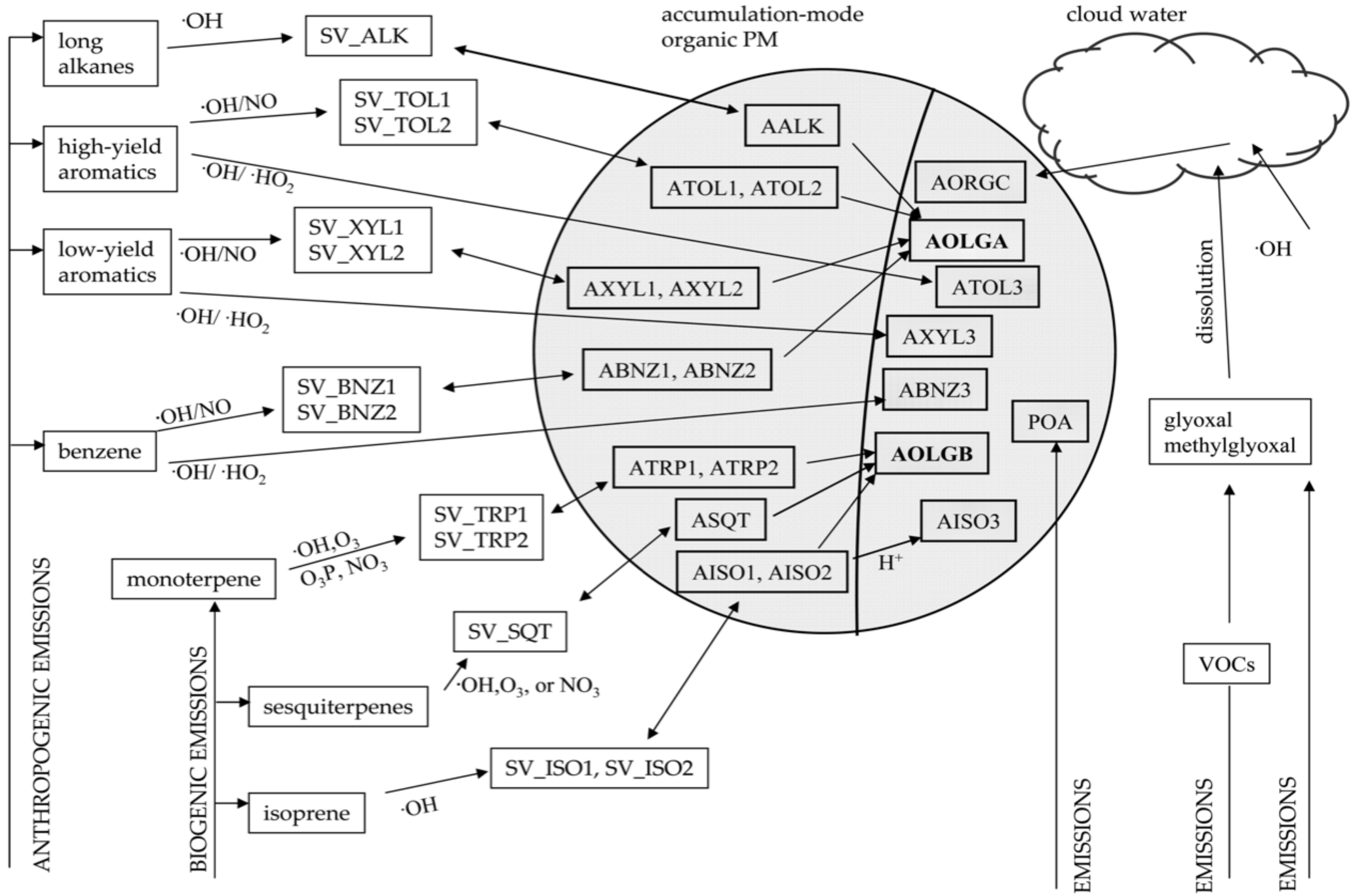
$$Y_i = M_o \left(\frac{\alpha_i K_{om,i}}{1+K_{om,i} M_o} \right)$$

$$Y = \sum_i Y_i = \sum_i M_o \left(\frac{\alpha_i K_{om,i}}{1+K_{om,i} M_o} \right)$$

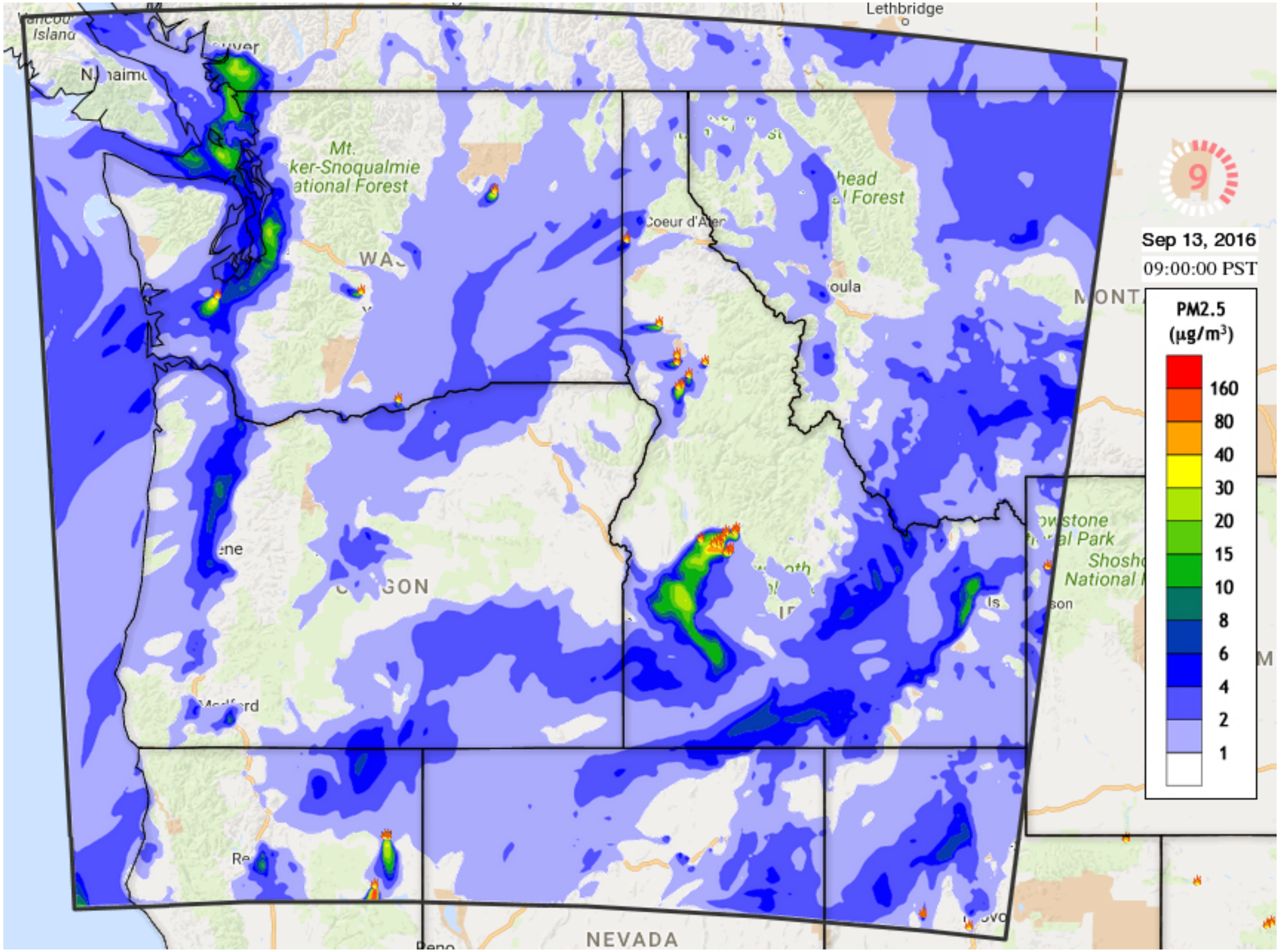
- Y_i = the yield
- M_o =organic aerosol mass concentration
- $K_{om,i}$=partitioning coefficient
- α_i = the proportionality constant.

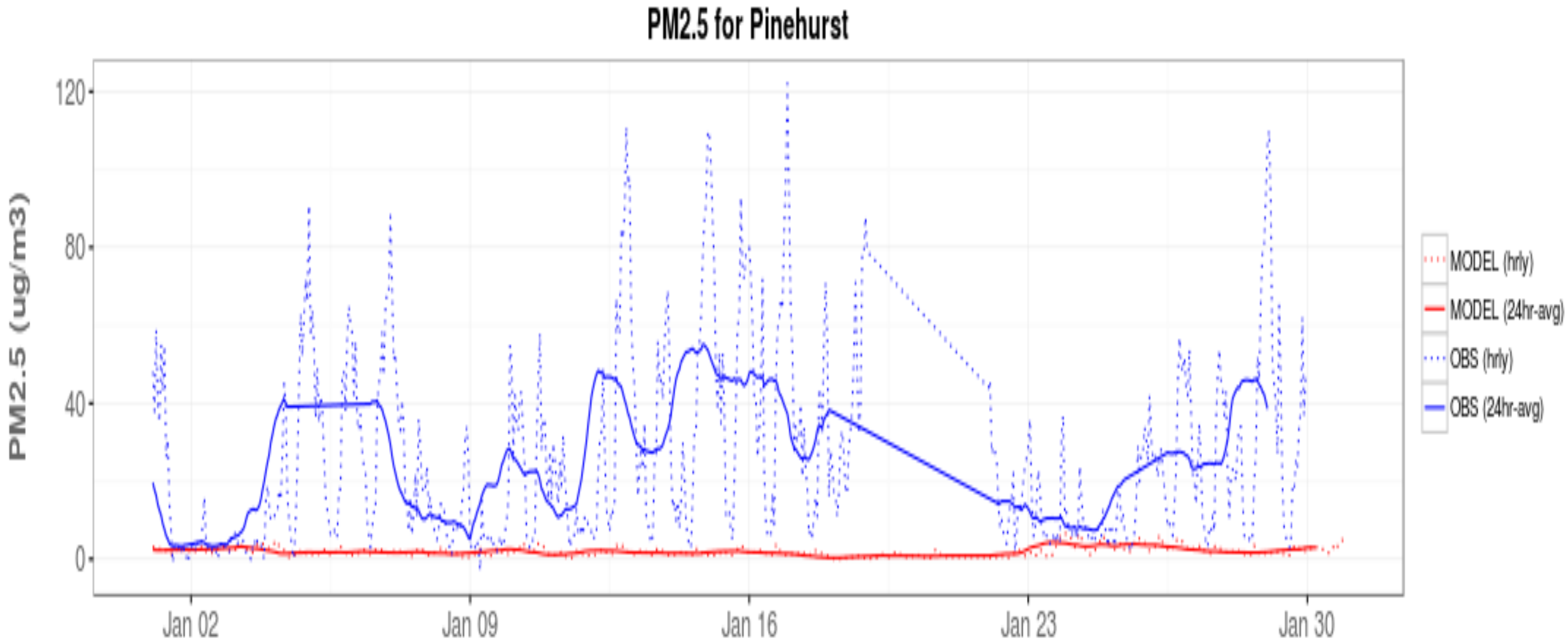
(Odum et al., 1996)

Schematic of the SOA module of CMAQ (Carlton et al., 2010).



$PM_{2.5}$ concentrations simulated by AIRPACT5 for September 13, 2016, at 9:00 a.m. PST.





Pinehurst: Comparison of observed hourly (blue dashed line) and 24-hour average (blue solid line) $PM_{2.5}$ concentrations against AIRPACT5 results (corresponding red lines) from January 1 to January 30, 2017.

Box Modeling

- Traditional photochemical box models (e.g. Barsanti, 2011): SOA
- SOA formation is still estimated with the "traditional two-product approach"
- Lack of measurements. Human assumptions (e.g. mixing layer height) may become the deciding factor in SOA calculations
- Transport (how big is the box area)
- Arbitrary

Challenges in Regulatory Projects

- The chemical and physical processes associated with SOA formation are complex
- Air quality models that simulate the complex processes in SOA formation are still in their infancy (Ziemann and Atkinson 2012), and despite considerable progress in recent years, a realistically predictive understanding of SOA formation does not exist, which represents a major research challenge in atmospheric science (Hallquist et al. 2009).

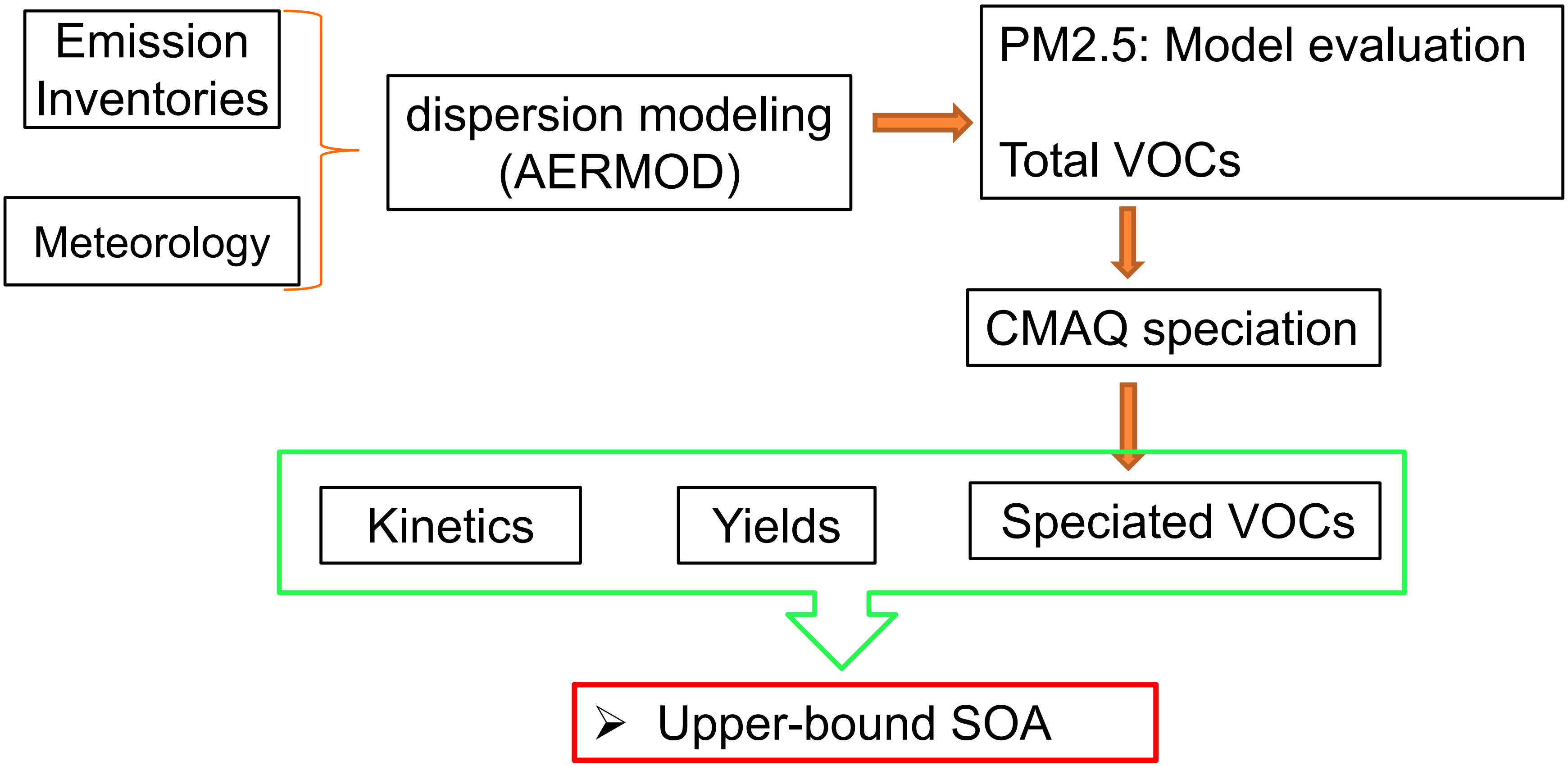
The formation, properties and impact of secondary organic aerosol: current and emerging issues

M. Hallquist[1], J. C. Wenger[2], U. Baltensperger[3], Y. Rudich[4], D. Simpson[5,6], M. Claeys[7], J. Dommen[3], N. M. Donahue[8], C. George[9,10], A. H. Goldstein[11], J. F. Hamilton[12], H. Herrmann[13], T. Hoffmann[14], Y. Iinuma[13], M. Jang[15], M. E. Jenkin[16], J. L. Jimenez[17], A. Kiendler-Scharr[18], W. Maenhaut[19], G. McFiggans[20], Th. F. Mentel[18], A. Monod[21], A. S. H. Prévôt[3], J. H. Seinfeld[22], J. D. Surratt[23], R. Szmigielski[7], and J. Wildt[18]

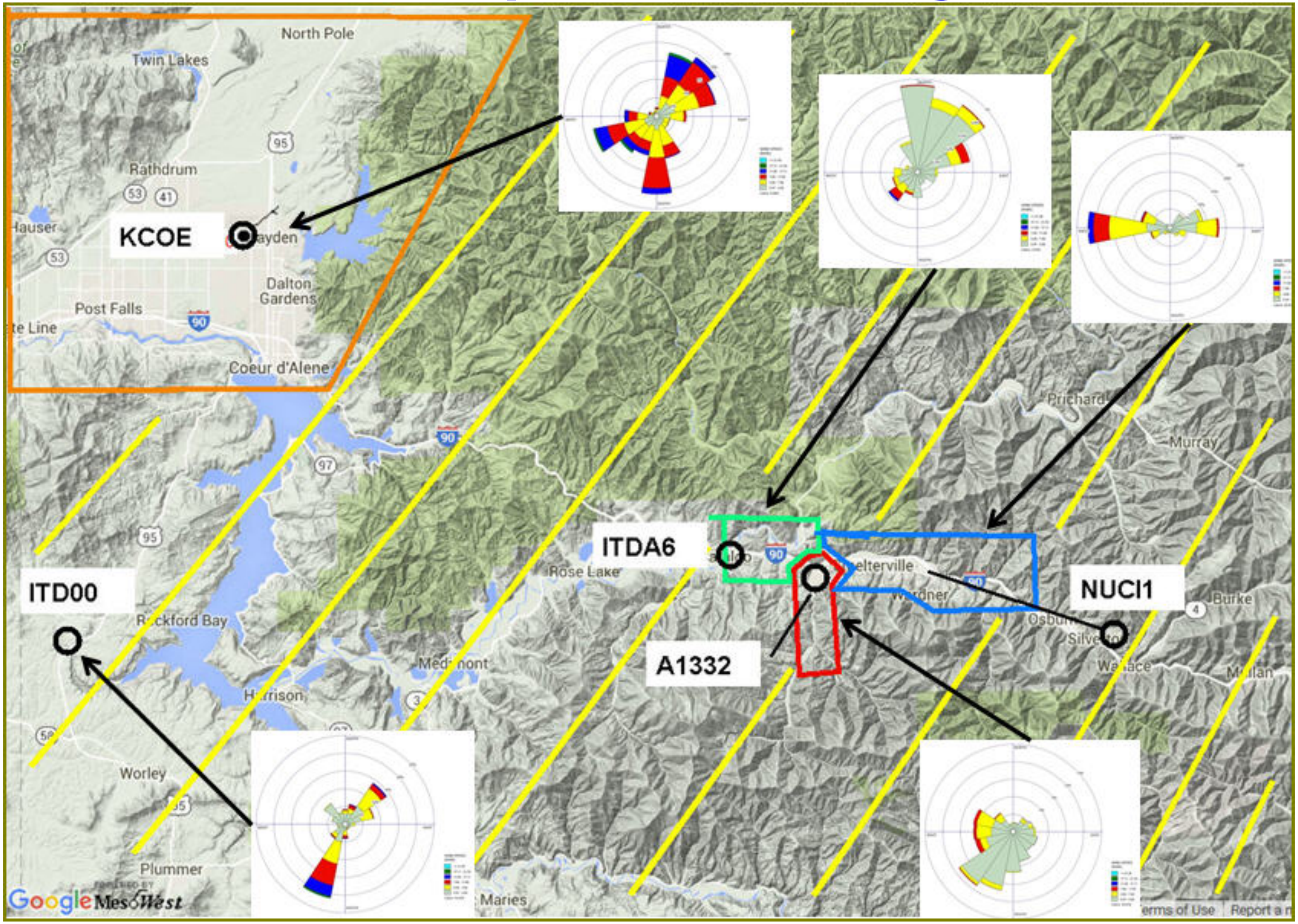
More Challenges in Regulatory Projects

- Precursor demonstrations for a nonattainment area:
  - (a) **Comprehensive precursor demonstration** (comprehensive refers to all source contributions combined)
    - ✓ **Concentration-based contribution analysis**: **If the contribution of the precursor (SOA) < 0.2 μg/m^3**), the EPA may approve the demonstration so that the state will not be required to control emissions of the relevant precursor from existing sources in the attainment plan.
  - (b) **Major stationary source** (i.e. > 100 tons per year) precursor demonstration
  - (c) **nonattainment new source review** (NNSR) precursor demonstration
- Legal issue: **What if SOA is underestimated**?
- Upper-bound SOA concentration
- SIP: 18 months
- **No VOC or SOA** measurements

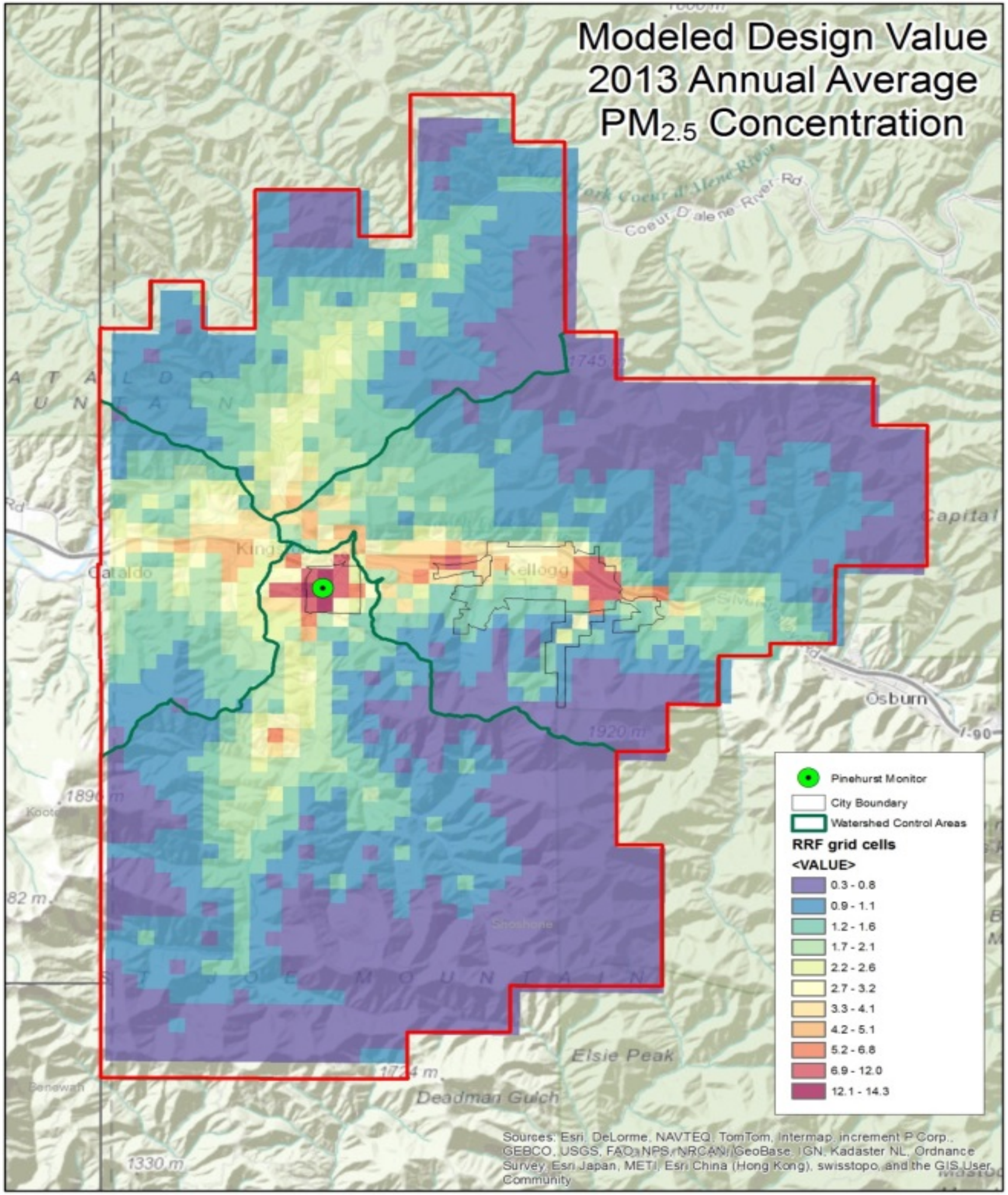
Our Approach



Dispersion Modeling

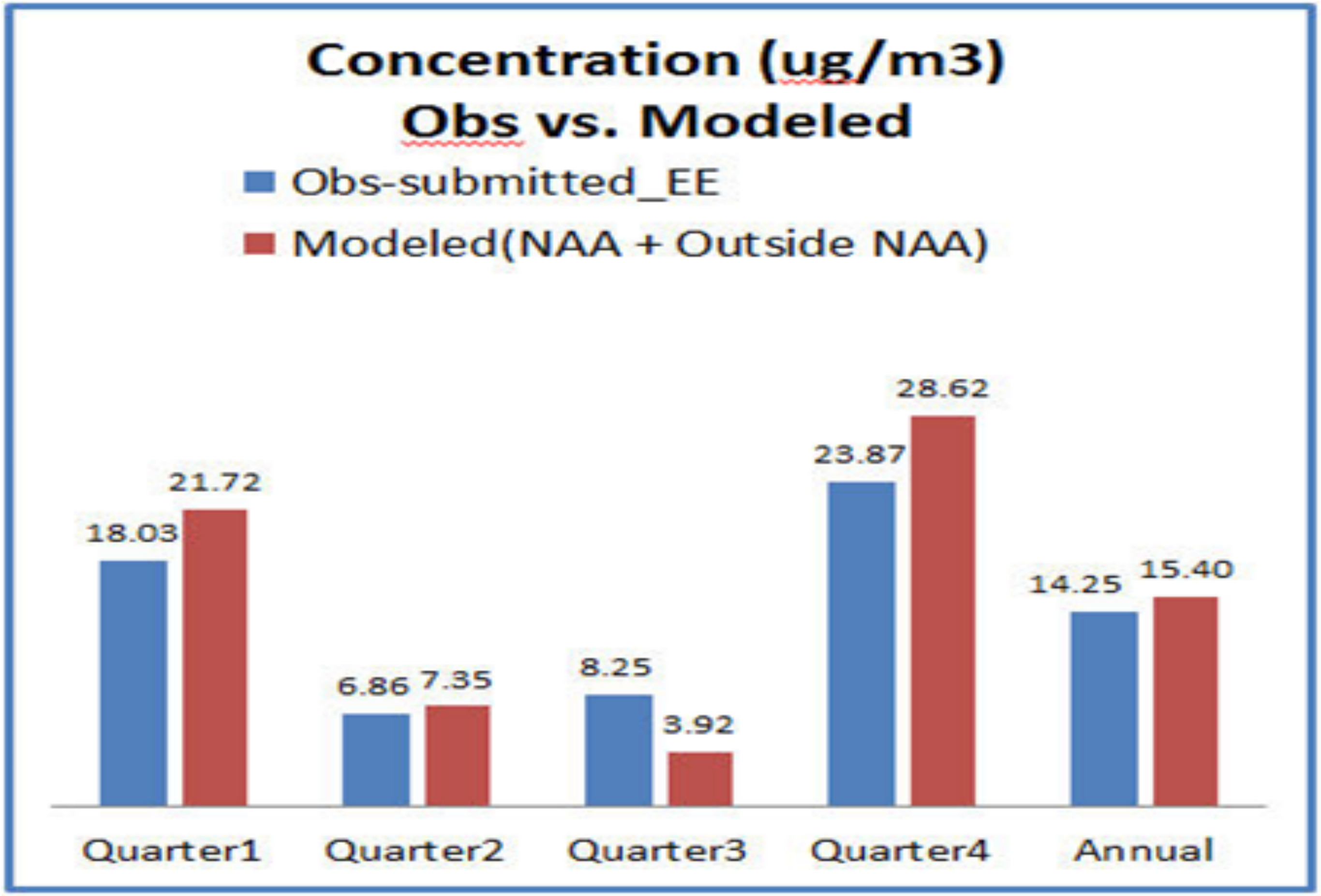


Representative meteorological sites with wind roses representing meteorological regions in the AERMOD modeling.



Spatial distribution of AERMOD-simulated annual $PM_{2.5}$ concentrations

Pinehurst: Quarterly modeled and observed $PM_{2.5}$ concentrations



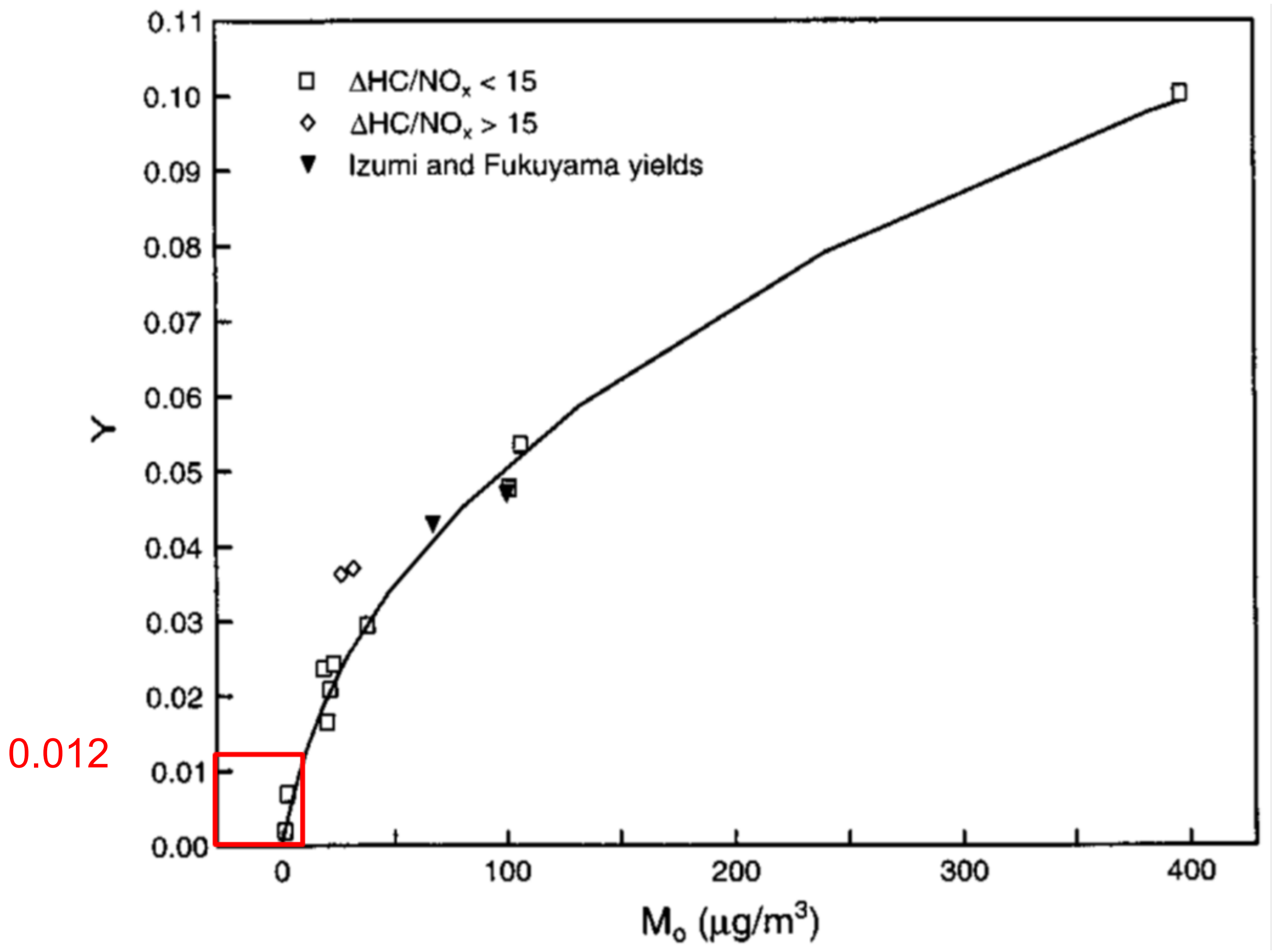
Concentrations (μg/m^3) of precursor species at the Pinehurst site

Lumped VOCs in Pinehurst
SAPRC-07 chemical mechanism in CMAQ

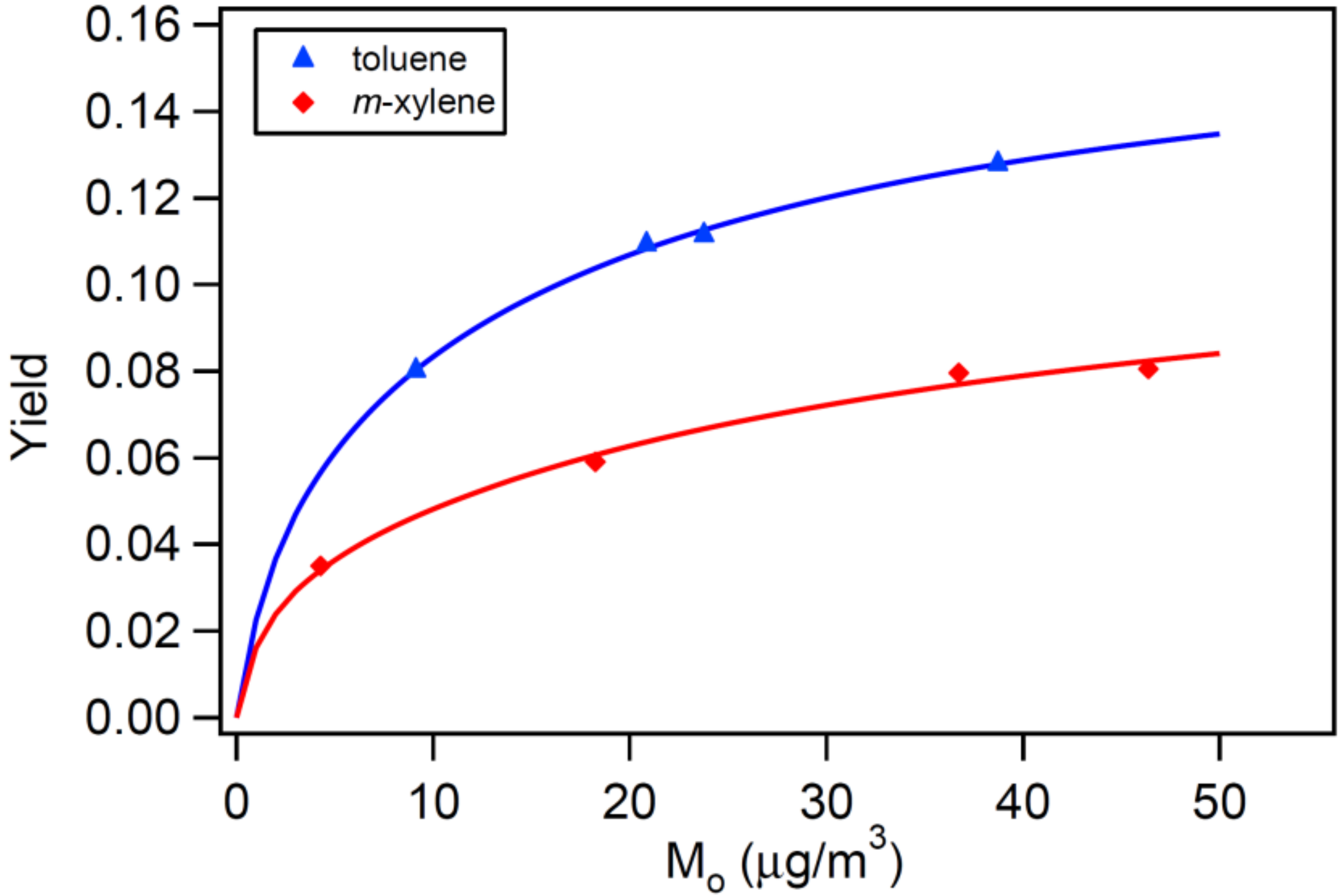
Species ID[a]	Species	Concentrations of all Sources	Concentrations of only Point Sources
ARO1	Toluene	1.59	0.04
ARO2	Xylene	2.87	0.01
BENZ	Benzene	0.80	0.01
ALK5	Alkanes	11.73	0.10
TERP	Terpenes	0.84	0.47
SUM		17.83	0.63

a. Species categories in CMAQ5 include ARO1 (high-yield aromatics represented by toluene), ARO2 (low-yield aromatics represented by xylene), BENZ (benzene), ALK5 (long-chain alkanes), and TERP (terpenes).

Aerosol yields for m-xylene (Odum et al., 1996).



Yield curves for toluene and m-xylene (Ng et al. 2007)



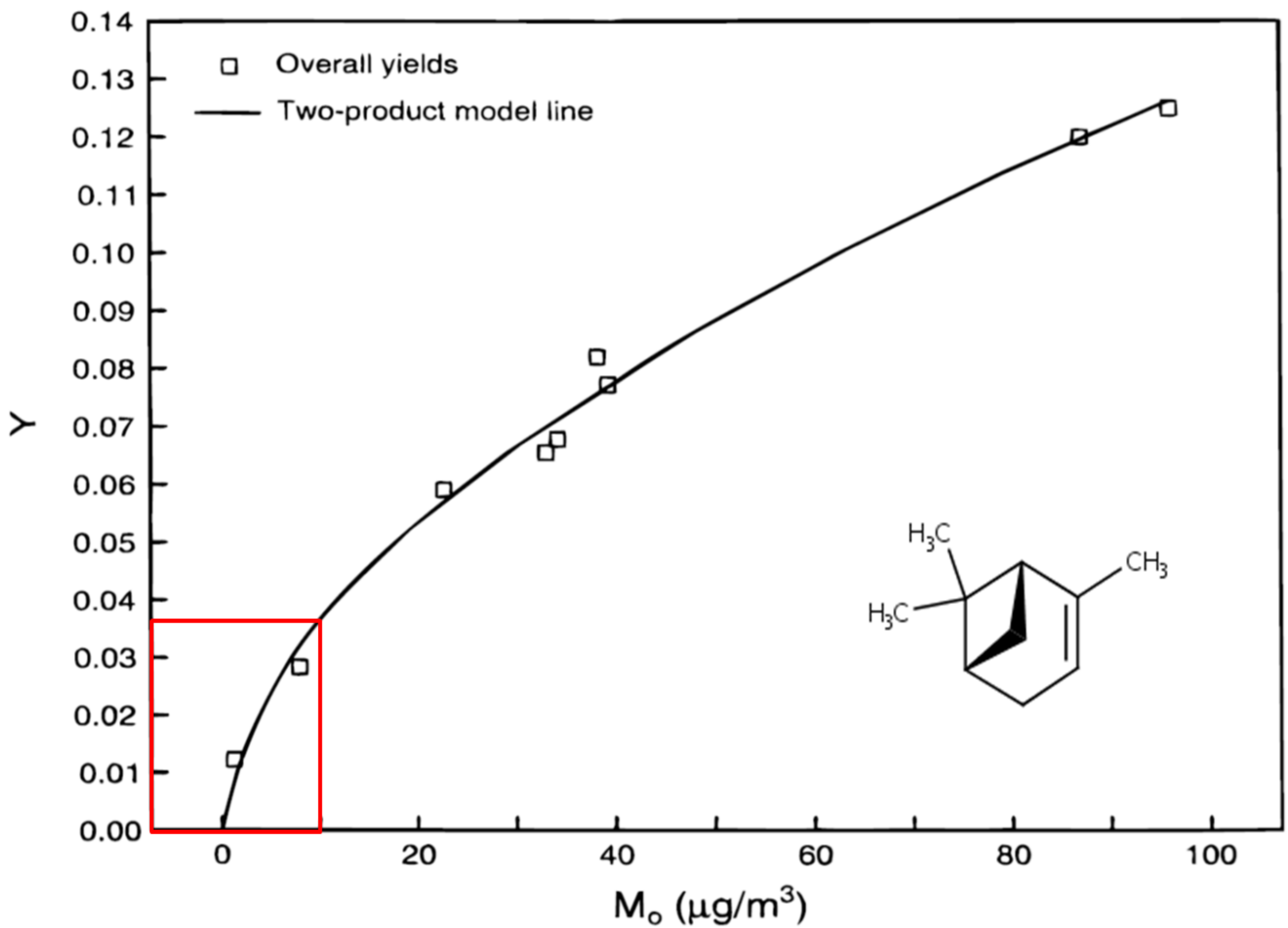
Benzene (Borrás and Tortajada-Genaro 2012)

- The results showed that SOA yield of benzene ranged from 1% to 3% at M_o for WSV.
- The highest yield among all conditions

SOA yields of alkanes (Gentner et al. 2012)

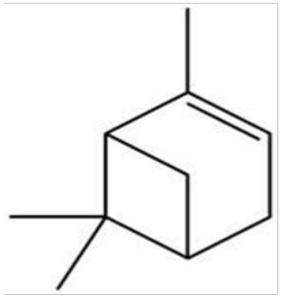
Carbon Number	Straight Chain Alkanes	Branched Alkanes	Cycloalkanes (Single Straight Alkyl Chain)	Cycloalkanes (Branched or Multiple Alkyl Chains)	Bicycloalkanes
8	0.0006	0.0001	0.0015 ± 0.0011	0.0002 ± 0.0002	—
9	0.0012	0.0002	0.0031 ± 0.0020	0.0005 ± 0.0003	0.0005 ± 0.0002

Yield curves for α-pinene (C10H16) (Odum et al., 1996)

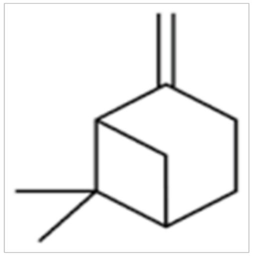


Terpenes (Zhao et al. 2015).

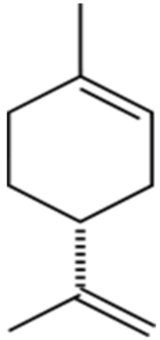
(a) α-pinene,

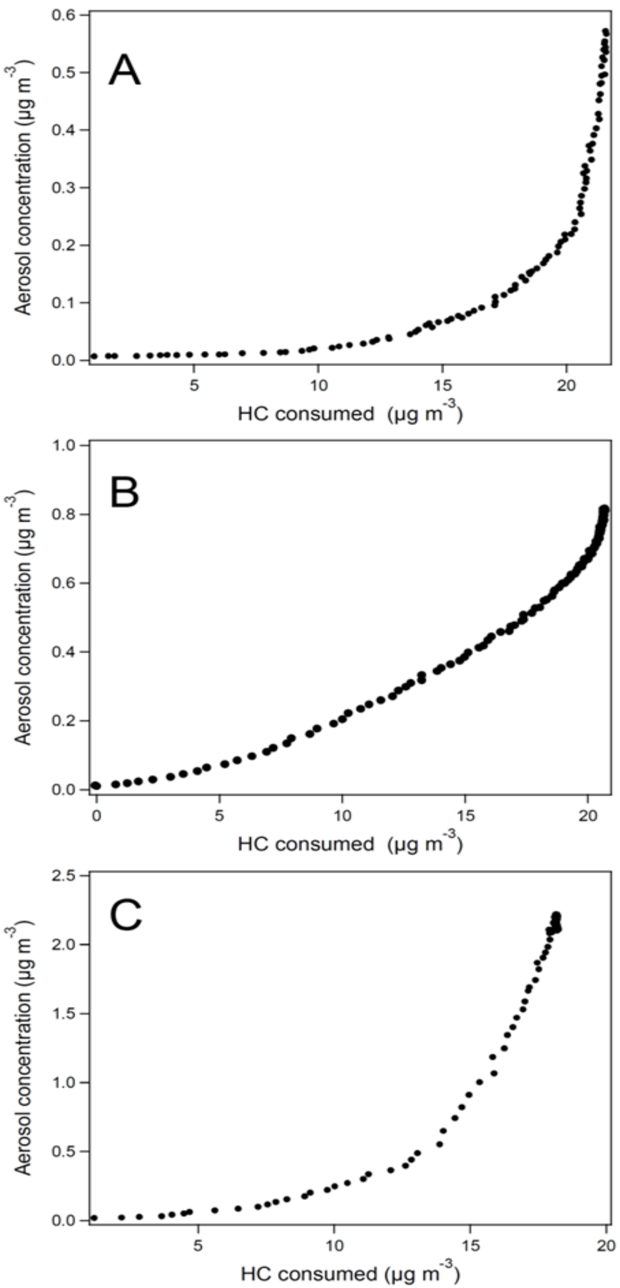


(b) β-pinene



(c) limonene





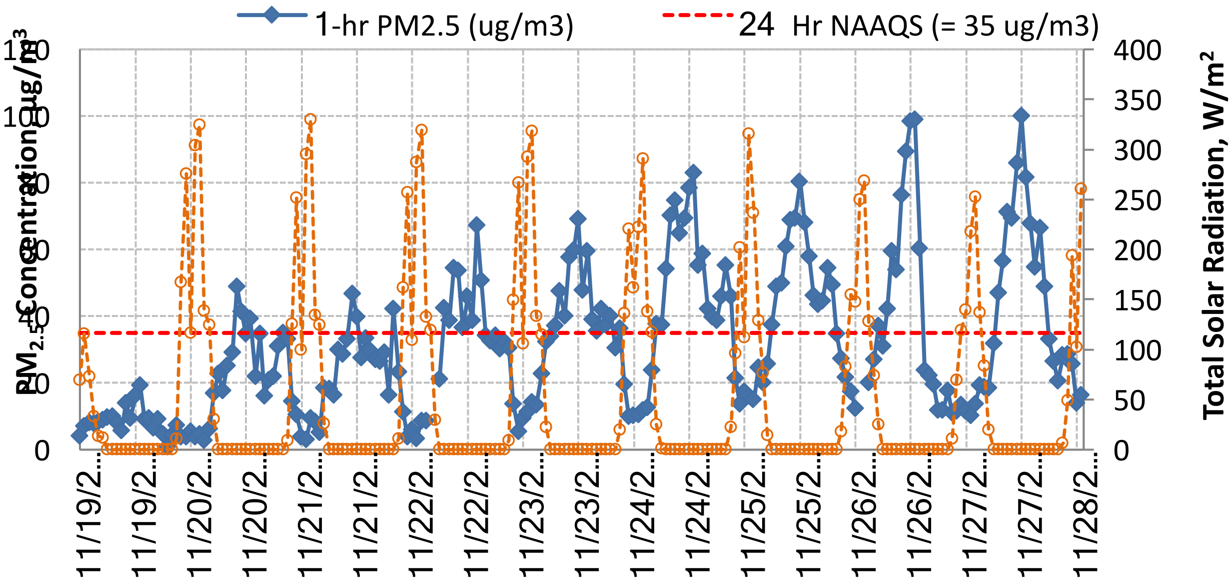
The ratio of a VOC that has reacted: $Ratio_i = 1 - e^{-k_{i,OH}[OH]\Delta t}$

Species ID[a]	Species	K (cm3 molecule-1 s-1)	References	K used in WSV Study (cm3 molecule-1 s-1)	[OH] (molecules/cm-3)	Δt (hours)
ARO1	Toluene	5.6×10^{-12}	Ziemann and Atkinson 2012)	5.6×10^{-12}	1.5×10^{6}	24
ARO2	Xylene	2.3×10^{-11}	Atkinson and Aschmann 1989	2.3×10^{-11}		
BENZ	Benzene	1.23×10^{-12}	Warneke et al. 2004	1.23×10^{-12}		
ALK5	Alkanes	8.1×10^{-12}	Ziemann and Atkinson 2012	8.1×10^{-12}		
TERP	Terpenes	5.37×10^{-11}	Warneke et al. 2004	6.63×10^{-11}		
		7.89×10^{-11}	Warneke et al. 2004			

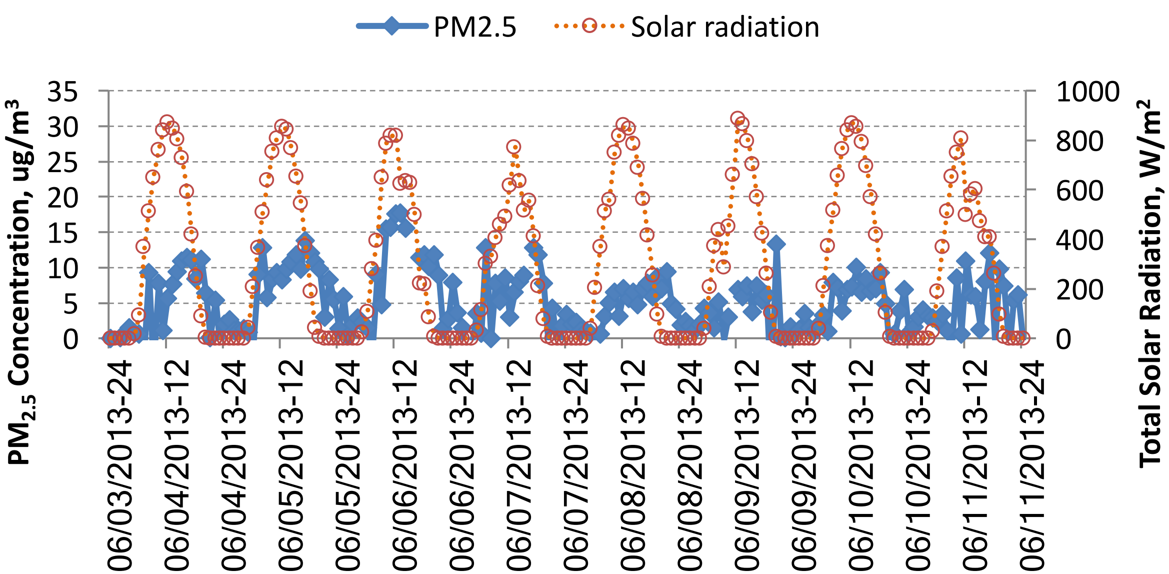
a. Species categories in CMAQ5 include ARO1 (high-yield aromatics represented by toluene), ARO2 (low-yield aromatics represented by xylene), BENZ (benzene), ALK5 (long-chain alkanes), and TERP (terpenes).

12-h daytime OH concentration (Seinfeld and Pandis 2016)

Pinehurst $PM_{2.5}$ and Solar Radiation



Pinehurst $PM_{2.5}$ and Solar Radiation - June



Upper-bound SOA

Species ID	Species	Reacted ratio	SOA (µg/m^3)	SOA % of Design Value
ARO1	Toluene	0.52	0.0667	0.539
ARO2	Xylene	0.95	0.0790	0.639
BENZ	Benzene	0.15	0.0035	0.028
ALK5	Alkanes	0.65	0.0066	0.054
TERP	Terpenes	1.00	0.0301	0.24
SUM			0.186	1.5

SUMMARY

- Final rule and draft $PM_{2.5}$ Precursor Demonstration Guidance: Implications for SOA
- Estimating SOA for regulatory projects is challenging
- An approach that combine emission inventories, meteorology, dispersion model, CMAQ speciation, yield, and kinetic
- Upper-bound SOA concentration
- Tool for places where photochemical models do not perform well