SECONDARY ORGANIC AEROSOL RESEARCH: CURRENT AND EMERGING ISSUES

Shaokai Gao
02/09/2016
Atlanta, Georgia
CRC Air Quality Research Needs Workshop

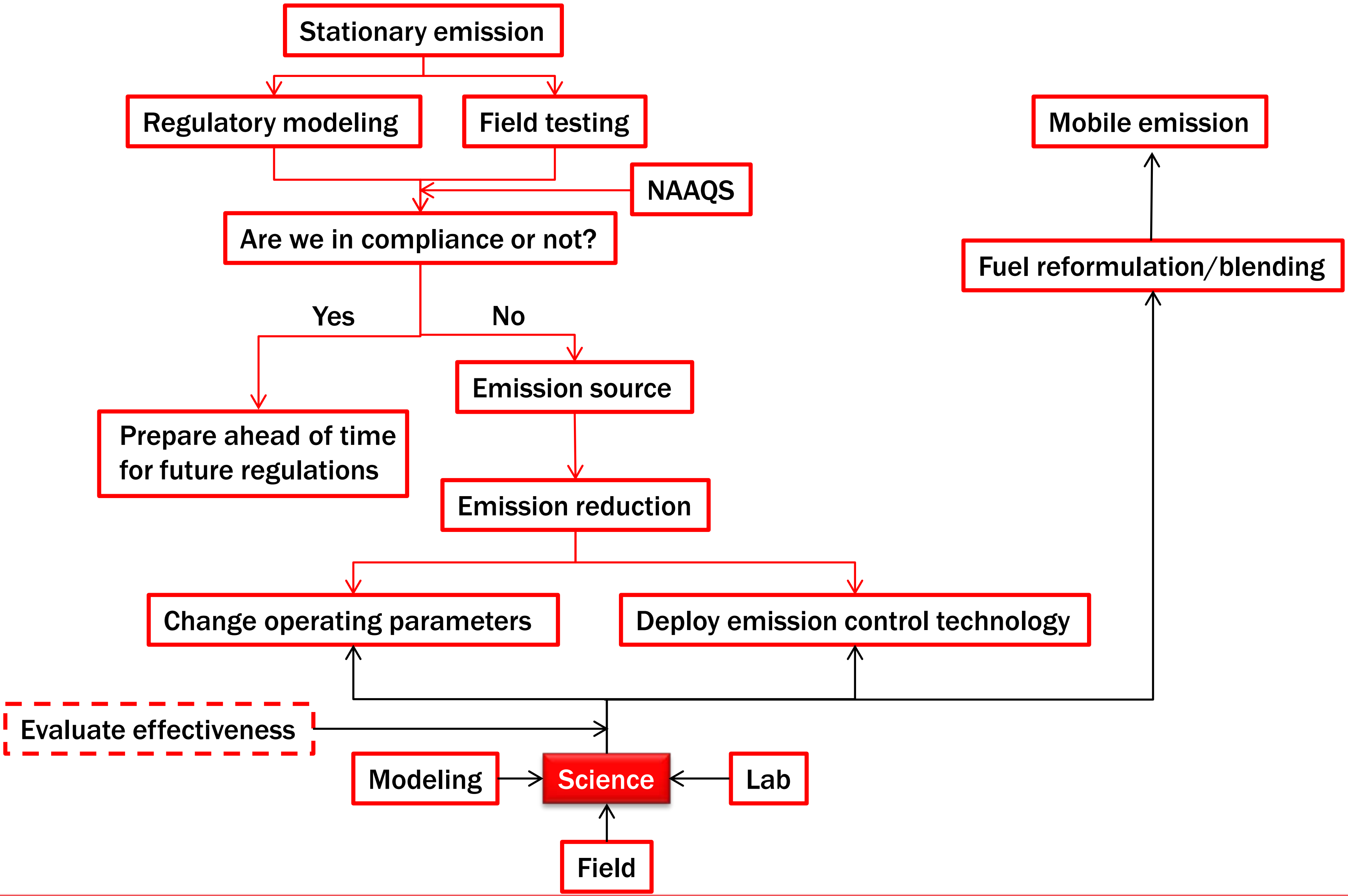
OUTLINE

- Why do we care?
  - U.S. oil and gas environmental expenditure
  - Regulations
- Current Research Needs
  - SOA Budget
  - SOA Modeling
  - SOA Formation
  - SOA Complexity
  - SOA Composition
- Summary

PHILLIPS 66 AIR PROGRAM

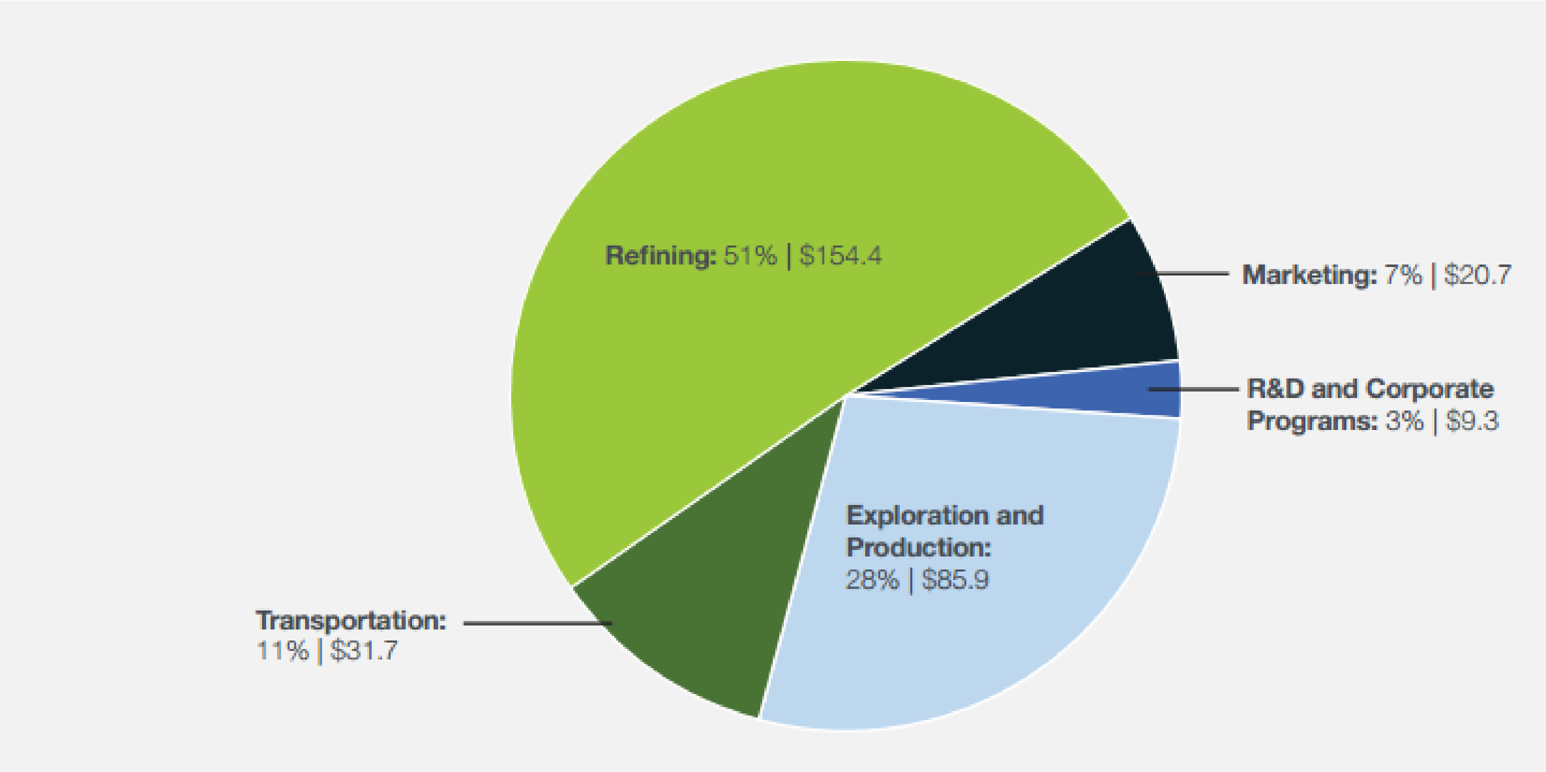
- Ambient Air Measurements
- Environmental Chamber Experiments
  - Nighttime chemistry
  - Outdoor chamber
- Modeling
- Business Unit Support

WHY DO WE CARE



WHY DO WE CARE – OIL & GAS ENVIRONMENTAL EXPENDITURE

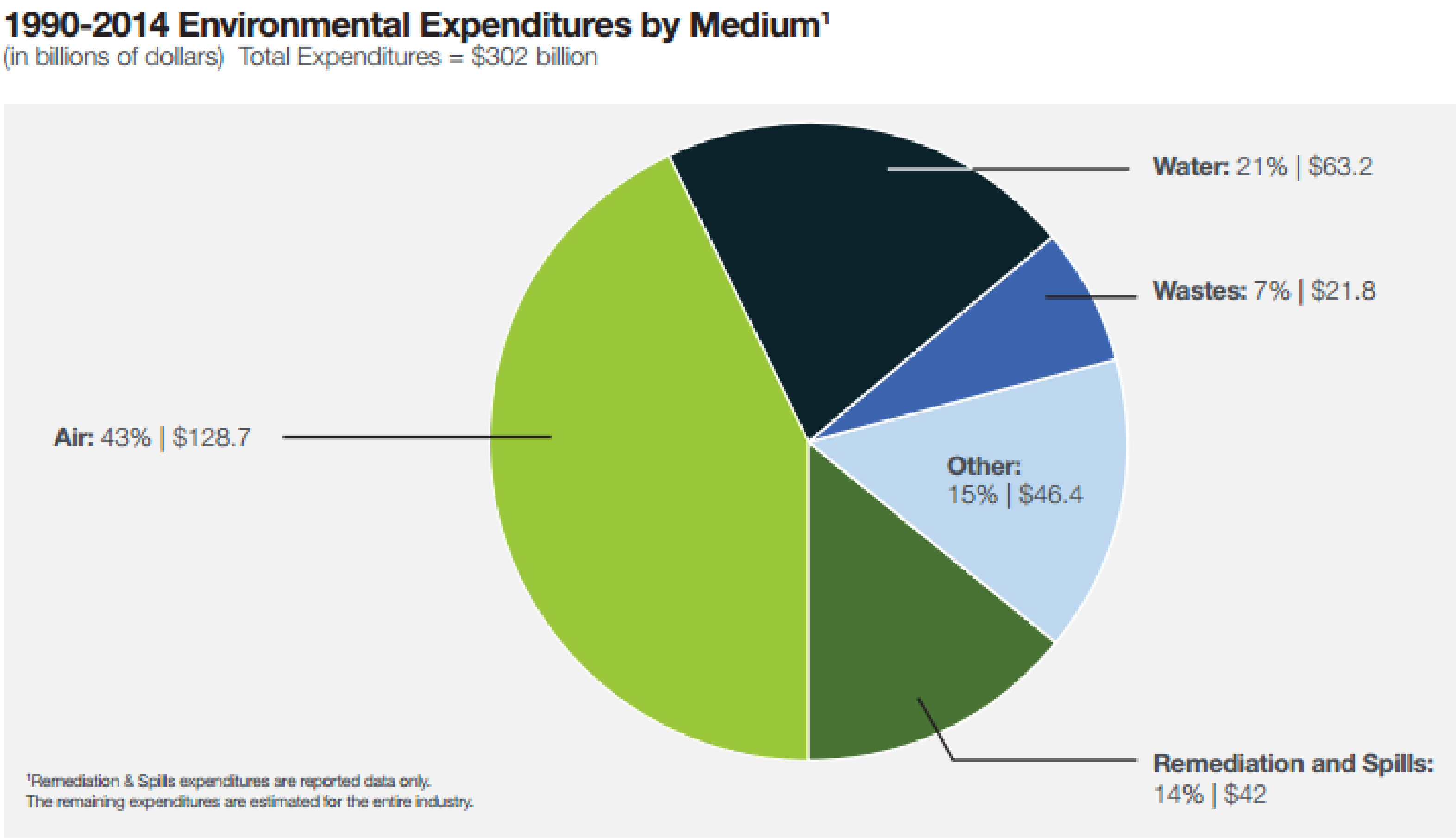
Spending on the Environment per Business Sector since 1990[1]
1990 - 2014: Total Expenditures = $302.0 Billion



[1] Remediation & Spills expenditures are included in the sector numbers and are reported data only.
The remaining sector expenditures are estimated for the entire industry

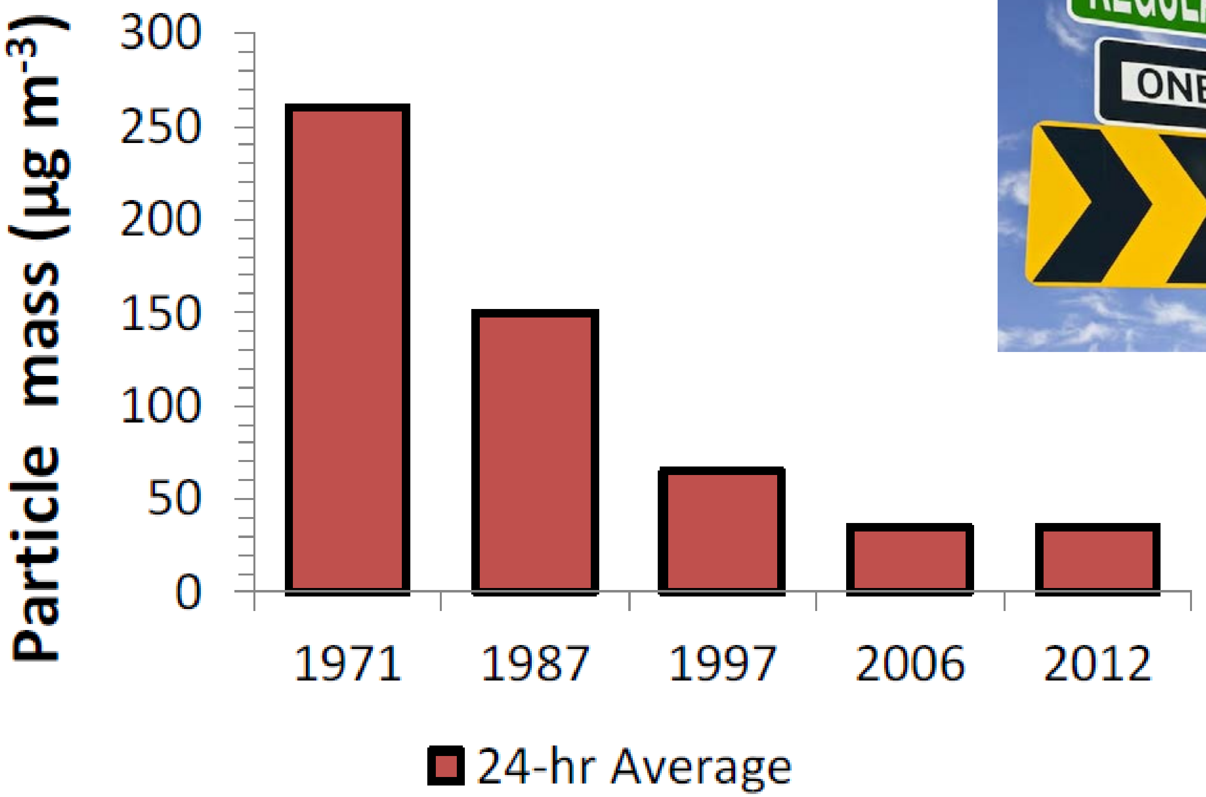
U.S. oil and gas industry environmental expenditures (1990-2014)

WHY DO WE CARE – OIL & GAS ENVIRONMENTAL EXPENDITURE



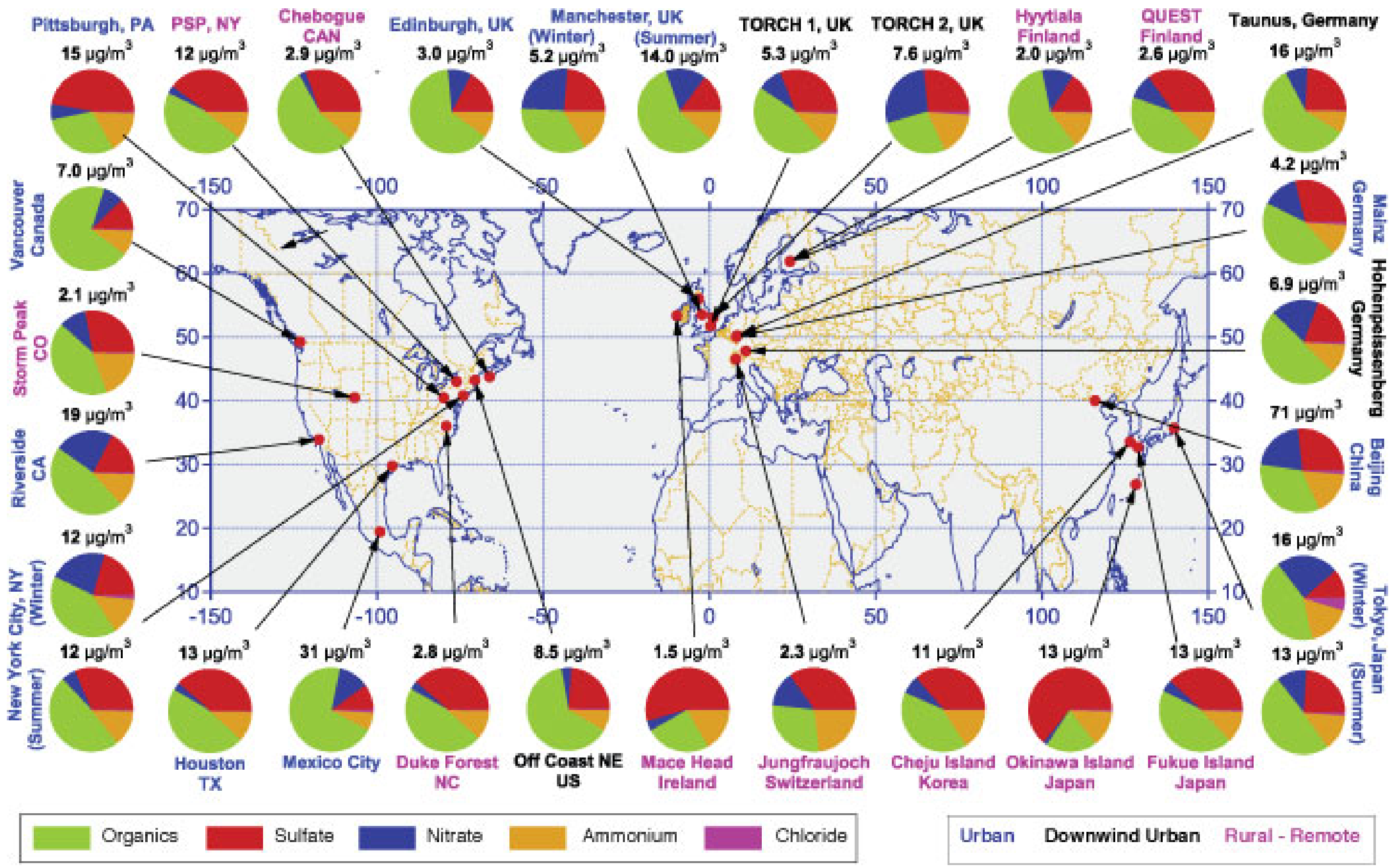
A majority of the investment – both historically and in 2014 – has focused on achieving reductions in airborne emissions

WHY DO WE CARE – HISTORICAL PM STANDARDS



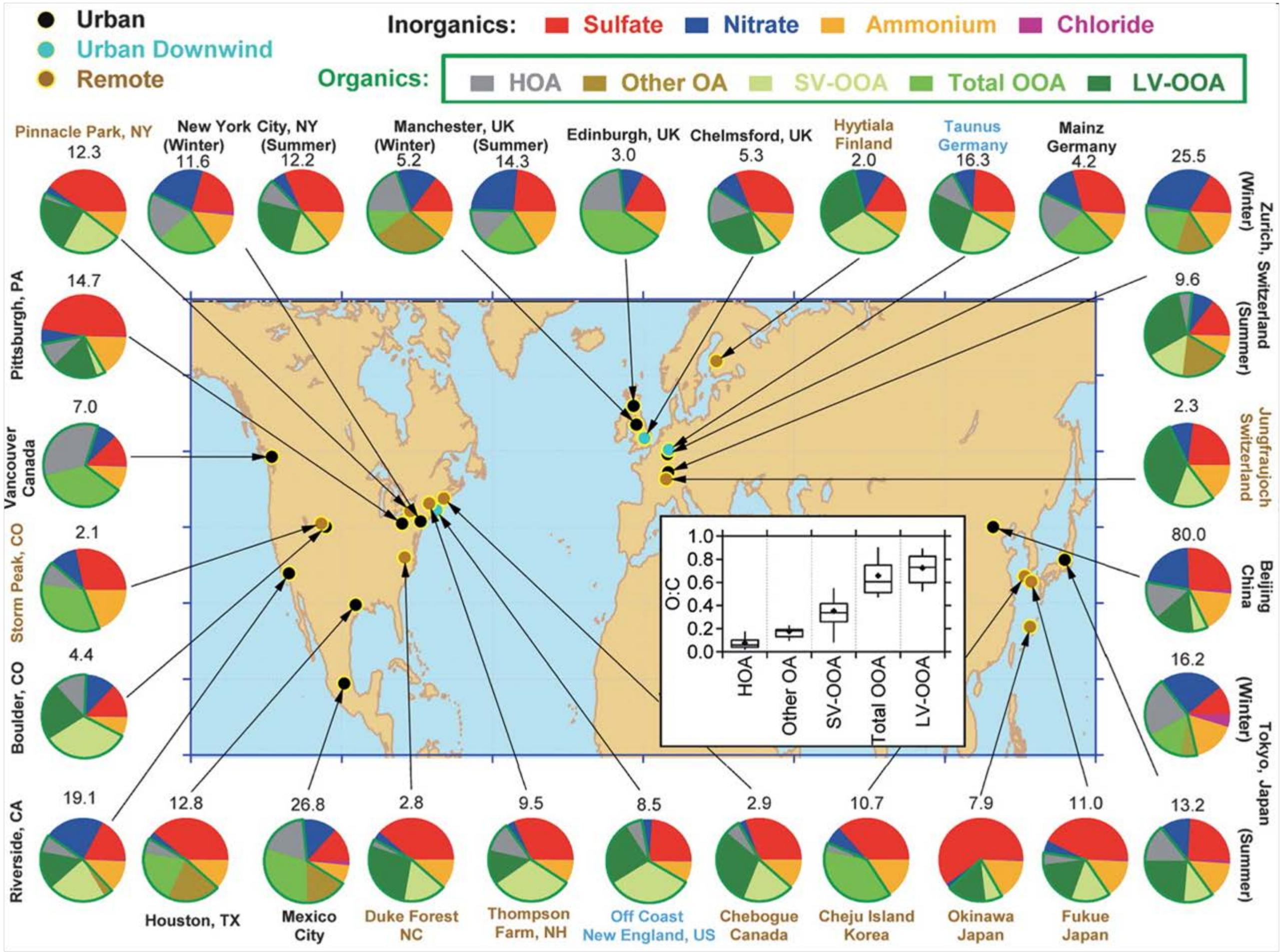
Industry faces more and more challenges to meet compliances in a changing regulatory landscape

WHY DO WE CARE –AEROSOL COMPOSITION



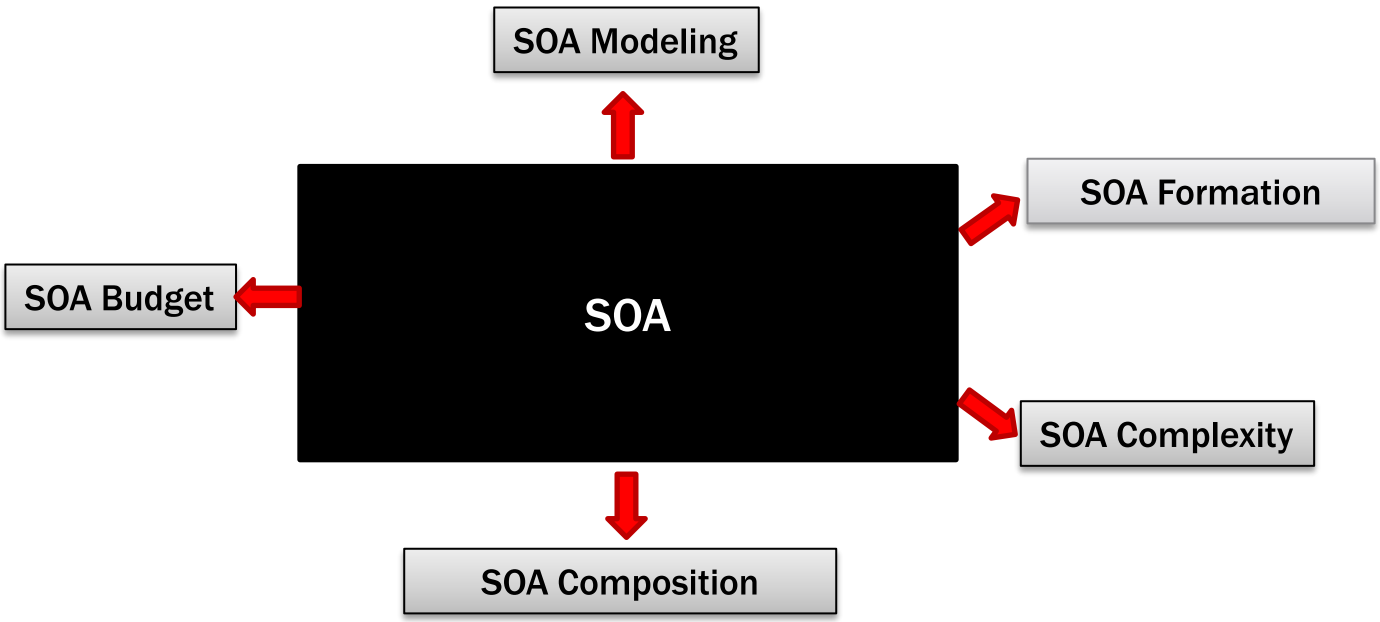
Organic material contributes significantly to $PM_{2.5}$ mass across the globe, and is least understood

WHY DO WE CARE – SECONDARY ORGANIC AEROSOL (SOA)



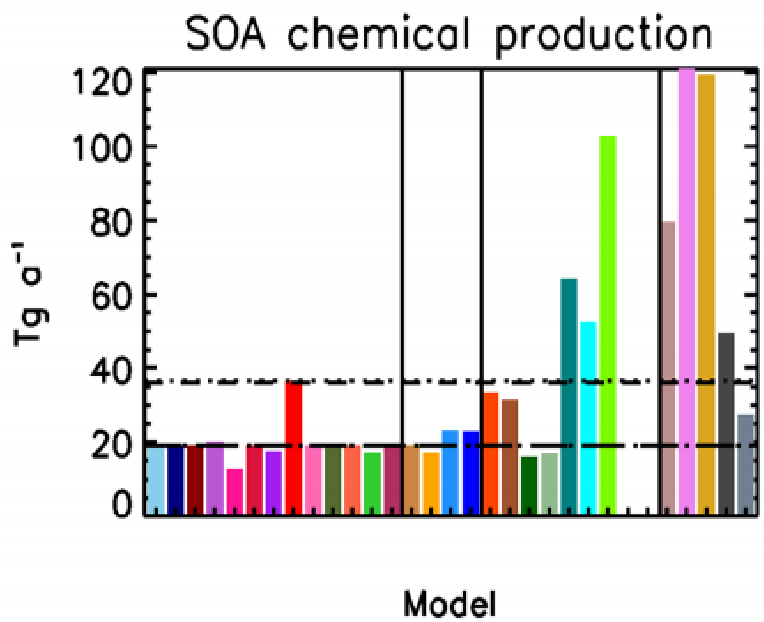
Secondary organic aerosols (SOA) take a large fraction of the total particulate matter

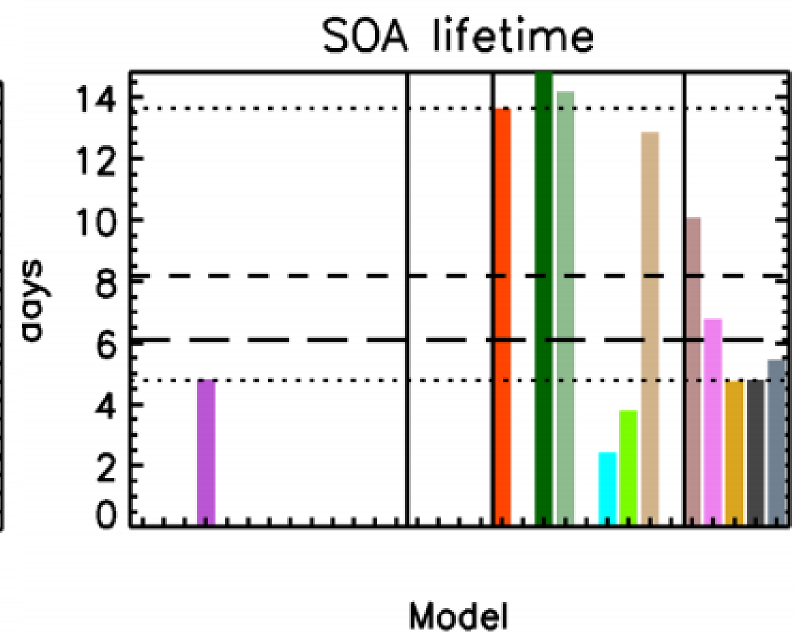
CURRENT RESEARCH NEEDS



The black box is still there waiting to be opened little by little

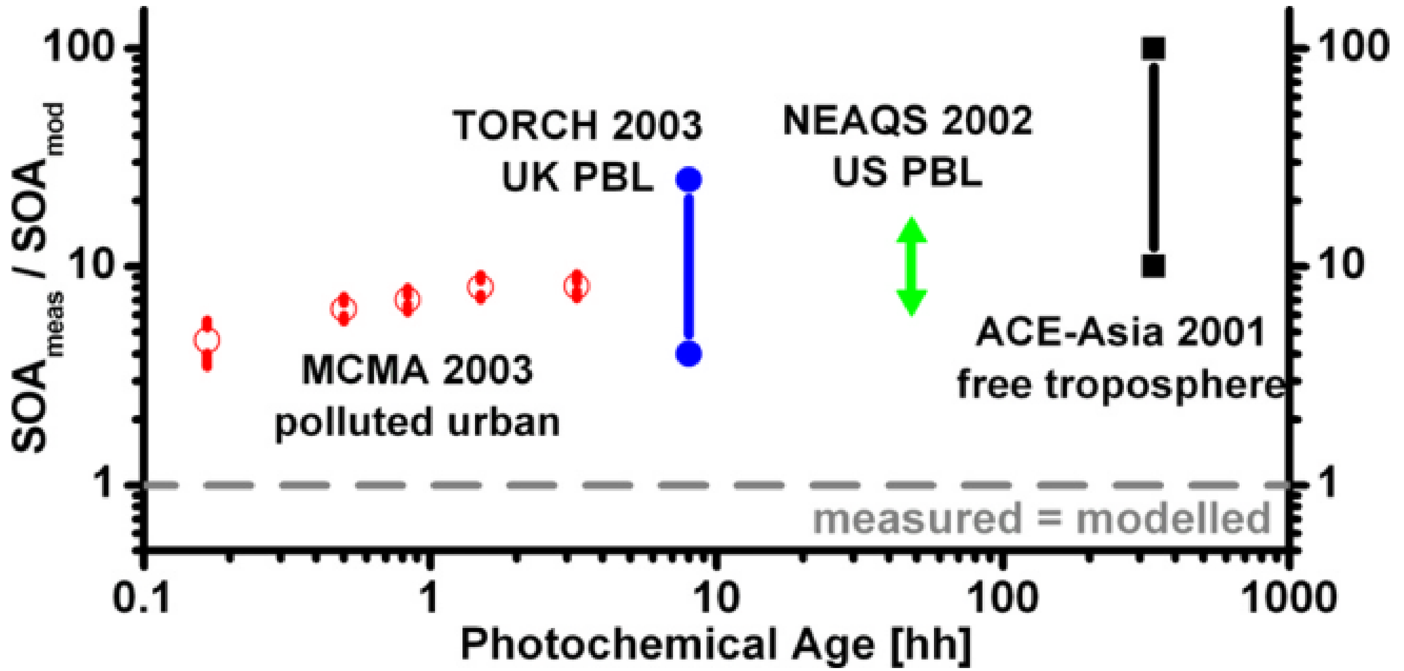
CURRENT RESEARCH NEEDS – SOA BUDGET





SOA formation/removal parameterization still needs to be improved

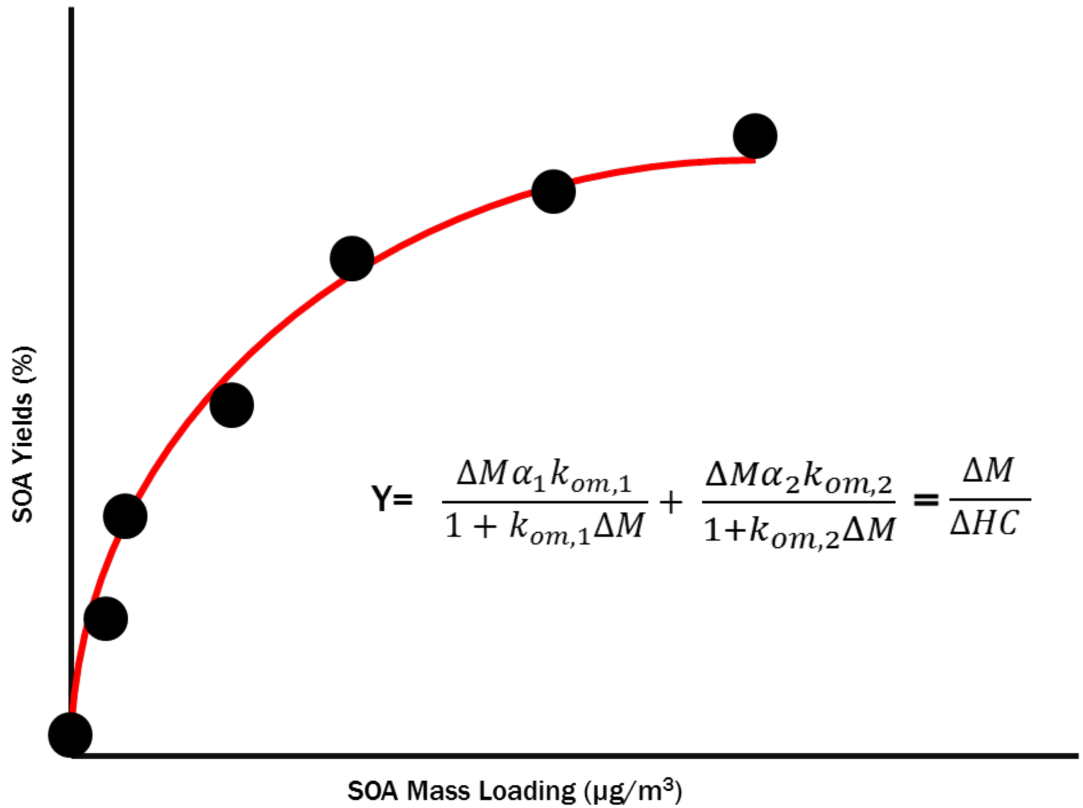
CURRENT RESEARCH NEEDS – SOA MODELING



Model can not reproduce the measured results

CURRENT RESEARCH NEEDS – SOA MODELING

MODELING SOA: 2-product Model (APPROACH #1)



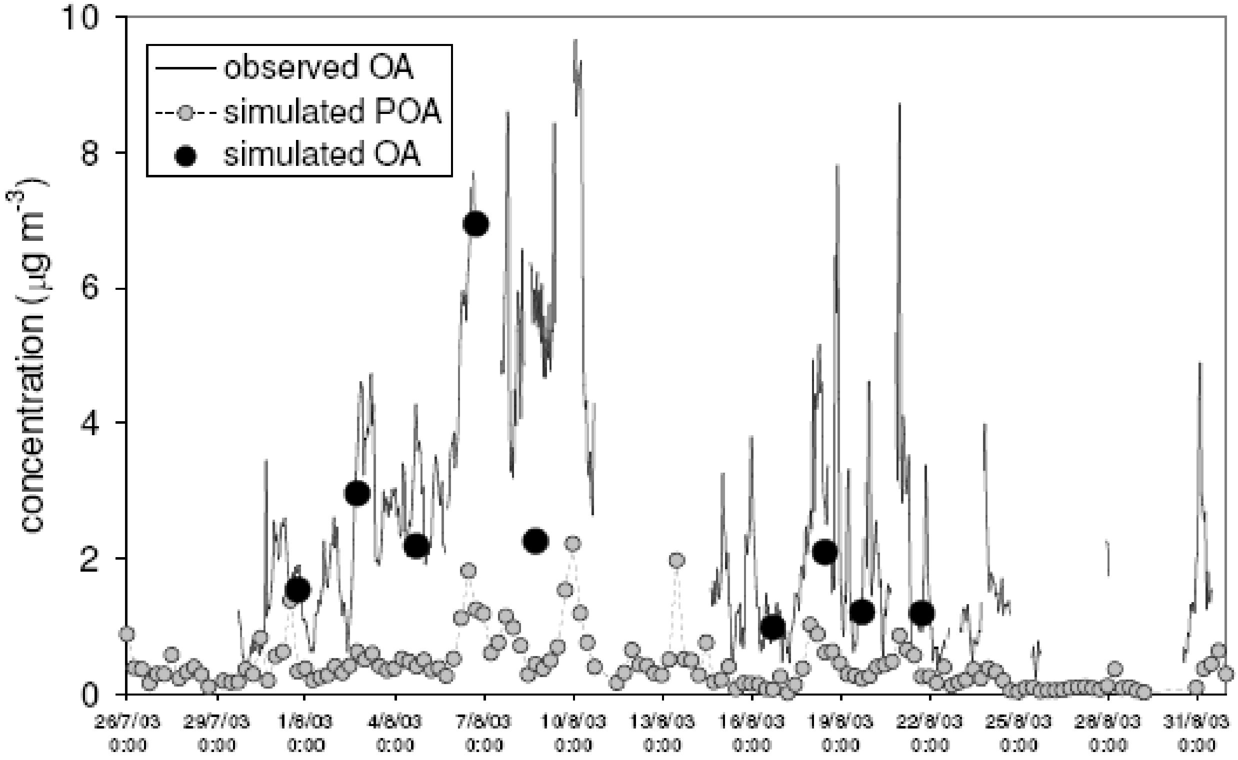
$$Y = \frac{\Delta M \alpha_1 k_{om,1}}{1 + k_{om,1}\Delta M} + \frac{\Delta M \alpha_2 k_{om,2}}{1 + k_{om,2}\Delta M} = \frac{\Delta M}{\Delta HC}$$

Chamber data provides direct modeling parameters (α_1, $k_{om,1}$, α_2, $k_{om,2}$)

2-product model was used in most global/regional models, gas phase adsorption to particle surfaces is typically neglected

CURRENT RESEARCH NEEDS – SOA MODELING

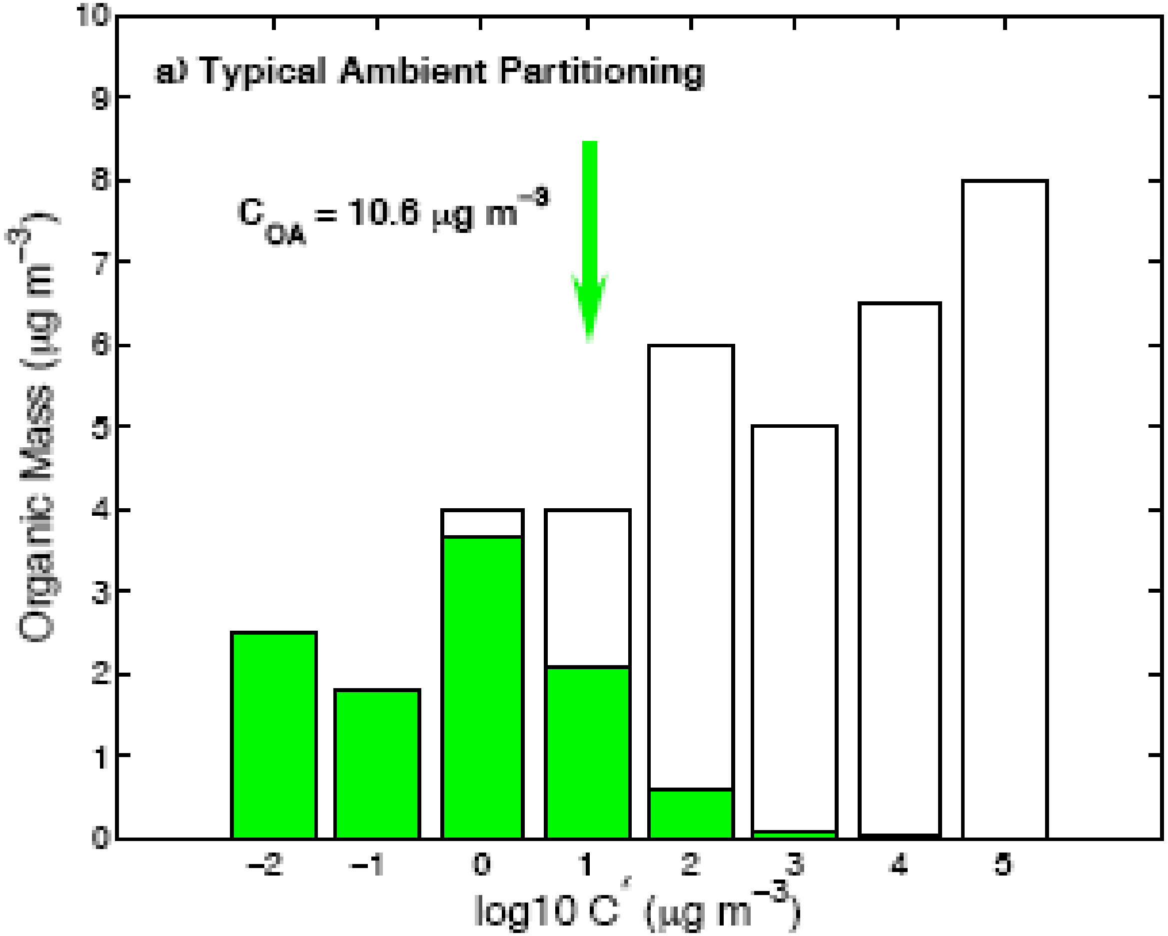
MODELING SOA: Explicit Chemistry (APPROACH #2)



Need to increase partitioning coefficients by factor of 500 to match with the observed data

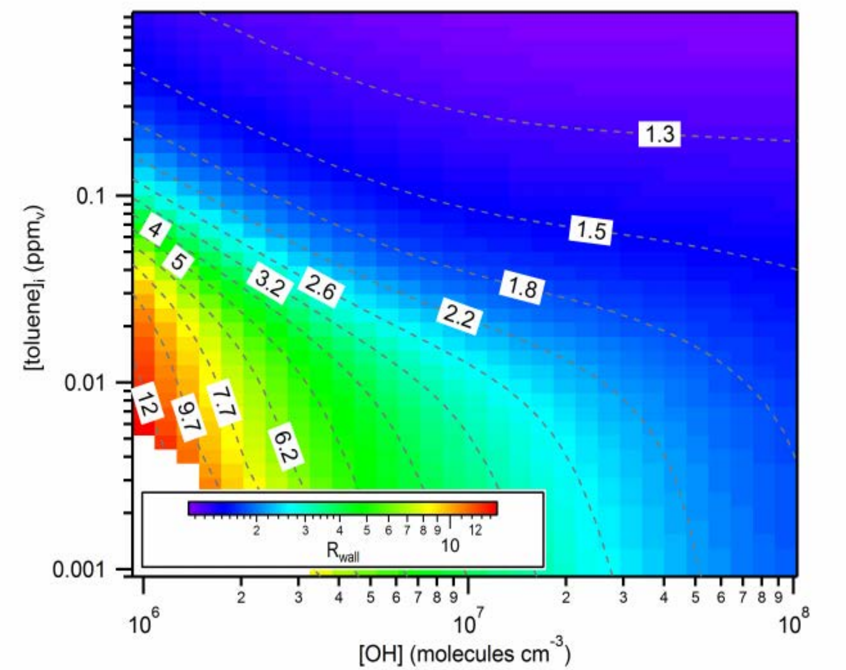
CURRENT RESEARCH NEEDS – SOA MODELING

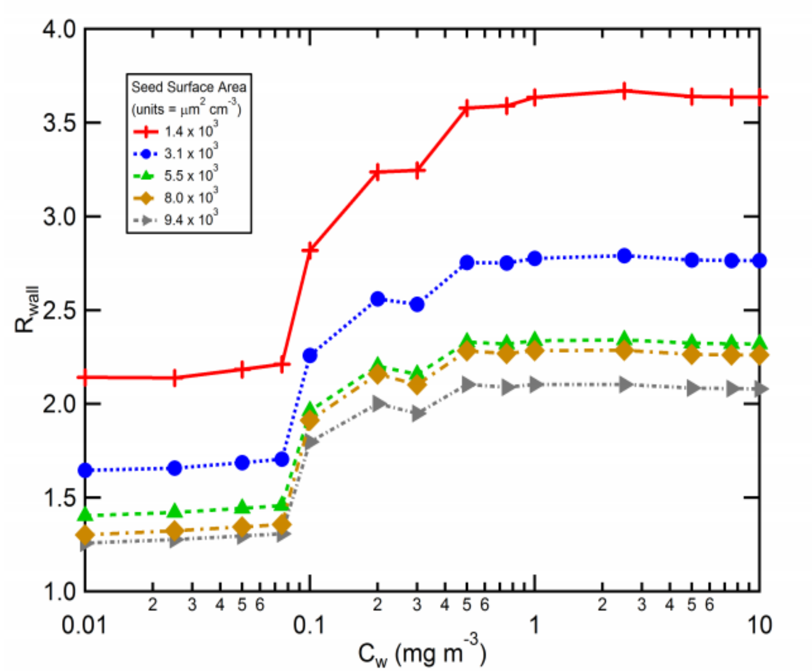
MODELING SOA: Volatility Basis Set (APPROACH #3)



CURRENT RESEARCH NEEDS – SOA FORMATION

Chamber Process: Vapor Wall Loss



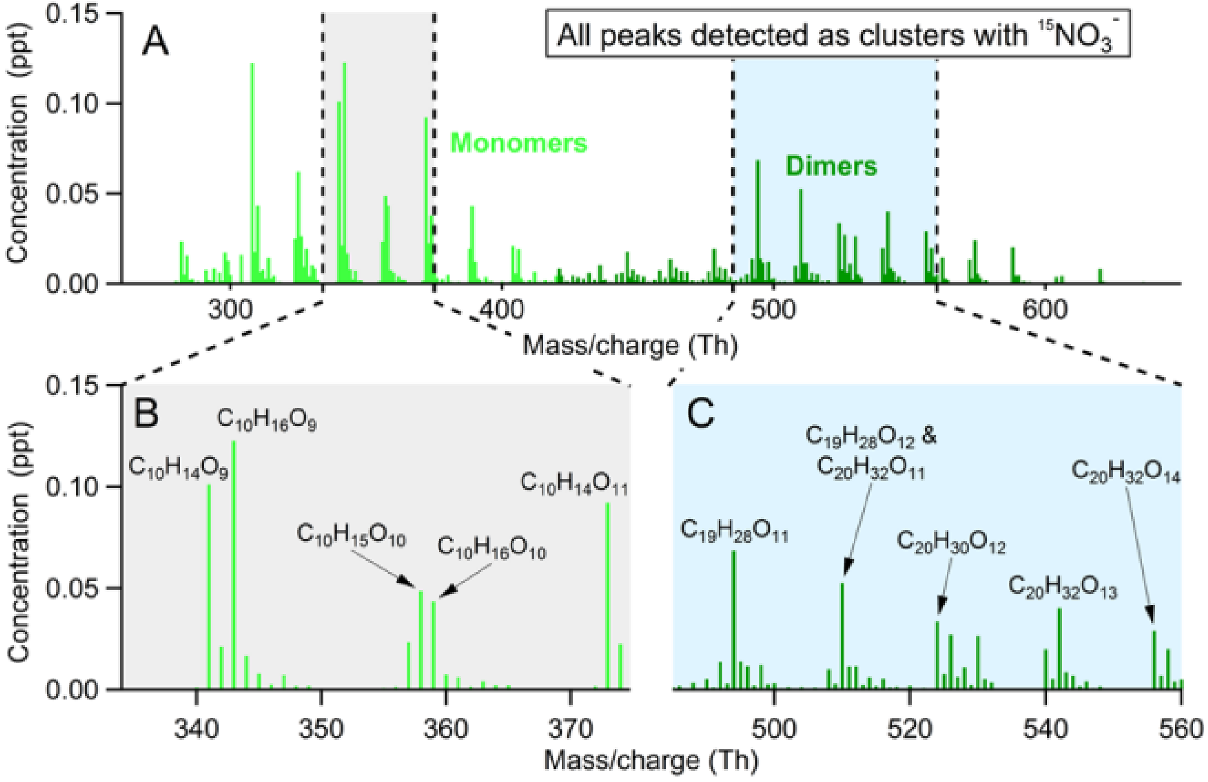


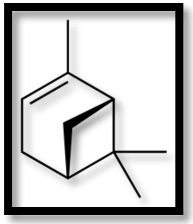
Chamber vapor wall loss could partially account for the disagreement between simulated and observed data

CURRENT RESEARCH NEEDS – SOA FORMATION

Reaction Pathway: Formation of Extremely Low Volatility Products

Mass spec from alpha-pinene ozonolysis

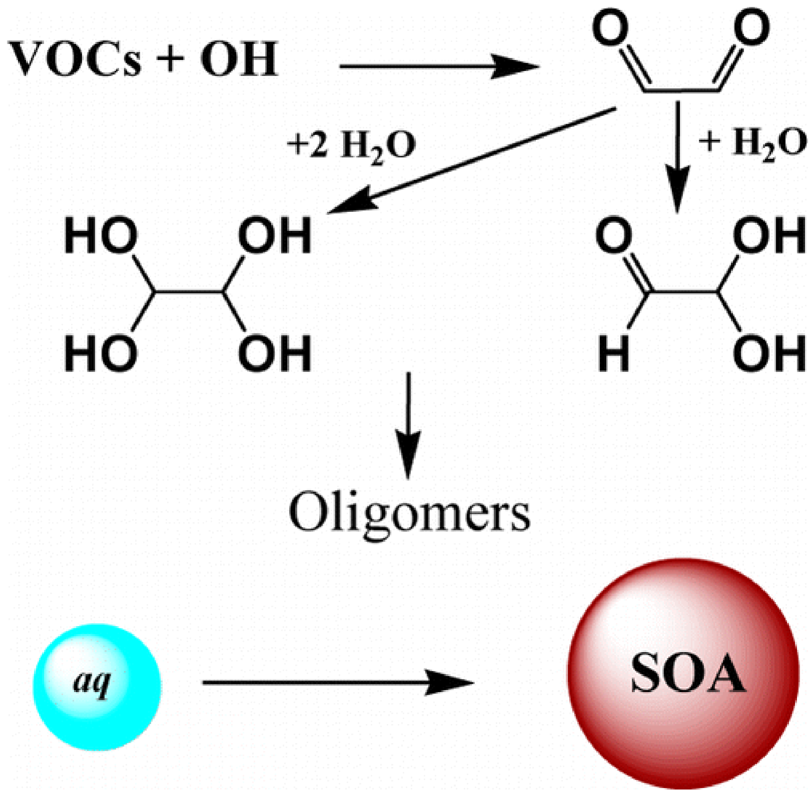




Source and composition for non-volatile organic vapors that contribute to SOA formation was poorly understood

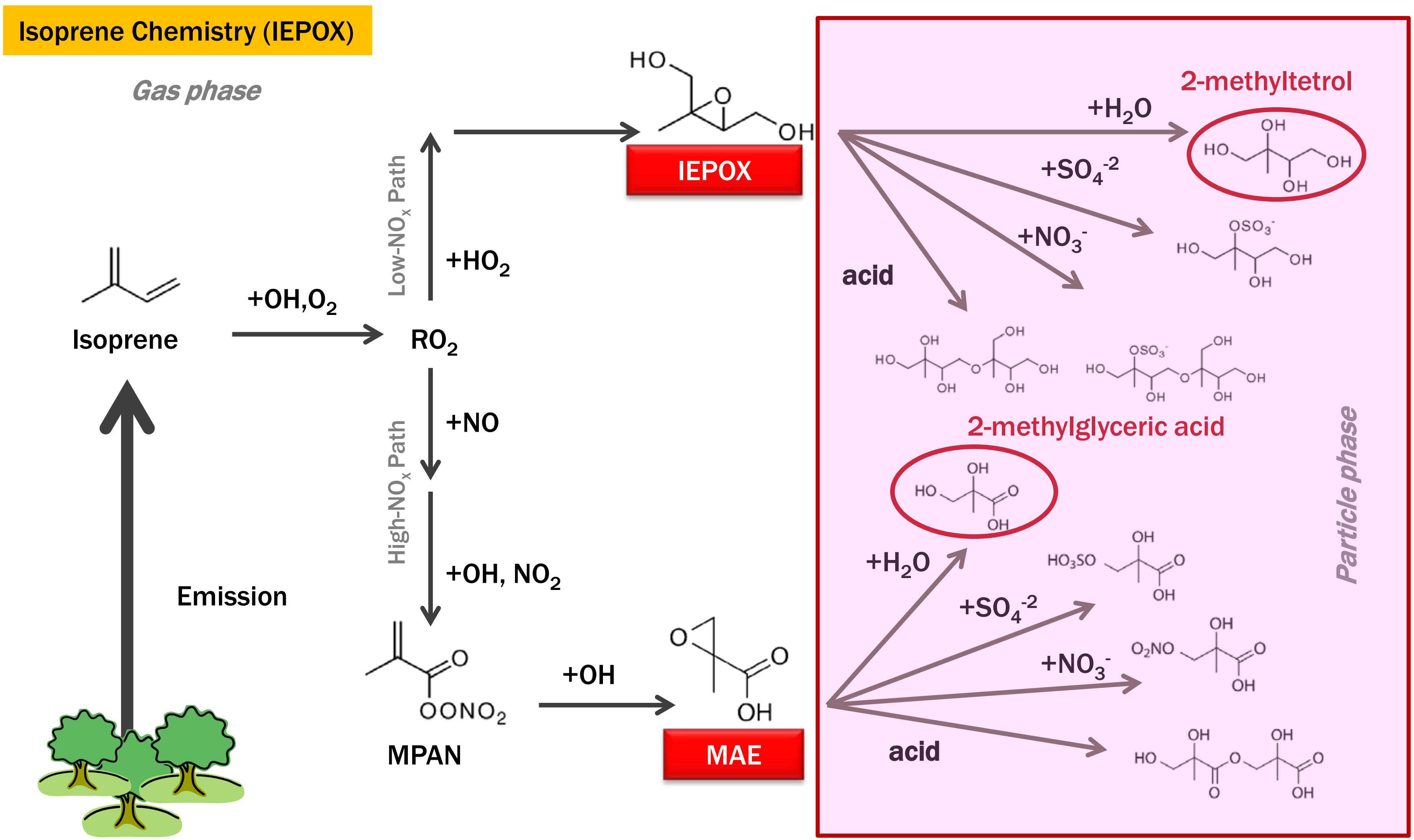
CURRENT RESEARCH NEEDS – SOA FORMATION

Reaction Pathway: Heterogeneous Chemistry
— Pathway for small molecules to contribute to SOA formation



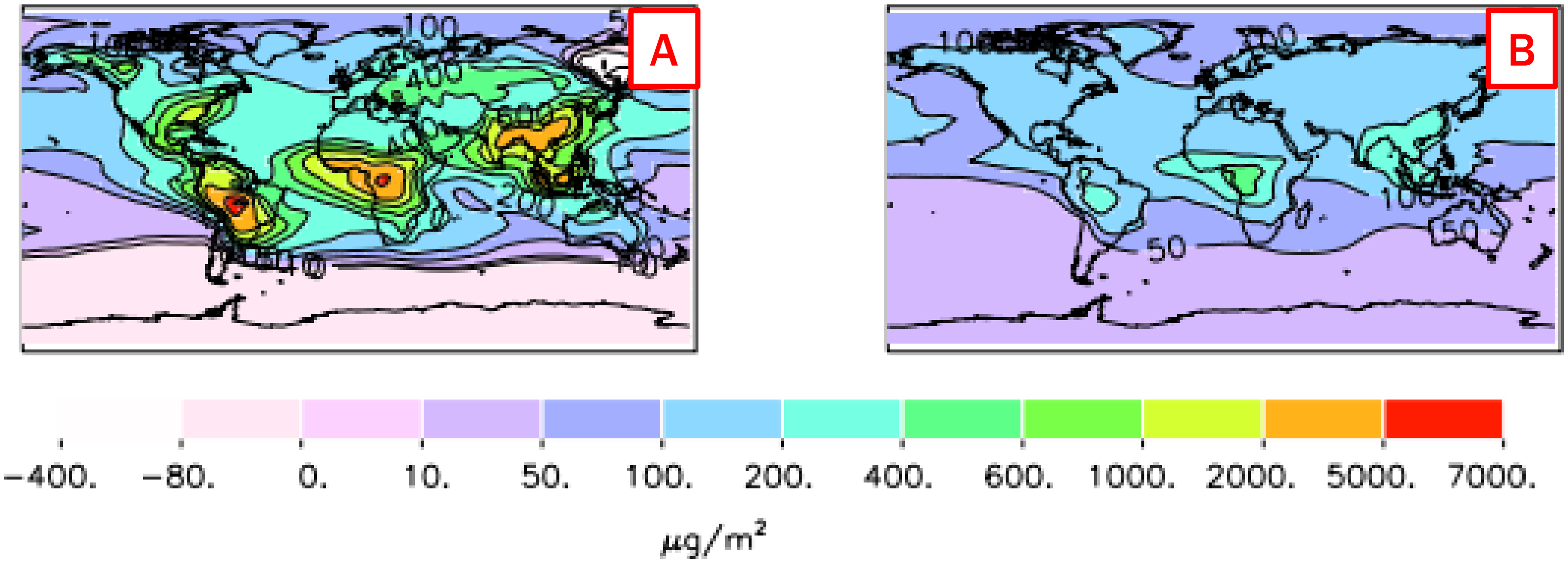
Heterogeneous chemistry of glyoxal on acidic solutions leads to SOA formation through hydration and oligomerization

CURRENT RESEARCH NEEDS – SOA FORMATION



CURRENT RESEARCH NEEDS – SOA FORMATION

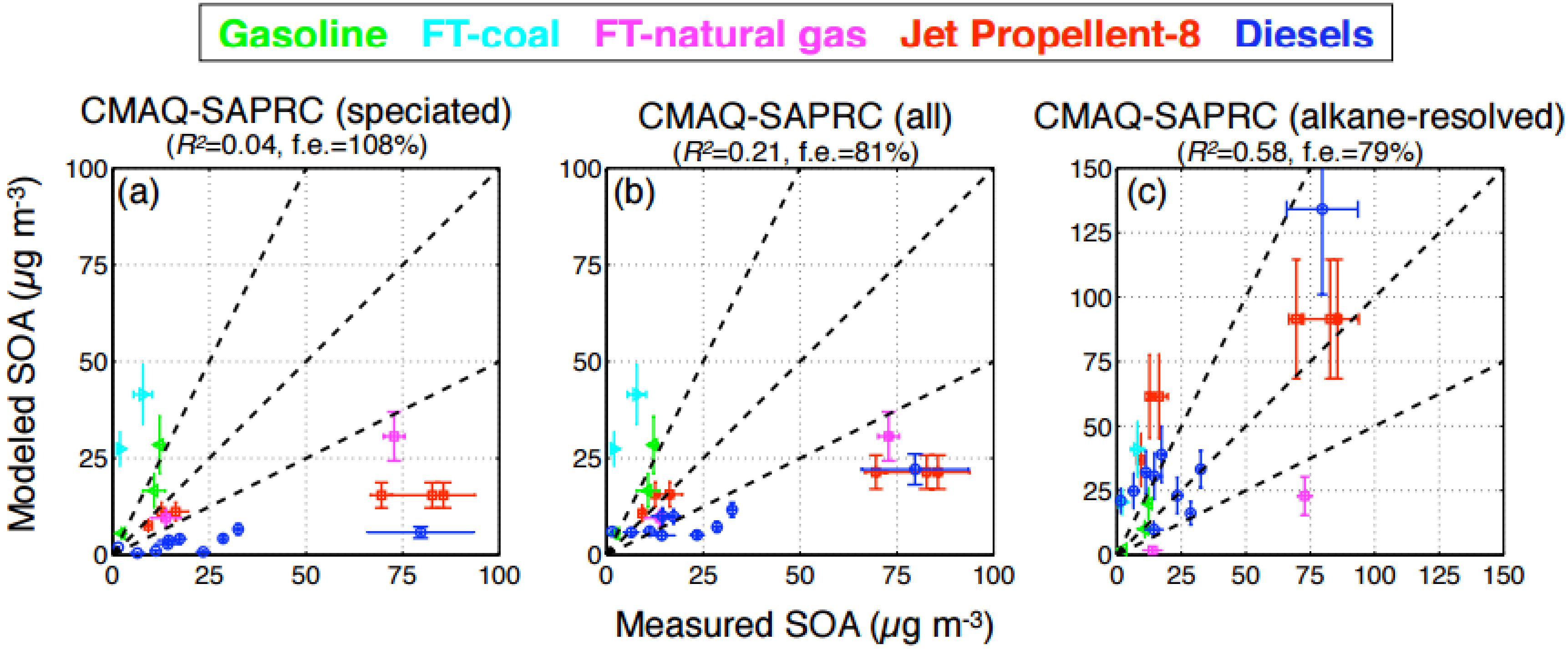
Biogenic and Anthropogenic Emission Interaction



(A) Modelled total column increase in SOA since the pre-industrial period
(B) Mass formed directly from anthropogenic SOA precursors

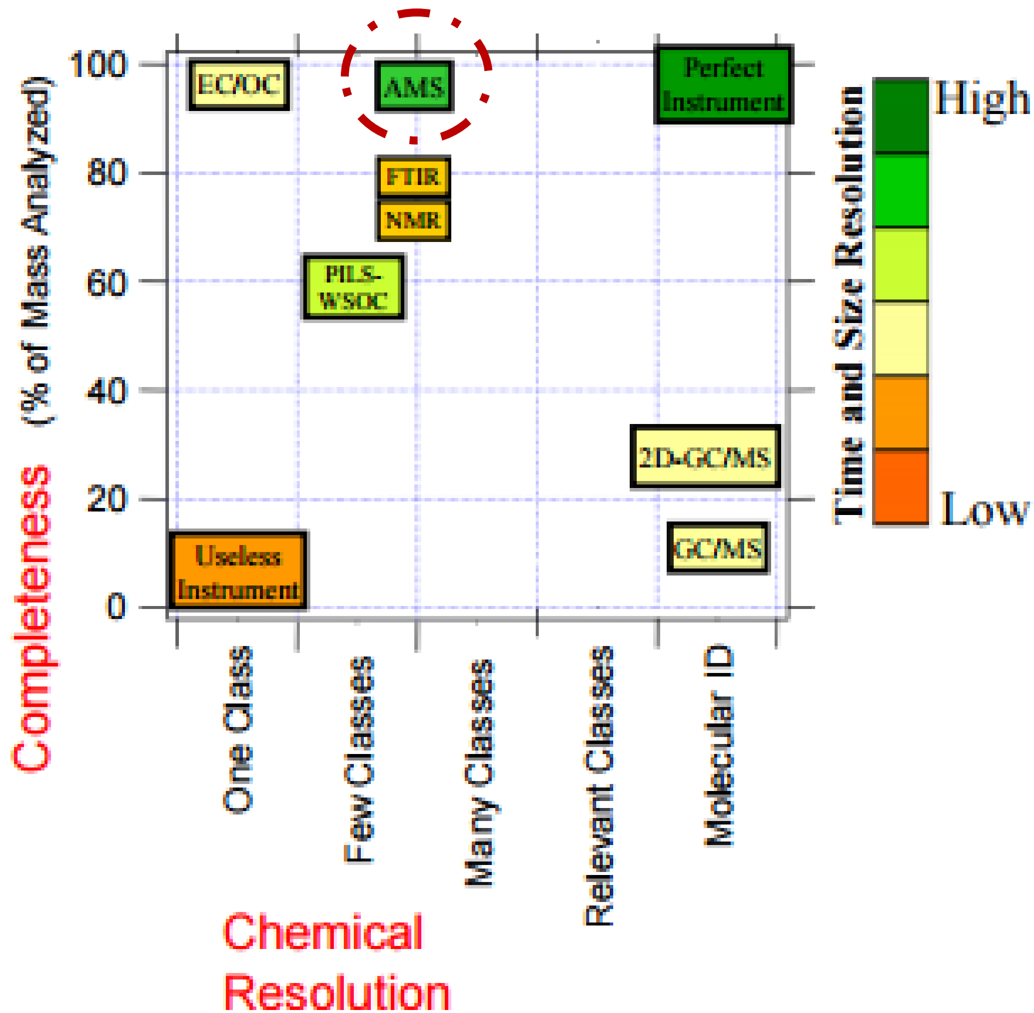
Enhancement of biogenic SOA through interaction with anthropogenic emissions

CURRENT RESEARCH NEEDS – DEAL WITH COMPLEXITY



Modeling performance for complex mixtures is poor when using the parameterization derived from single precursor chamber experiments

CURRENT RESEARCH NEEDS – MEASUREMENT OF COMPOSITION



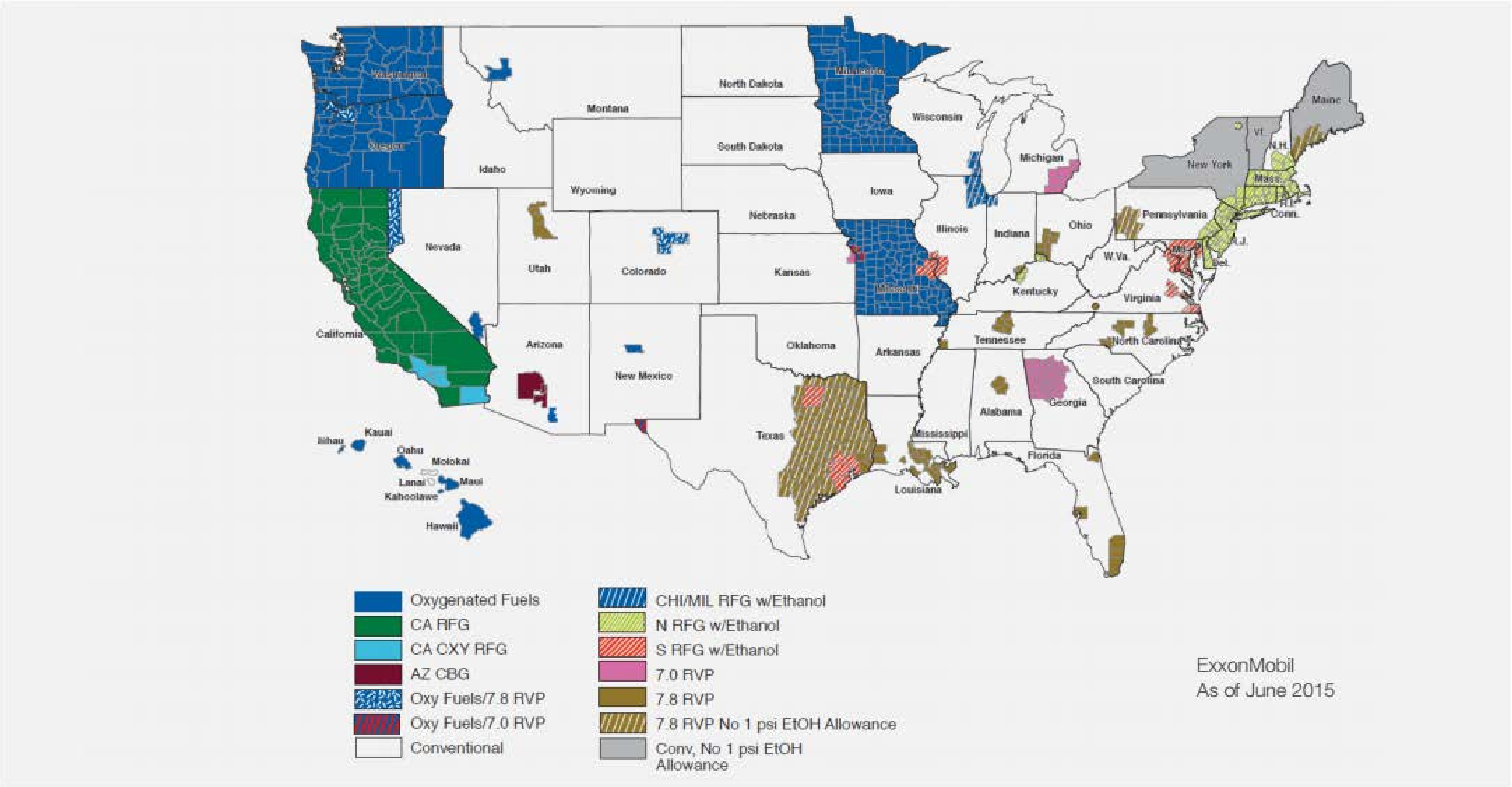
SUMMARY

- 1. SOA budget
- 2. Modeling of SOA
- 3. Fundamental understanding of processes leading to SOA formation
- 4. Dealing with complexity
- 5. Measurement of aerosol composition

- Back up slides

WHY DO WE CARE – FUEL REFORMULATIONS

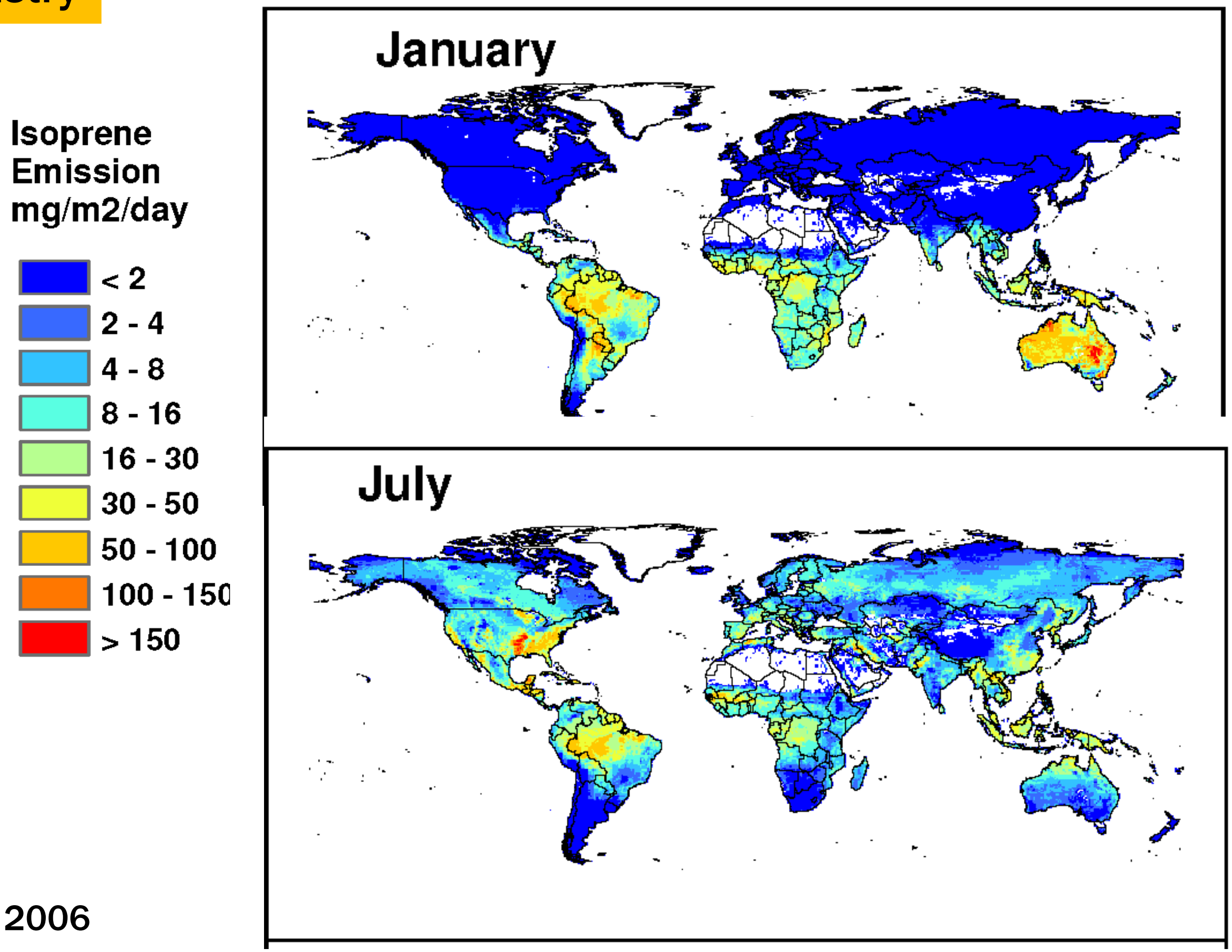
U.S. Gasoline Requirements



Note: This map is not intended to provide legal advice or to be used as guidance for state and/or federal fuel requirements, including but not limited to oxy fuel or RFG compliance requirements. API makes no representations or warranties, express or otherwise, as to the accuracy or completeness of this map.

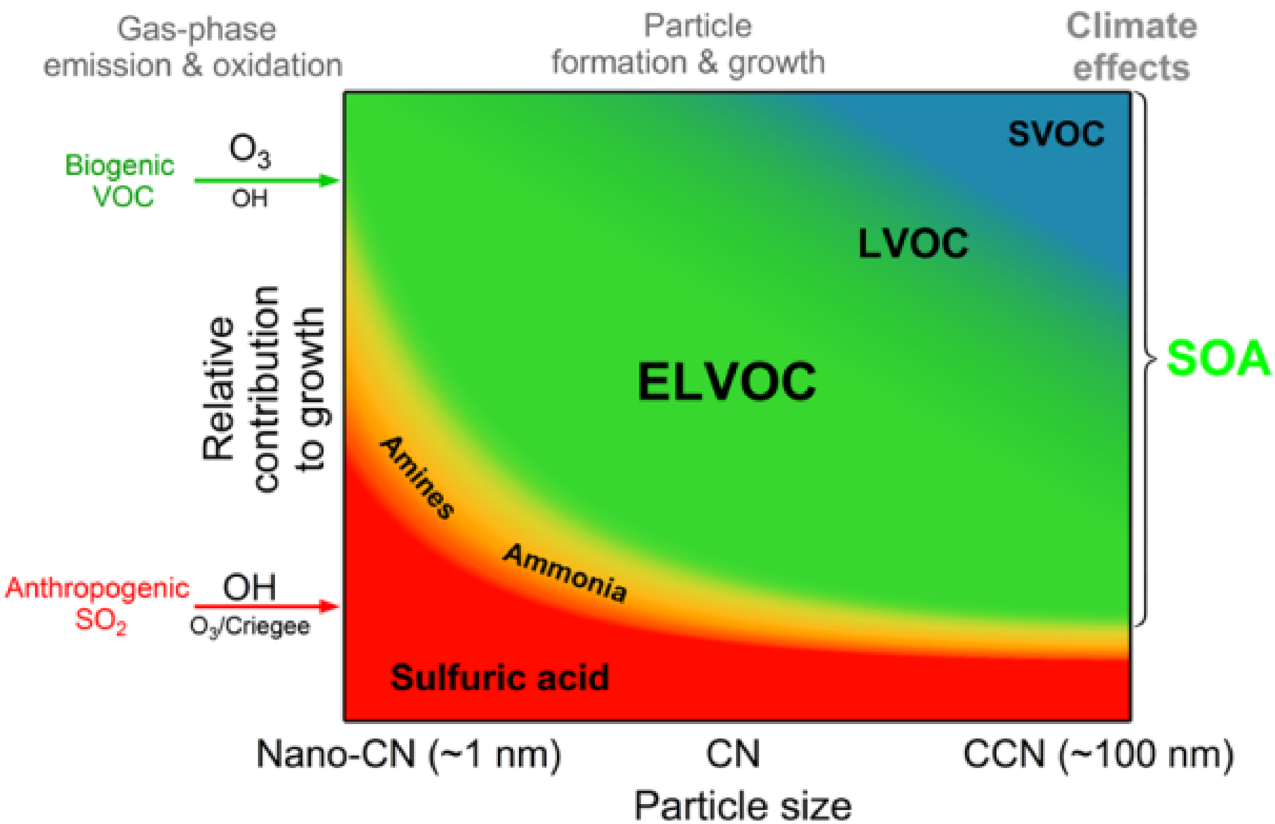
Environmental effect of reformulated fuel

Isoprene Chemistry

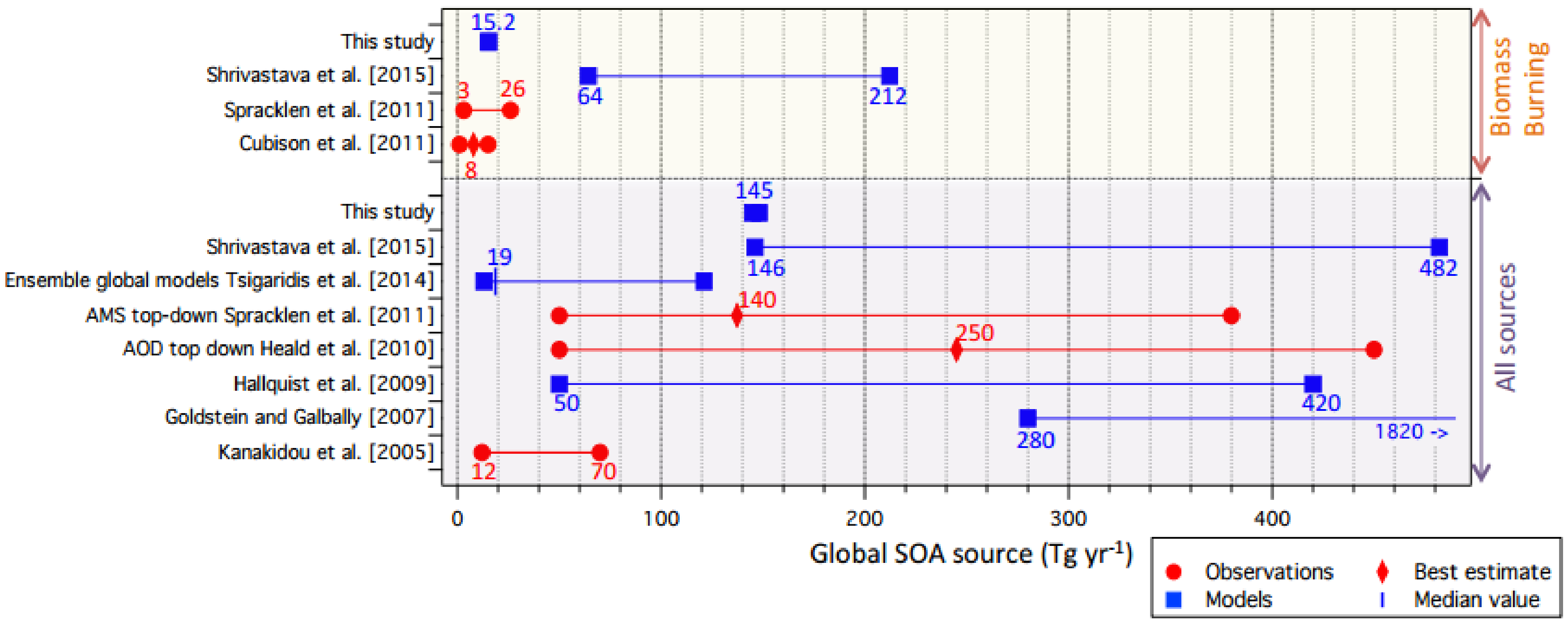


Guenther et al., 2006

Isoprene is the most abundant non-methane hydrocarbon in the atmosphere



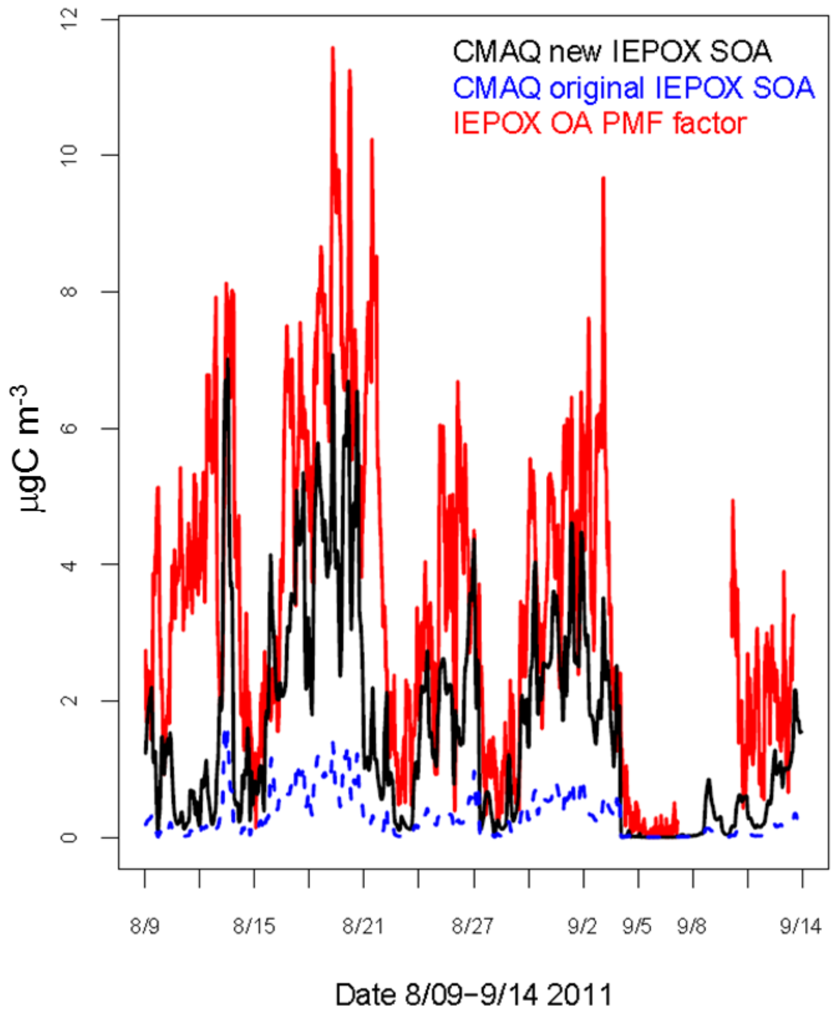
A schematic showing the role of ELVOC in the formation and growth of new particles, and their contribution to SOA in a boreal forest region



This study
Shrivastava et al. [2015]
Spracklen et al. [2011]
Cubison et al. [2011]
This study
Shrivastava et al. [2015]
Ensemble global models Tsigaridis et al. [2014]
AMS top-down Spracklen et al. [2011]
AOD top down Heald et al. [2010]
Hallquist et al. [2009]
Goldstein and Galbally [2007]
Kanakidou et al. [2005]
15.2
64
212
3
26
8
145
146
482
19
140
250
50
420
280
1820 ->
12
70
0
100
200
300
400
Global SOA source (Tg yr-1)
Biomass Burning
All sources
Observations
Models
Best estimate
Median value

CURRENT RESEARCH NEEDS – SOA FORMATION

Isoprene Chemistry (IEPOX)



Isoprene chemistry needs to be better addressed to more accurately predict the biogenic SOA formation using CMAQ