Improved treatment of atmospheric organic particulate matter concentrations from biomass combustion emissions

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Research Team

Co-Principal Investigators:

Sonia M. Kreidenweis, Jeffrey L. Collett, Jr., and Colette L. Heald

Colorado State University

Co-Investigators:

Wei Min Hao

USDA Forest Service Fire Sciences Laboratory

Doug Worsnop, Timothy Onasch, Jesse Kroll, and Achim Trimborn

Aerodyne Research Inc.

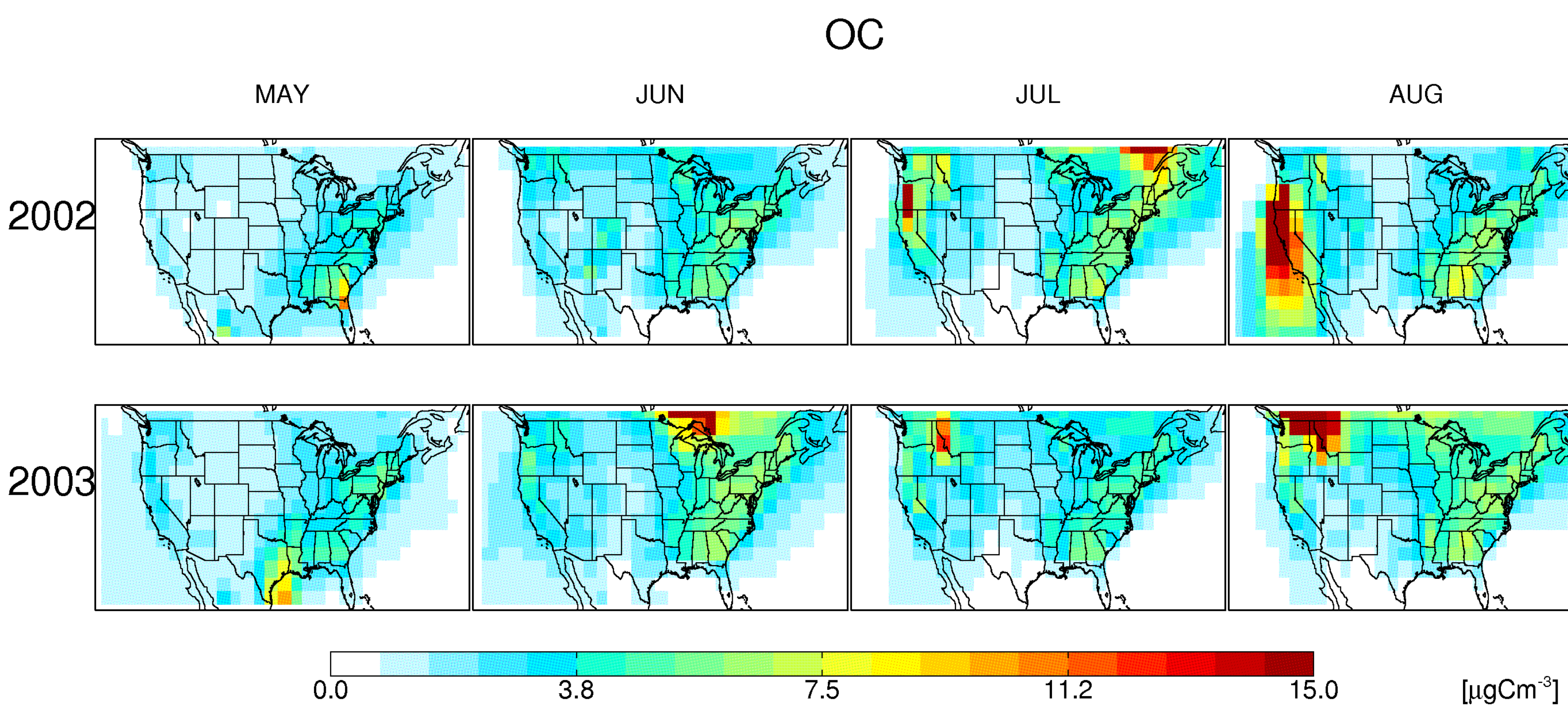
Jose-Luis Jimenez

University of Colorado

Premise

- Biomass burning (BB) in the U.S., from both wild and prescribed fires, is an important yet poorly-characterized source of organic aerosols
- Biomass burning emissions, like secondary organic aerosol (SOA), have constituents spanning a wide range of volatilities
  - Prior studies that developed source profiles are specific to the total aerosol mass concentrations used in those studies
    - In particular, aerosol "yields" at low mass concentrations may be biased, leading to model errors
    - Temperature dependence of volatilities have not been characterized
  - Models do not have emissions estimates for semivolatile species that may undergo oxidation in the atmosphere
    - May be one source of "missing carbon"
  - Stabilities of commonly-used BB tracers, like levoglucosan, against dilution / transport have not been unequivocally demonstrated

GEOS-Chem (current inventories)



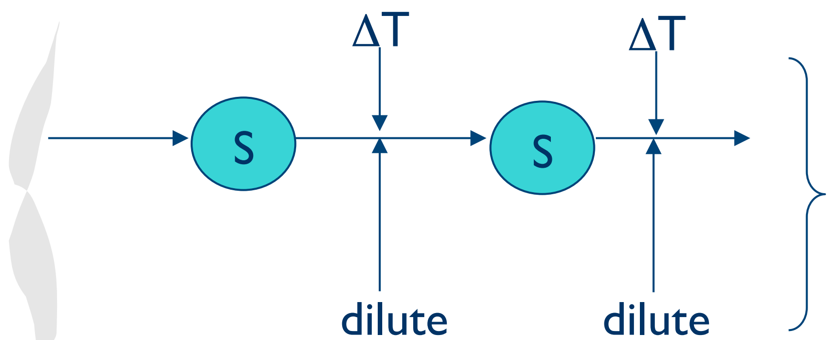
Fire is an important contribution to particulate organic carbon across the US

Project Objectives

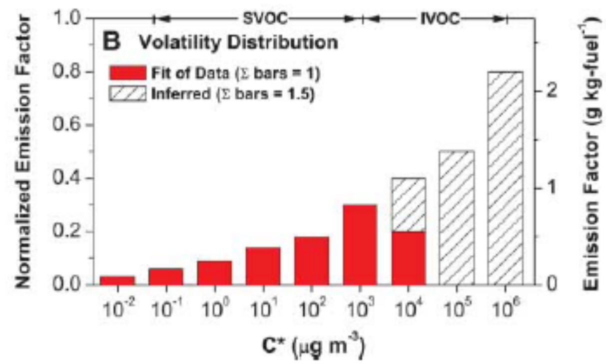
Study the role of biomass-burning emissions in U.S. air quality:

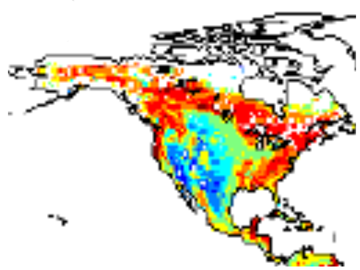
- Measure volatility distributions, as functions of both dilution and temperature, of open biomass burning emissions
  - test a variety of fuel types relevant to U.S. air quality
- Interpret data using semivolatile partitioning models
- Implement and test new biomass-burning emissions maps and partitioning models in large-scale model runs

Approach



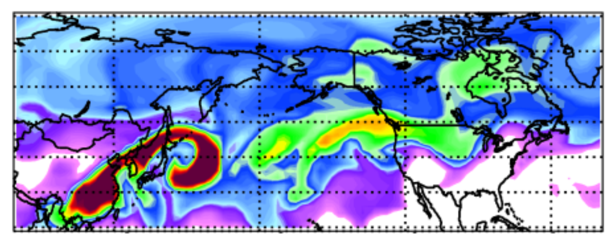
Robinson et al., *Science*, 2007



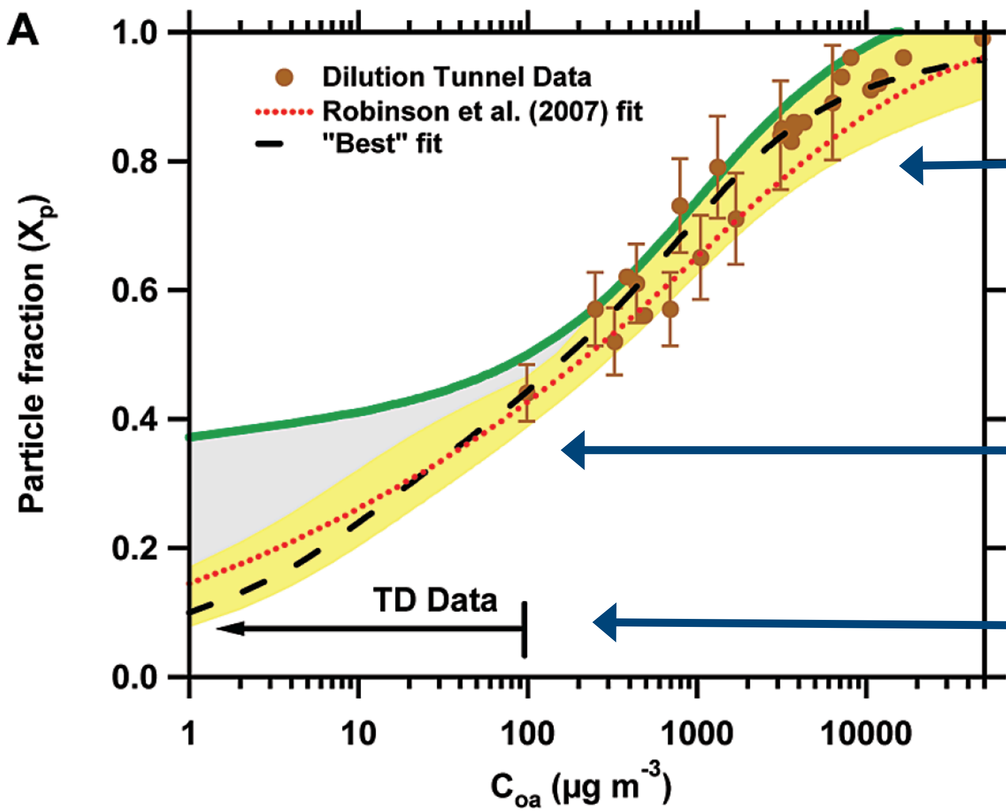


Van der Werf et al. (2006) BB emissions map

GEOS-Chem



Prior work: Estimates of volatility of smoke emissions generated in wood stoves



filter-based measurements used for high aerosol mass concentrations

Isothermal dilution data not available for ambient aerosol mass concentrations

Used thermodenuder measurements to constrain fit at low aerosol concentrations

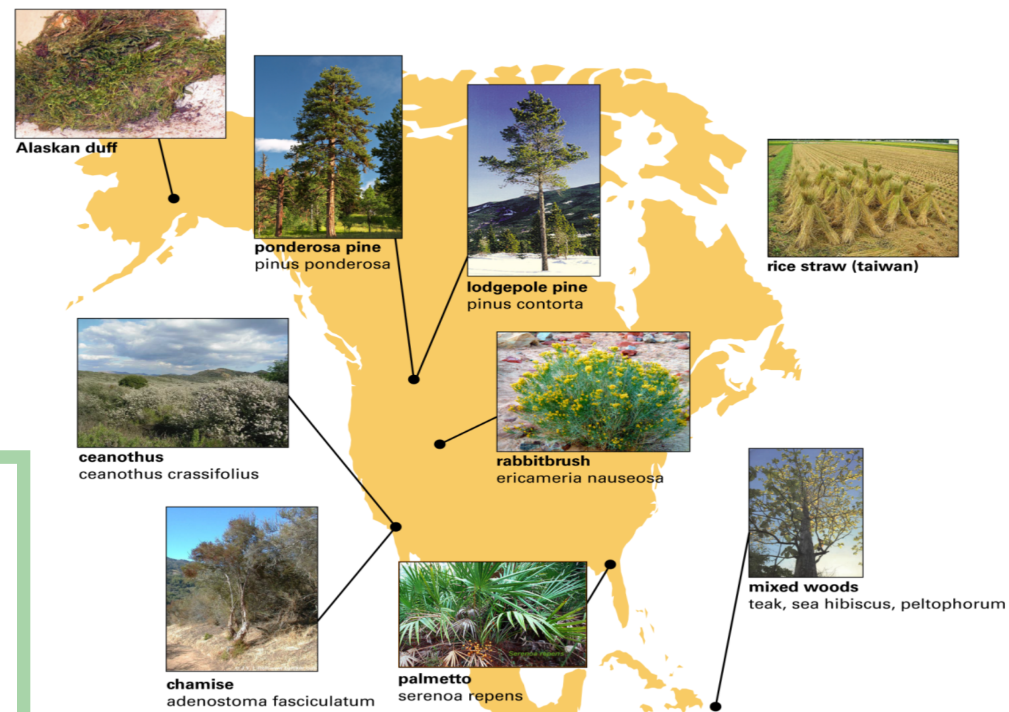
Grieshop et al., *ES&T*, 2009

Fire Lab at Missoula Experiments (FLAME I & II, 2006 / 2007)

Our STAR experiments build upon this series of smoke properties studies

USFS / USDA Fire Sciences Lab
Missoula, MT
http://www.firelab.org/

- **Joint Fire Science Program**
- Physical, optical and chemical properties of **open biomass burning emissions**
- EFs, source profiles for FLMs
- Focus on W and SE US fuels



plant images courtesy santa monica mountains trails council, bay area hicker, alberta parks and recreation, daniel kirk, food and agriculture organization of the United Nations

FSL Burn Chamber

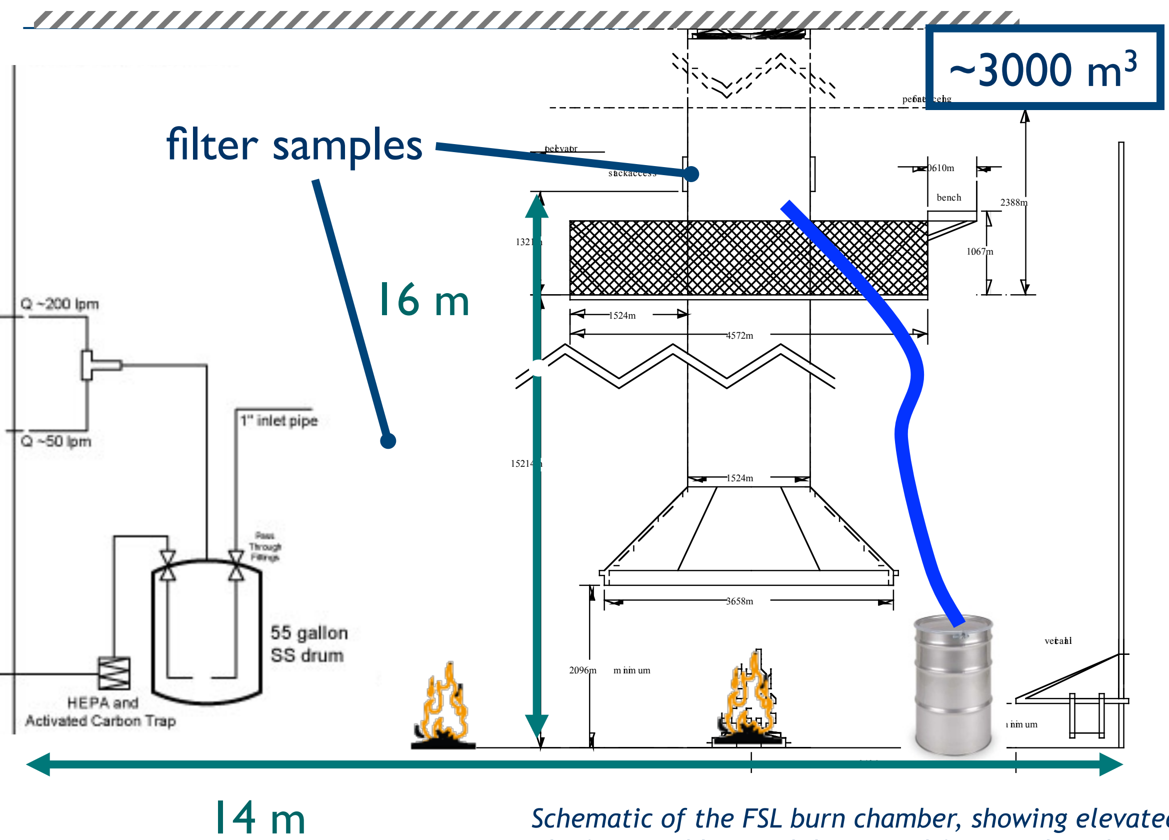
stack burns

chamber burns

optical properties,
hygroscopicity,
CCN activity,
continuous OC/EC,
and other

Particle and Gas Phase Instruments in Viewing Room

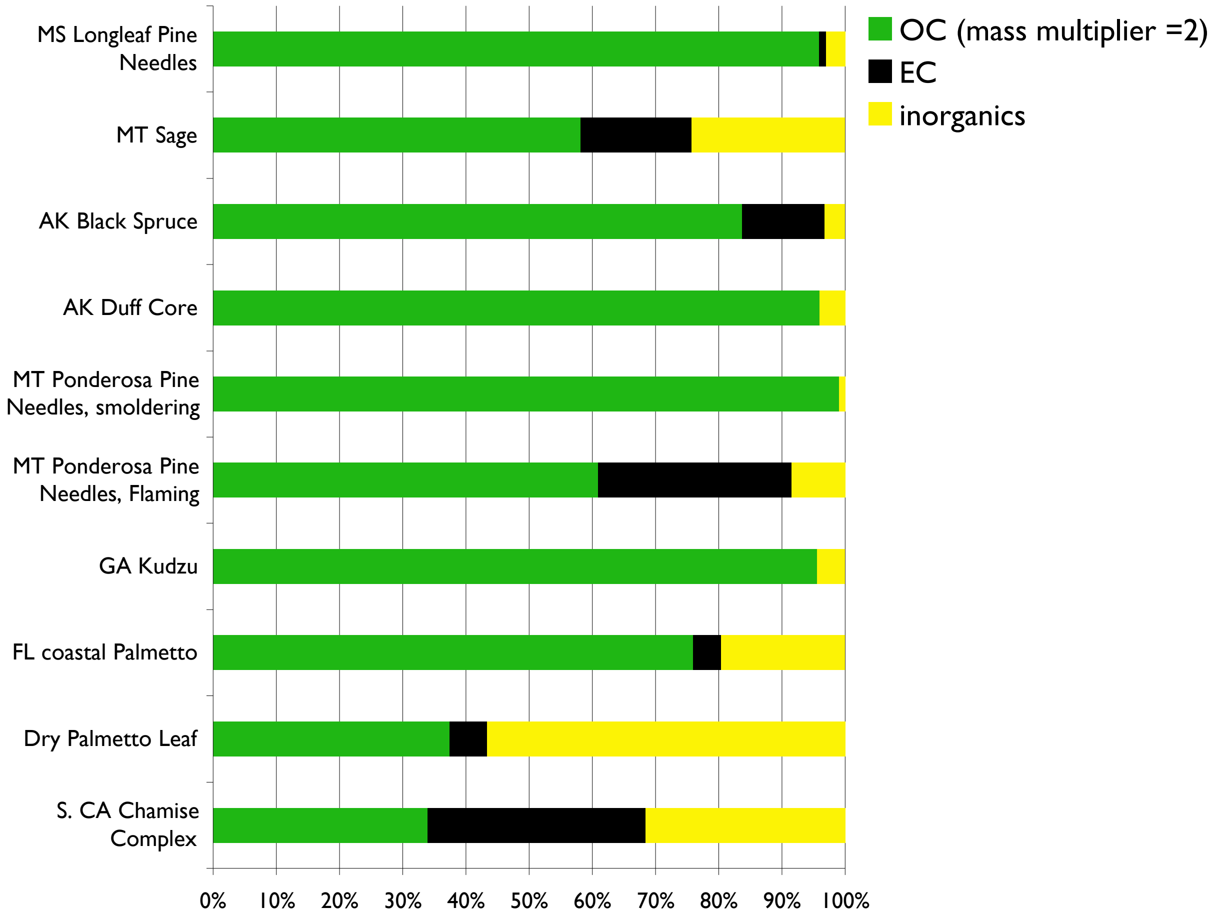
Multiple AMS, volatility AMS



256 burns
35 unique plant species
44 total fuels

Schematic of the FSL burn chamber, showing elevated platform and line and drum used for sampling during stack burns.

Example smoke compositions

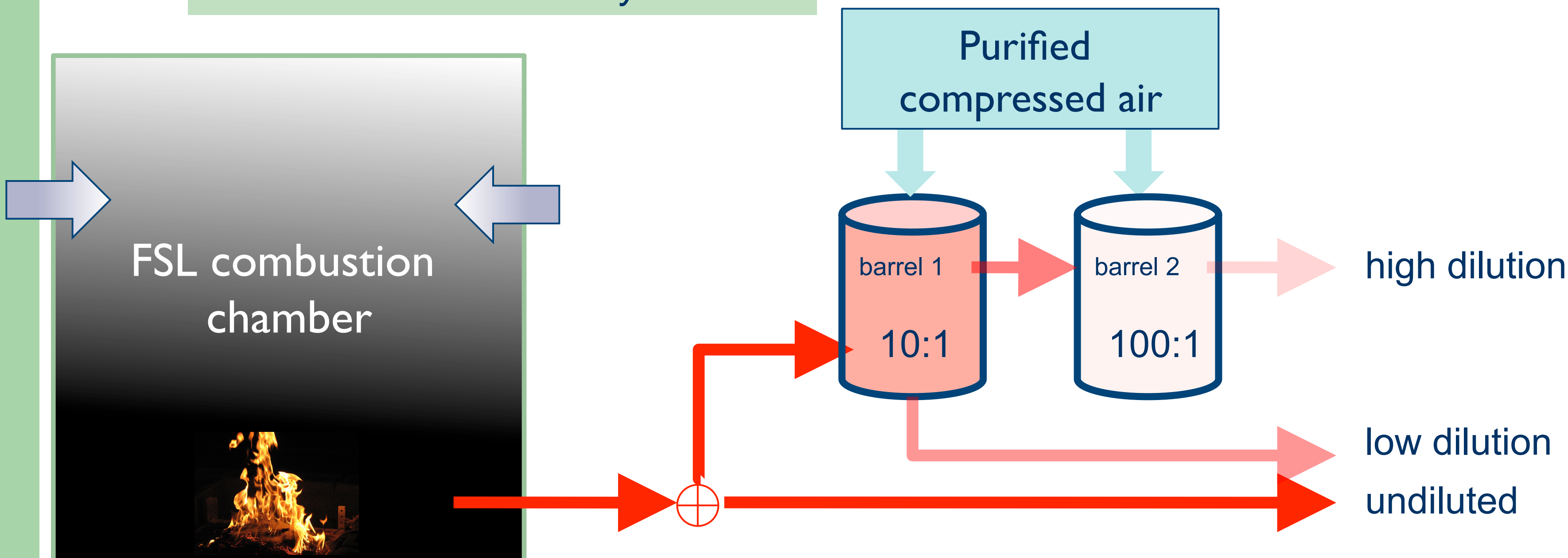


Sept/Oct 2009 experiment design

- Choose fuels that produce variable inorganic / organic and variable levoglucosan levels
- Stack burns for EFs
- Hi-vol filter measurements during burns
- Tracer gas monitoring during burns to characterize dilution ratios in chamber itself
- **Design partitioning experiments to**
  - **cover several orders of magnitude in [OC], including to very low concentrations (~1 μg m^{-3})**
  - **cover range of temperatures, using thermal denuder**
  - **Controlled, continuous-flow dilution system**
- **HR-ToF-AMS:**
  Time-resolved measurements key new feature in chamber burns

Experimental strategy

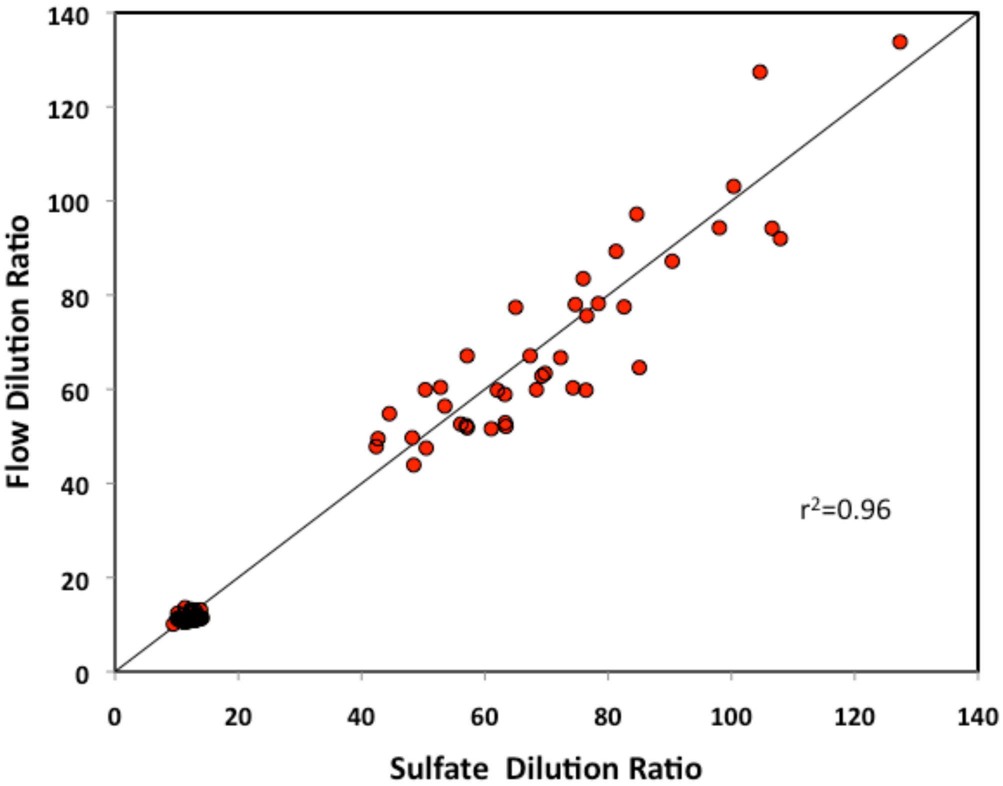
isothermal dilution system



+ thermal processing of all streams

26 chamber burns
16 fuels

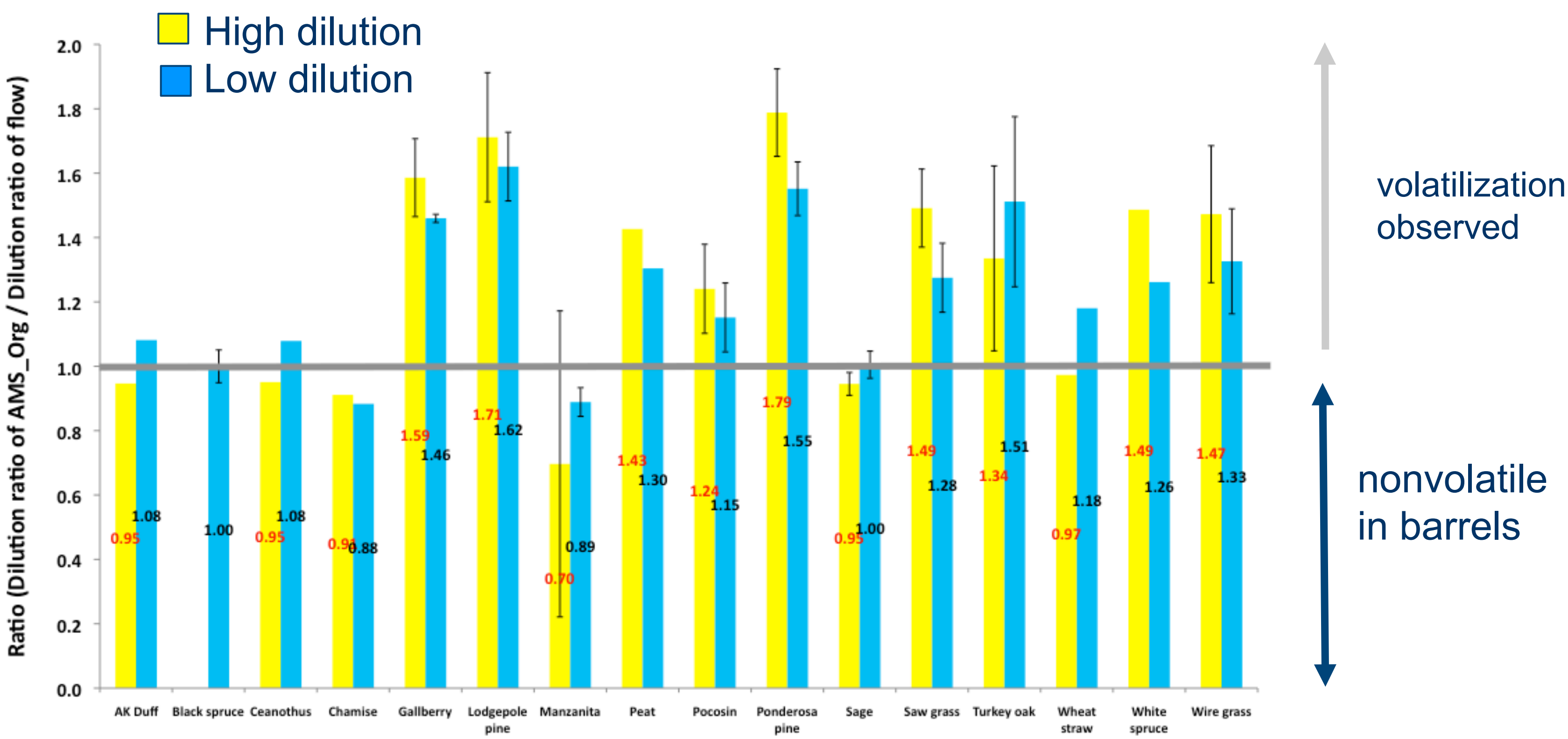
Active dilution system



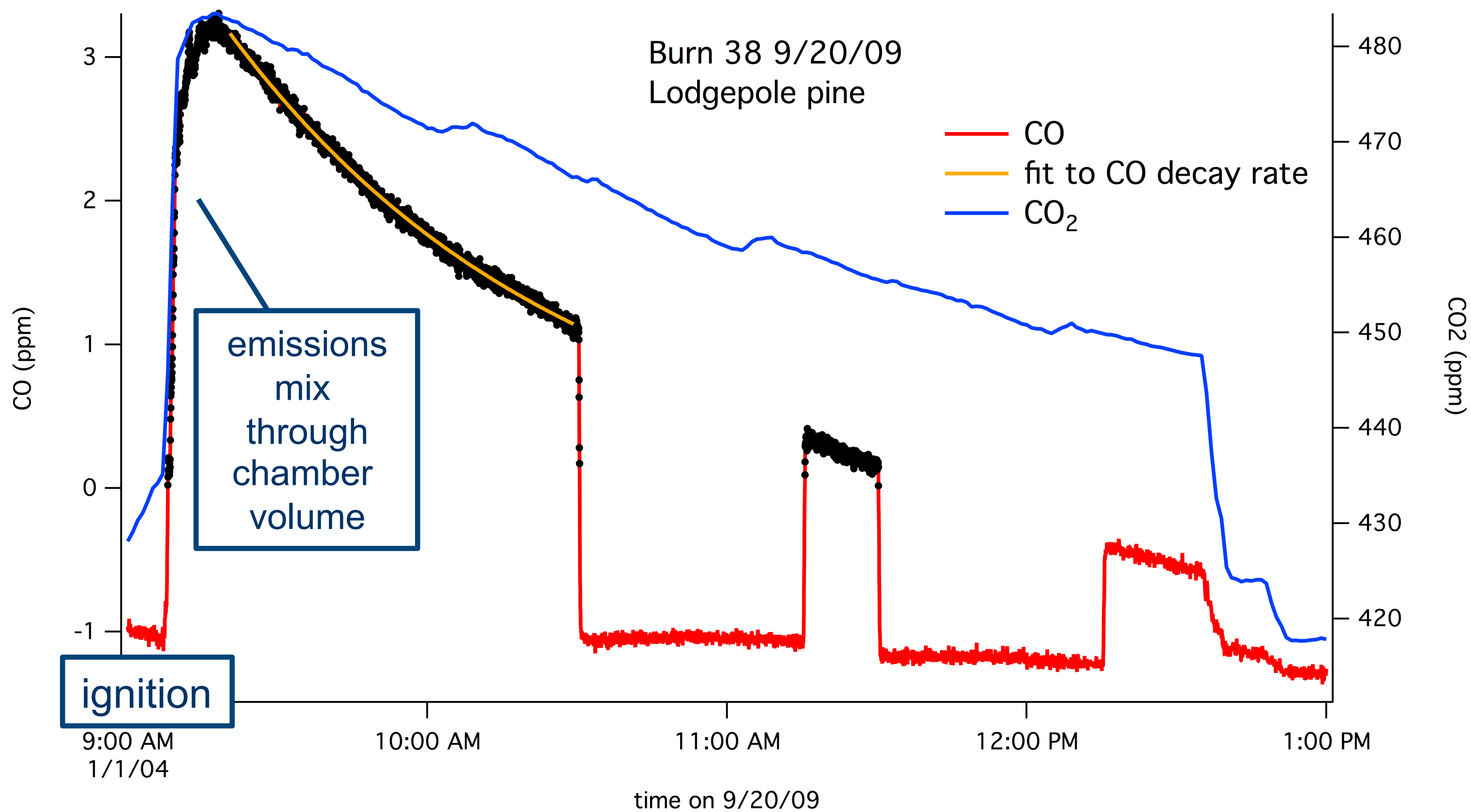
Dilution ratios computed from measured flow rates agreed well with those estimated from ratios of sulfate in the diluted and undiluted streams

→ High confidence in low concentration measurements

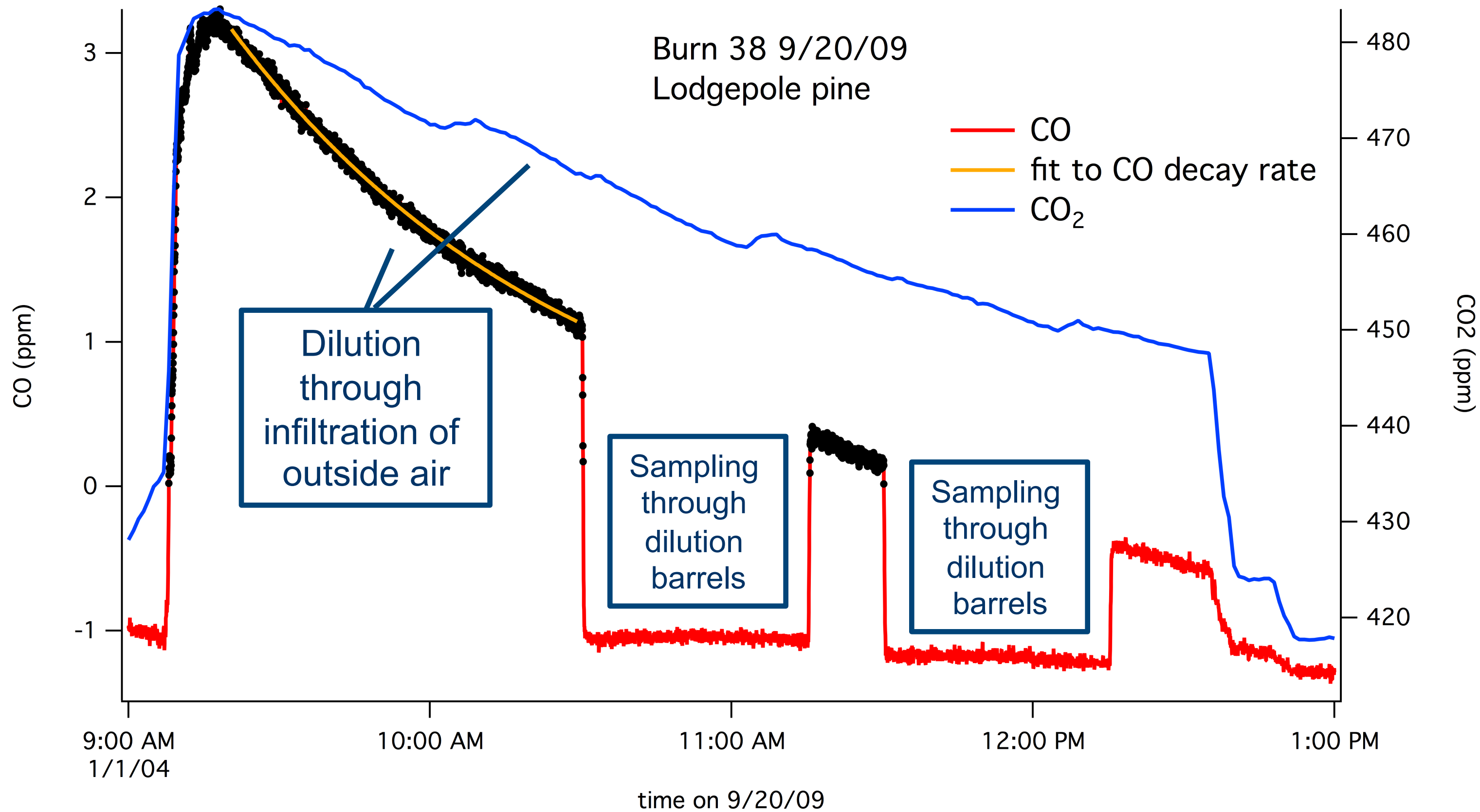
We observed a range of volatility behavior in the active dilution system



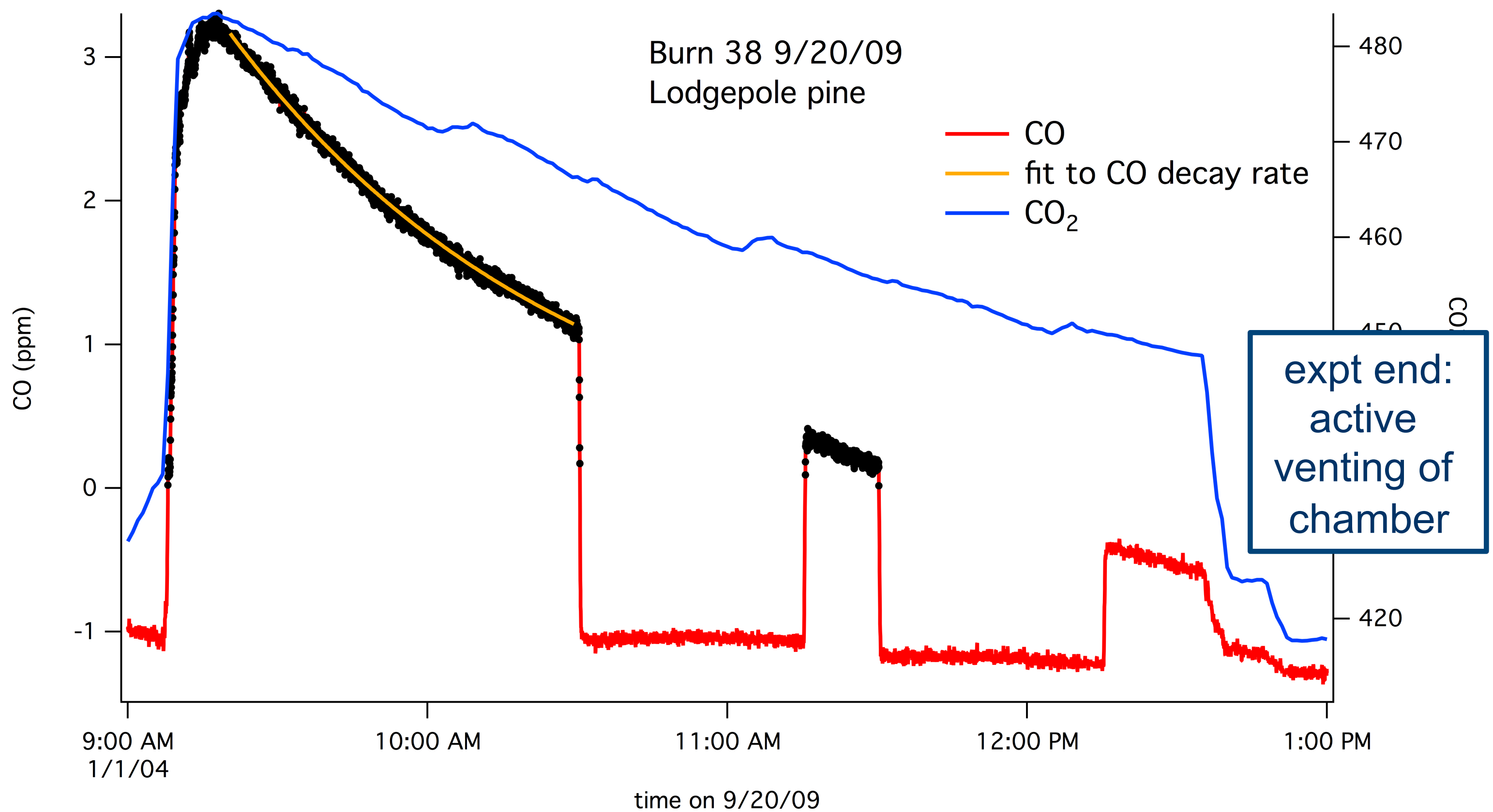
Dilution in main chamber



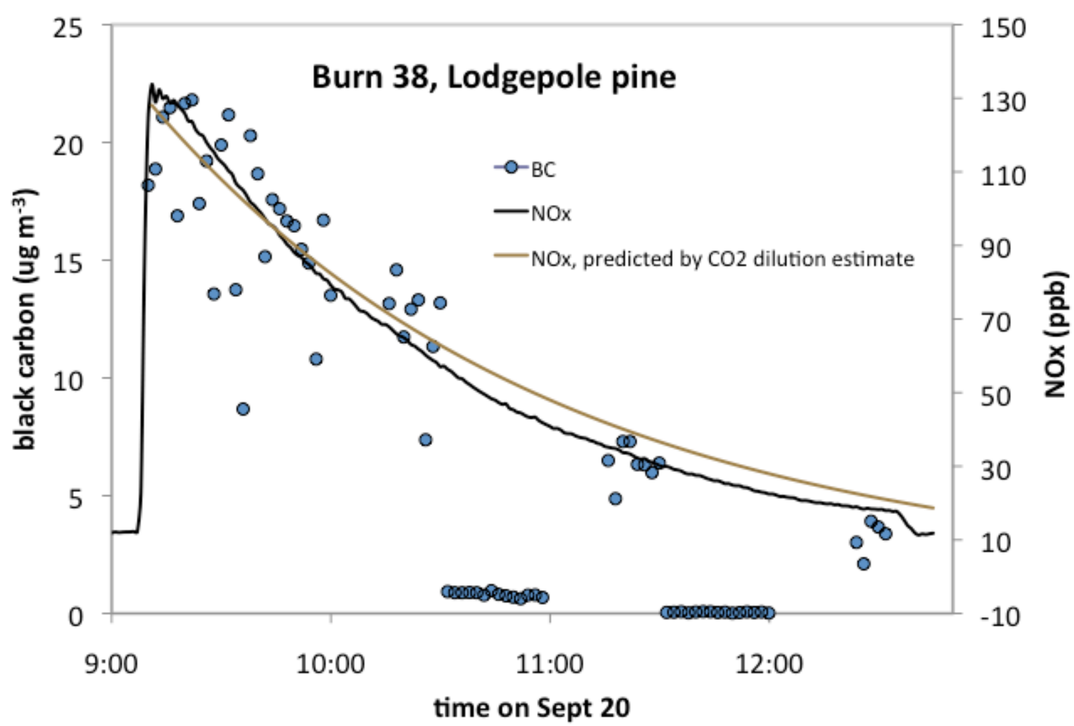
Dilution in main chamber



Typical experimental timeline

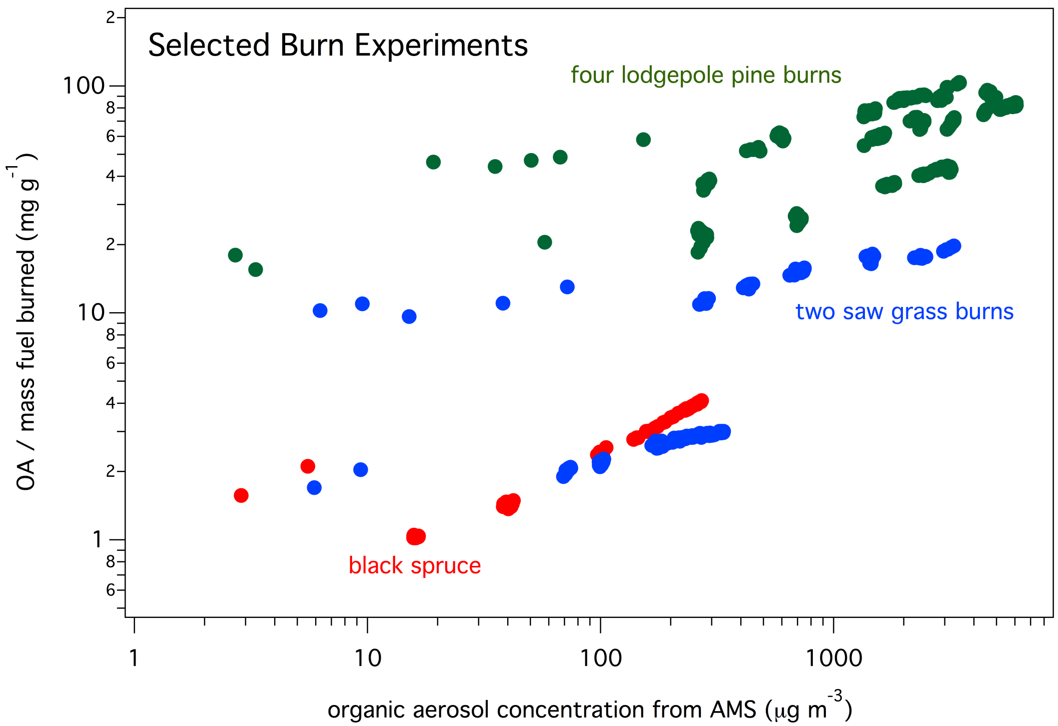


Predicted chamber dilutions match observations (gases and particles)



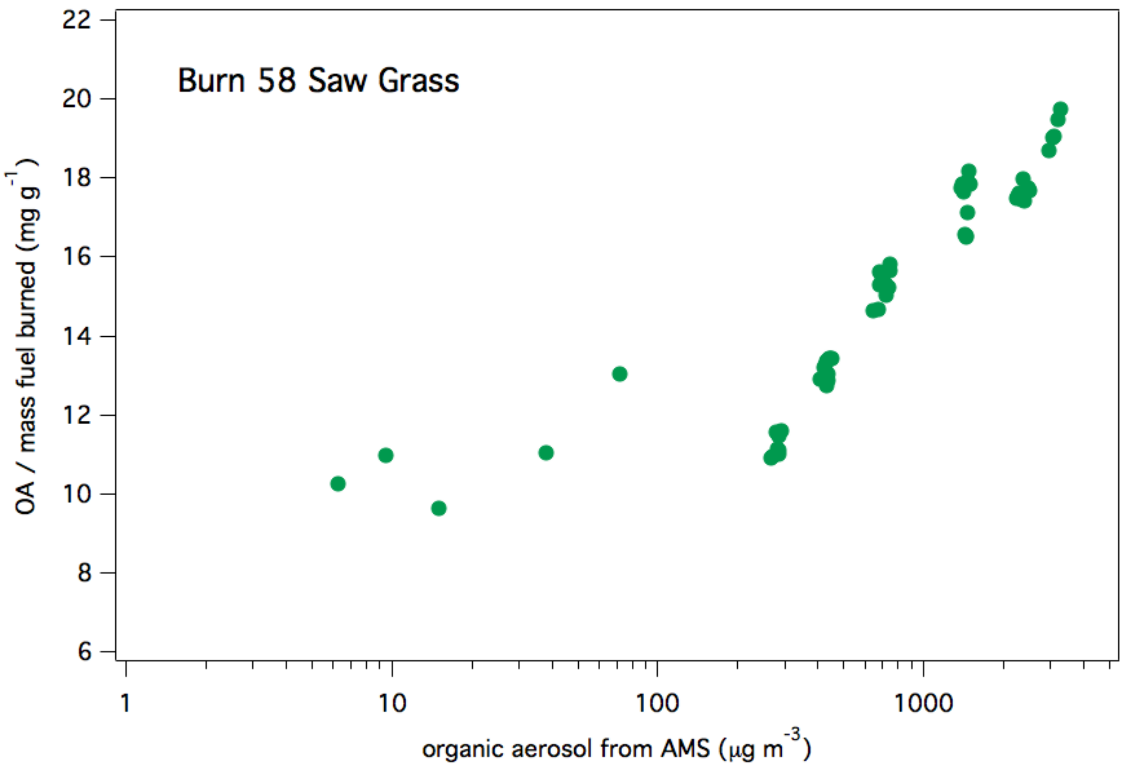
- Corrections for additional particle losses to wall appear unnecessary
- In the following, we have used the apparent dilution of sulfate aerosol (from AMS) to adjust the total available organic material

Partitioning data



- "Particle fraction" is expressed as the ratio (organic aerosol) / (mass fuel burned)
- Large range in emissions fuel-to-fuel
- Can have range even for same fuels (fuel moisture, other variables changing)

Example experiment



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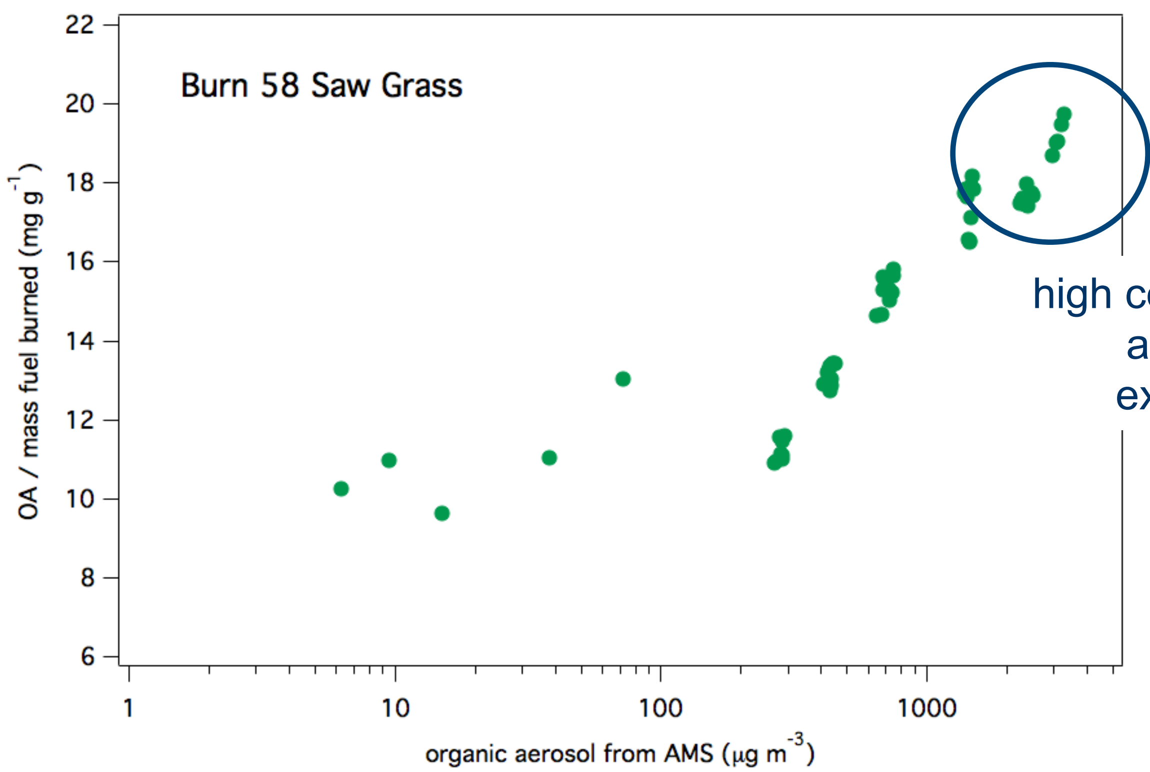
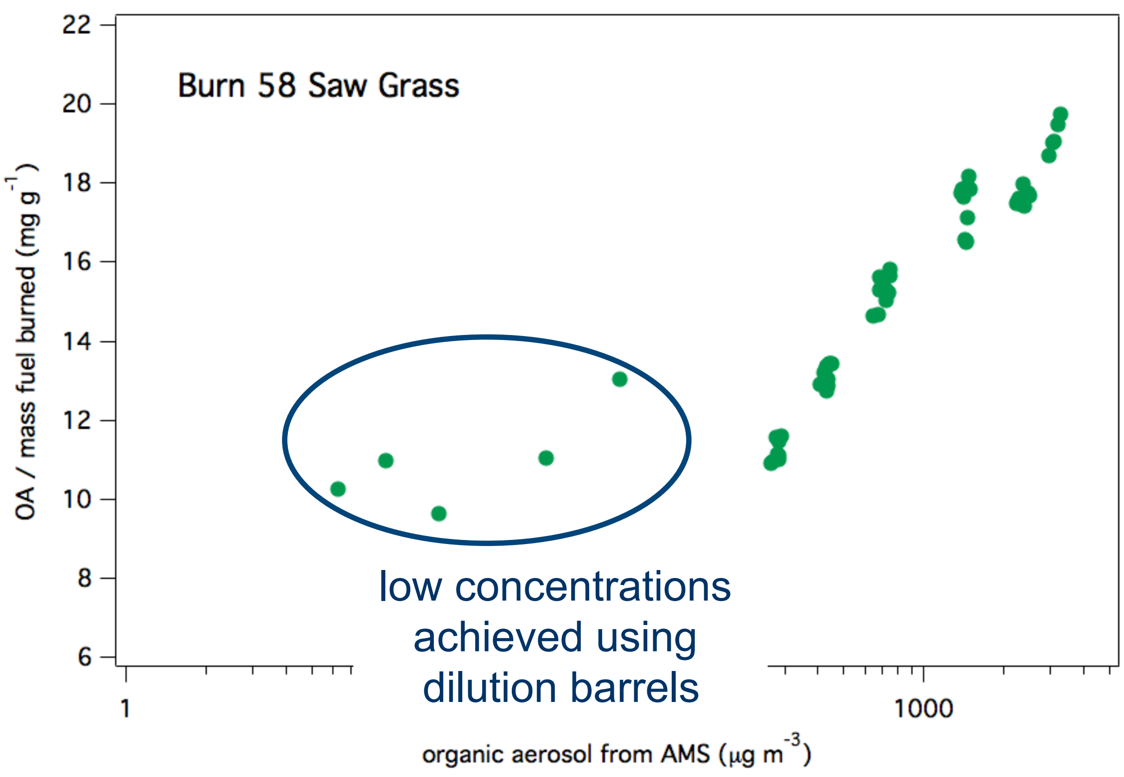


high concentrations at start of experiment

Example experiment



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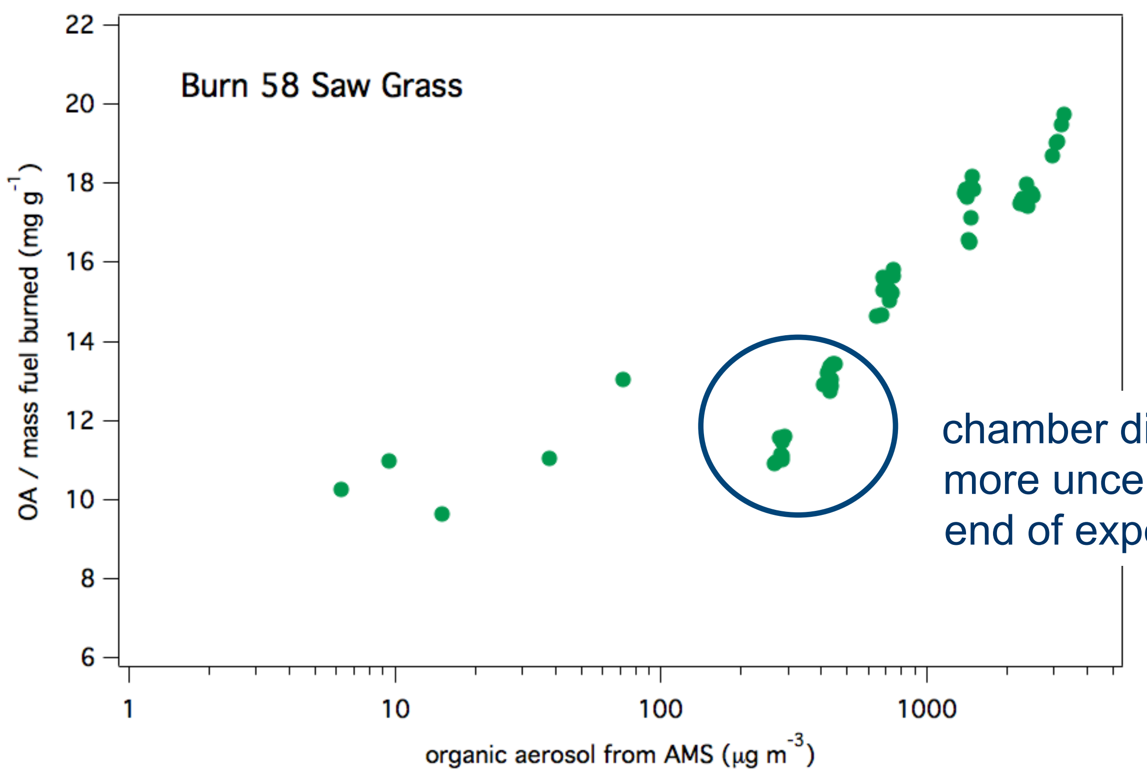
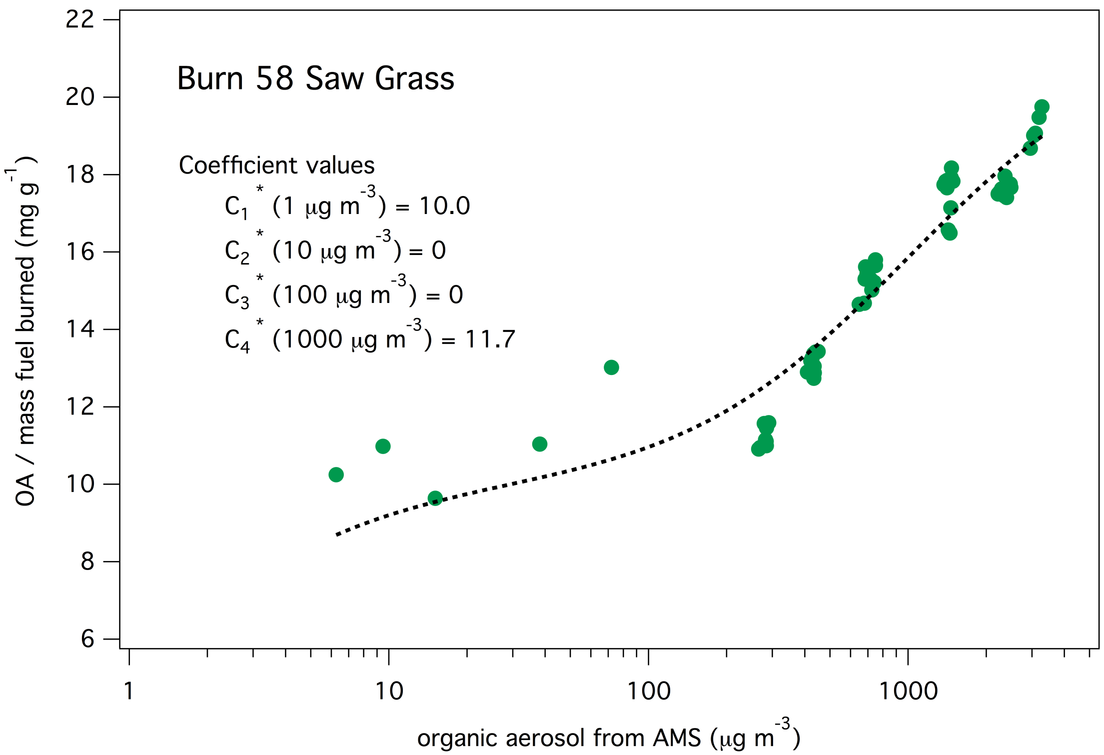


chamber dilutions more uncertain at end of experiment

Example fit to basis function



Data are fit with a four-parameter basis set:

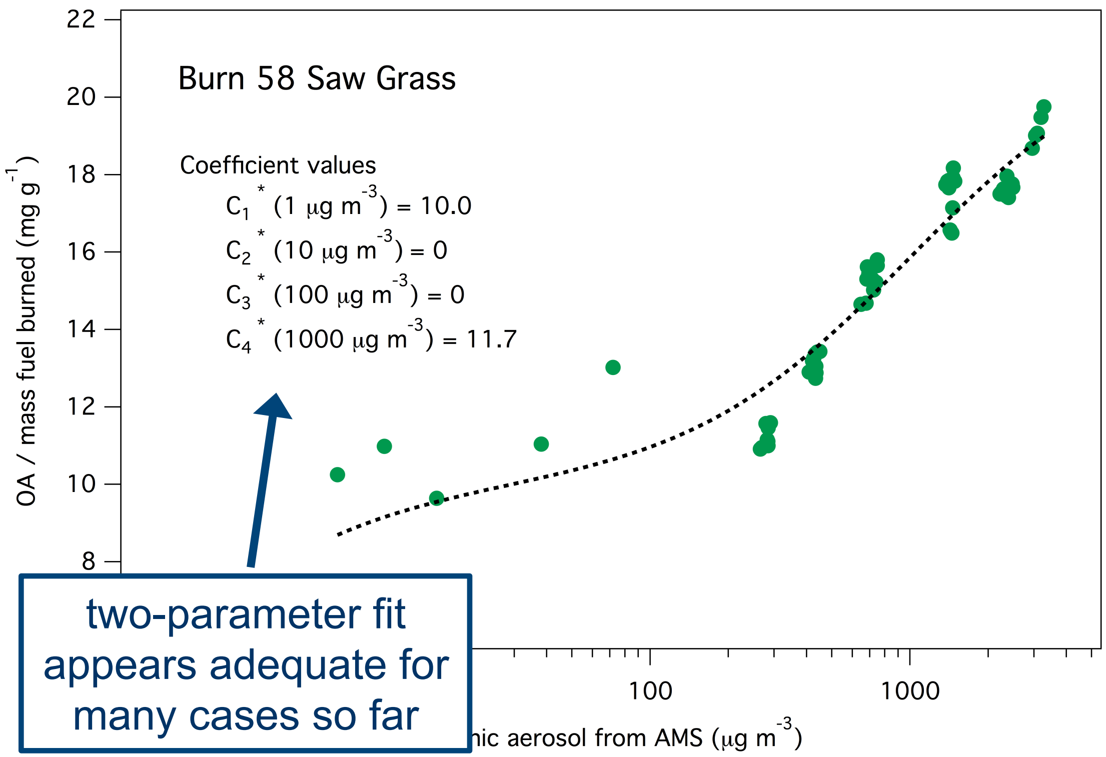
$$\xi = \sum_{i=1}^{n} C_i \xi_i$$

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}$$

The resulting partitioning coefficients are shown in the legend.

VBS: Donahue et al., *ES&T*, 2006

Example fit to basis function



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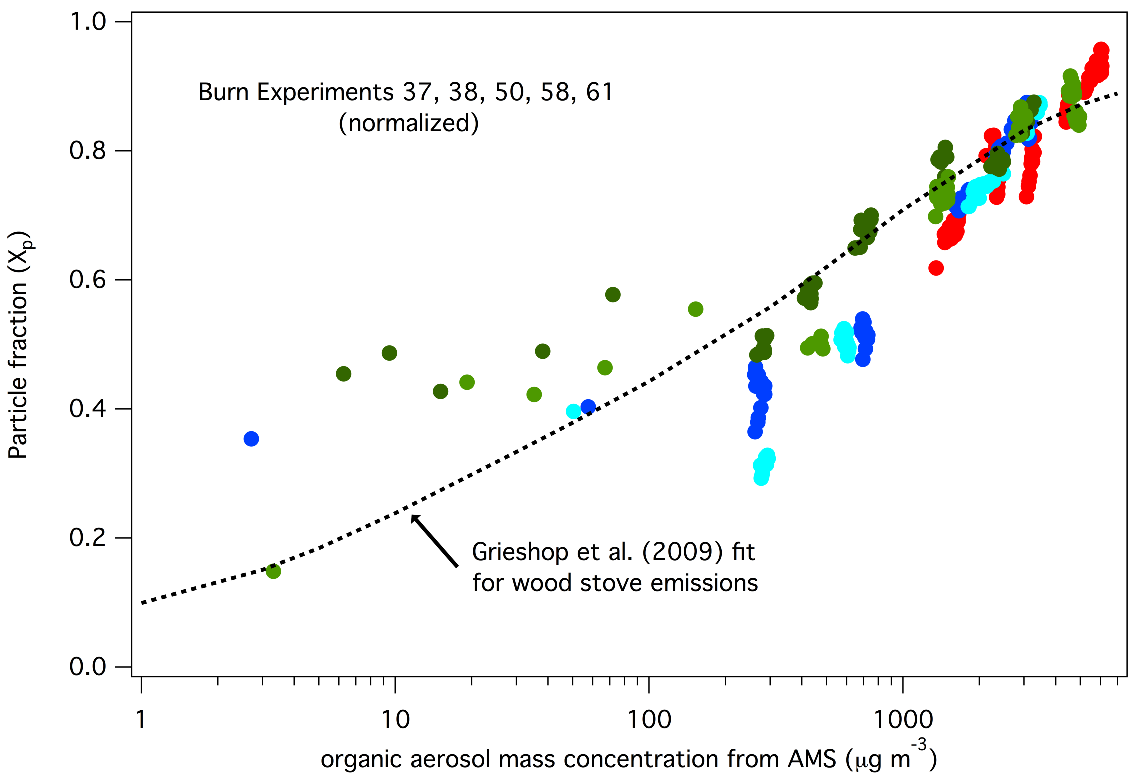
Comparison with Grieshop et al. (2009)



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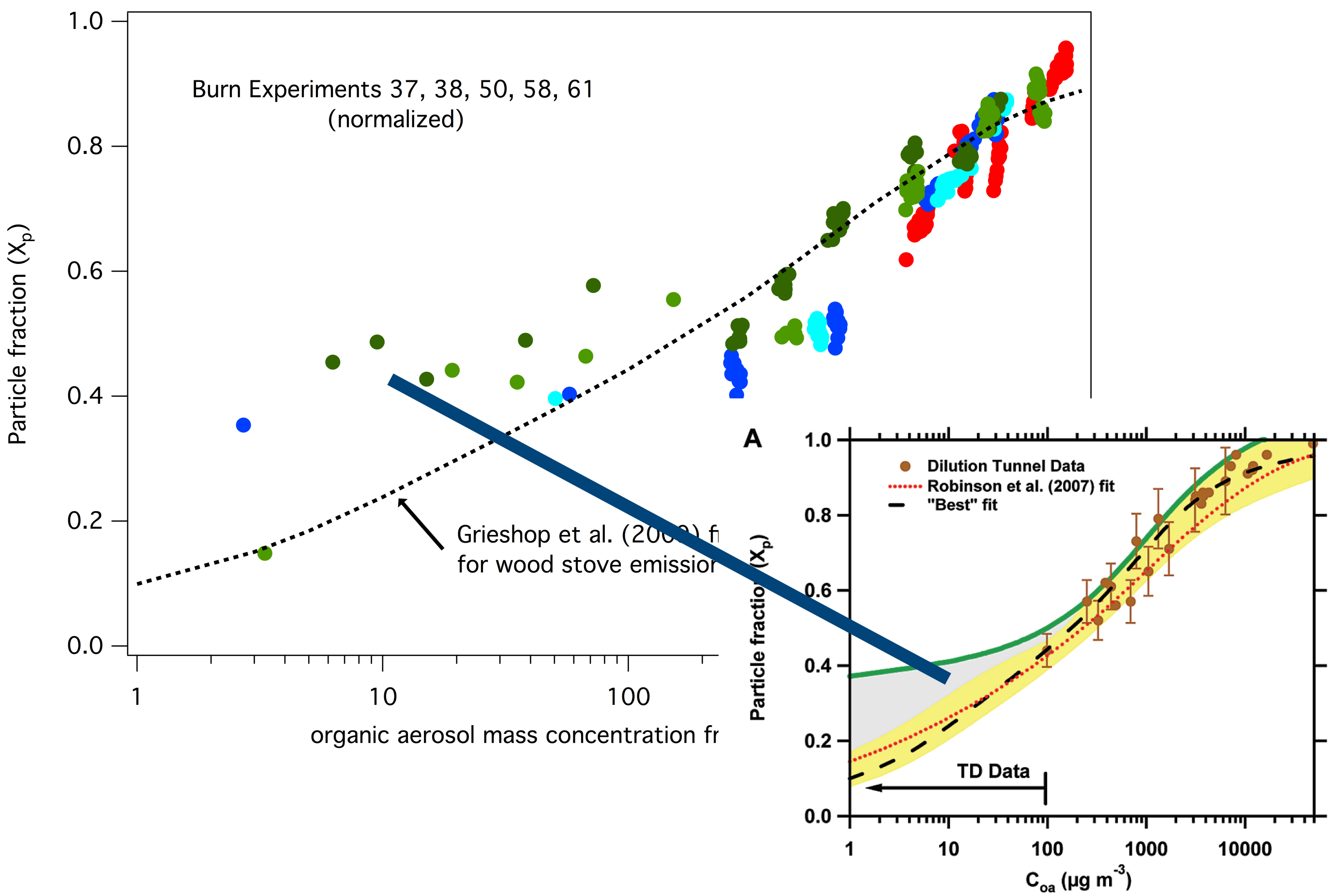
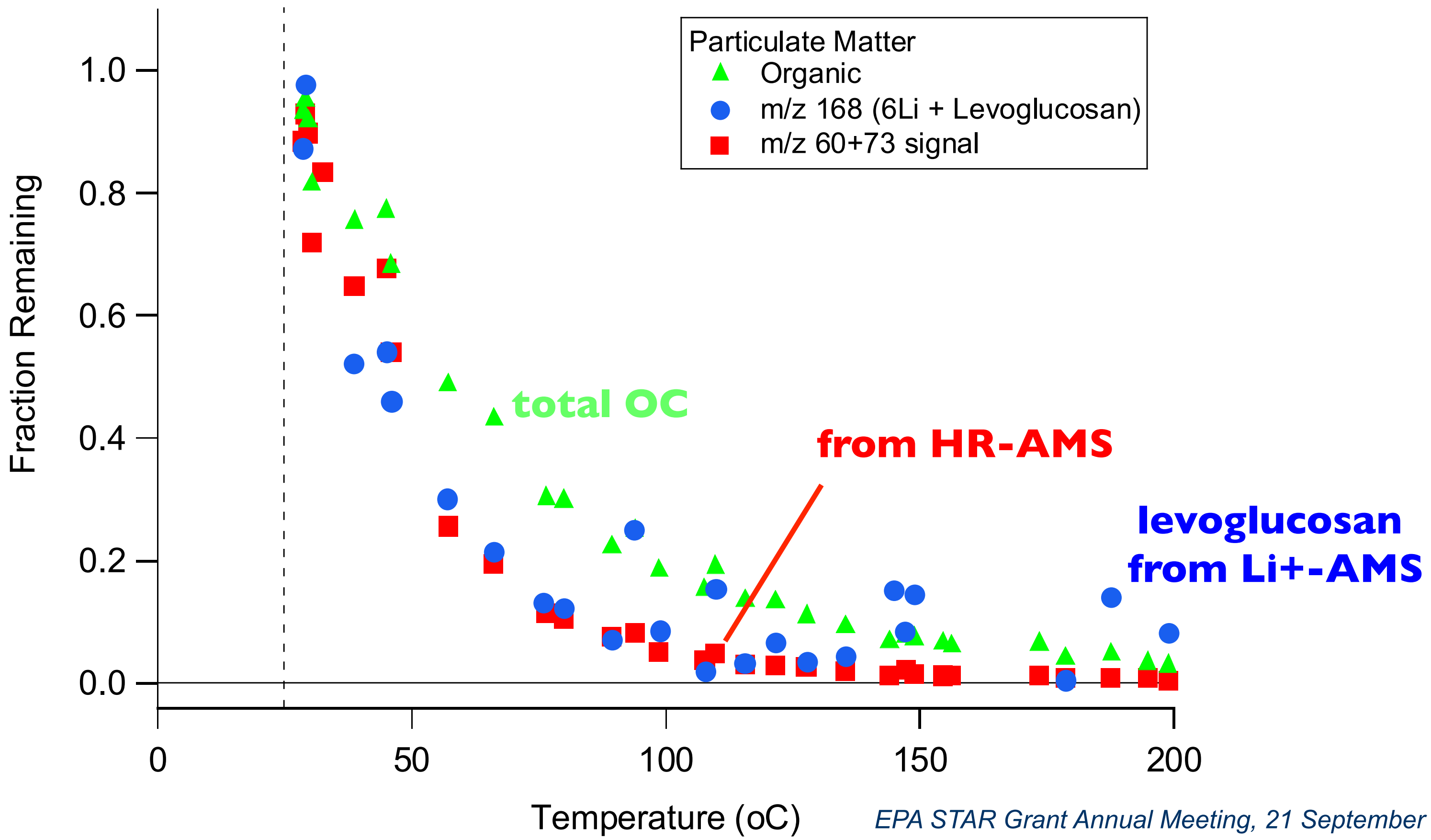


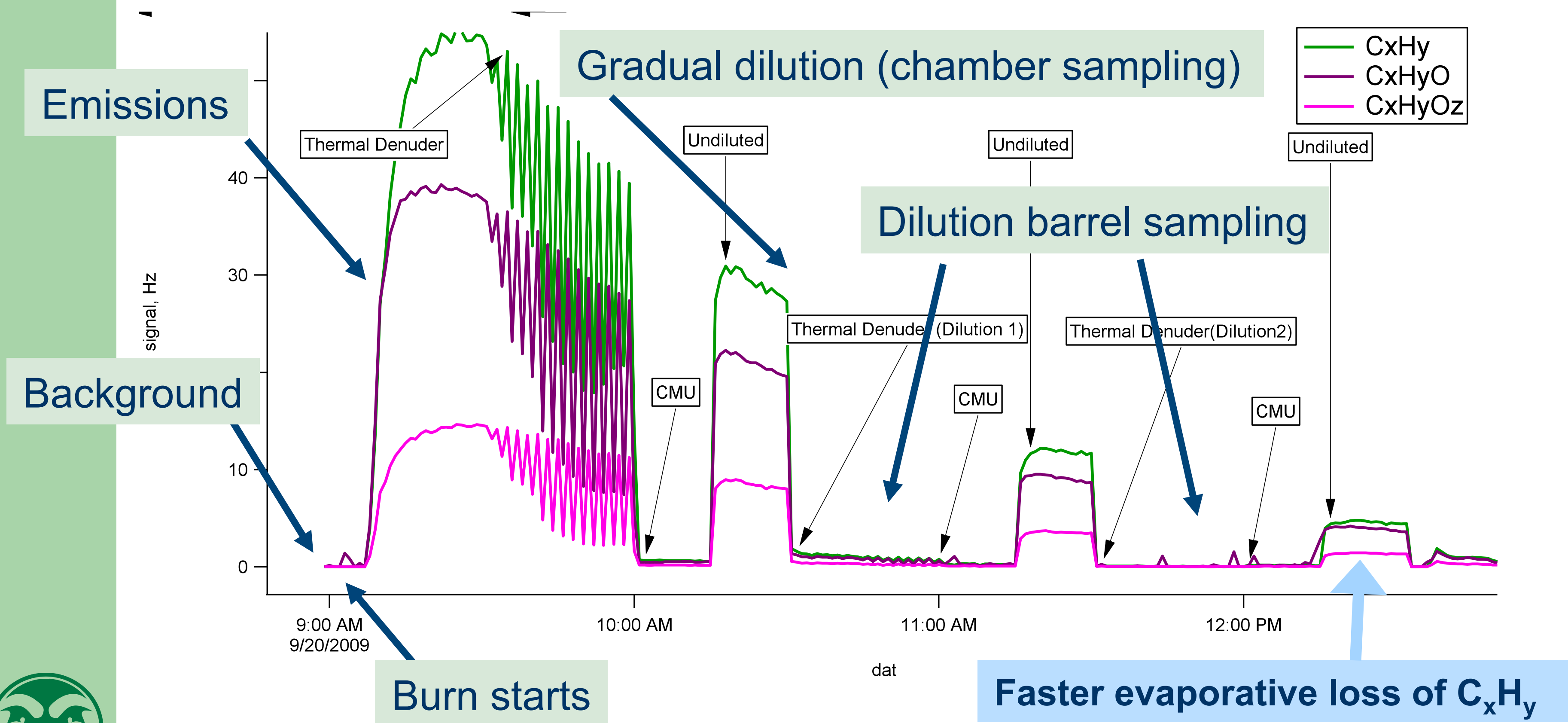
Ongoing analyses

- Processing of HR-ToF-AMS / thermodenuder data and merging with isothermal dilution data
  - create final, best-fit volatility distributions for use in modeling phase of our study
- O:C ratio changes with isothermal dilution and with temperature
  - O:C increases with aging in atmosphere; is smoke behavior consistent?
- Molecular markers and behavior under dilution
  - Levoglucosan from filters and in AMS
  - Tracer stability is a key issue in apportionment modeling

Volatility of molecular markers?



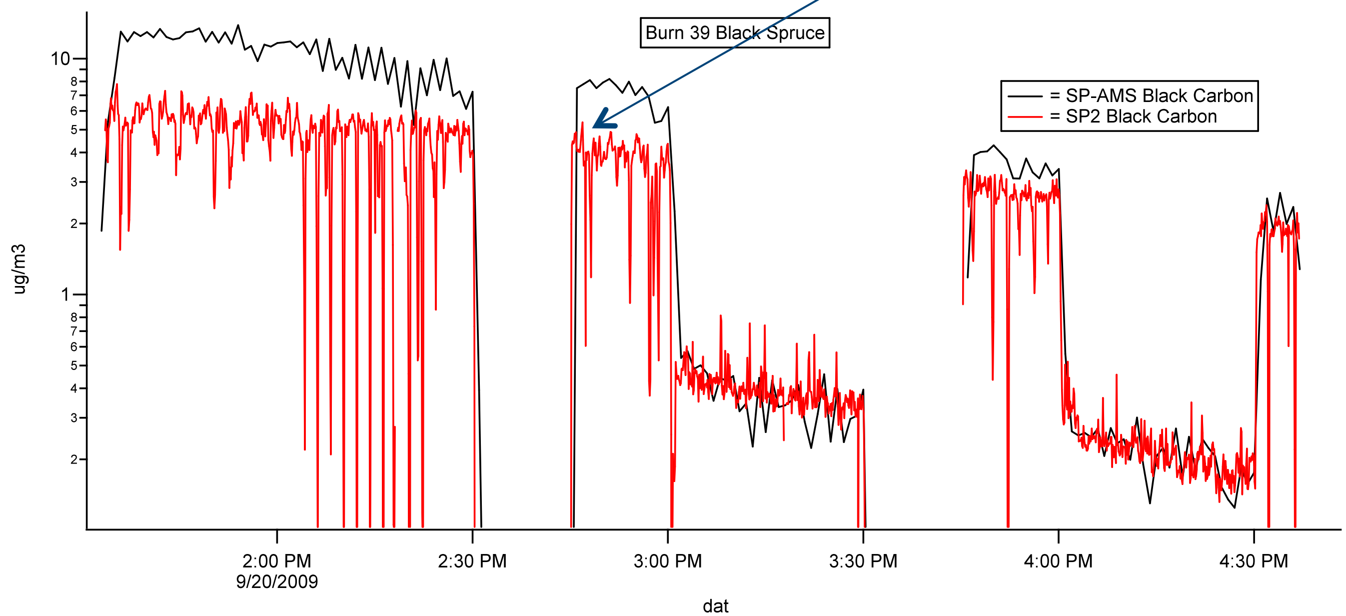
AMS timelines for various fragment classes



Add-on experiments: black carbon

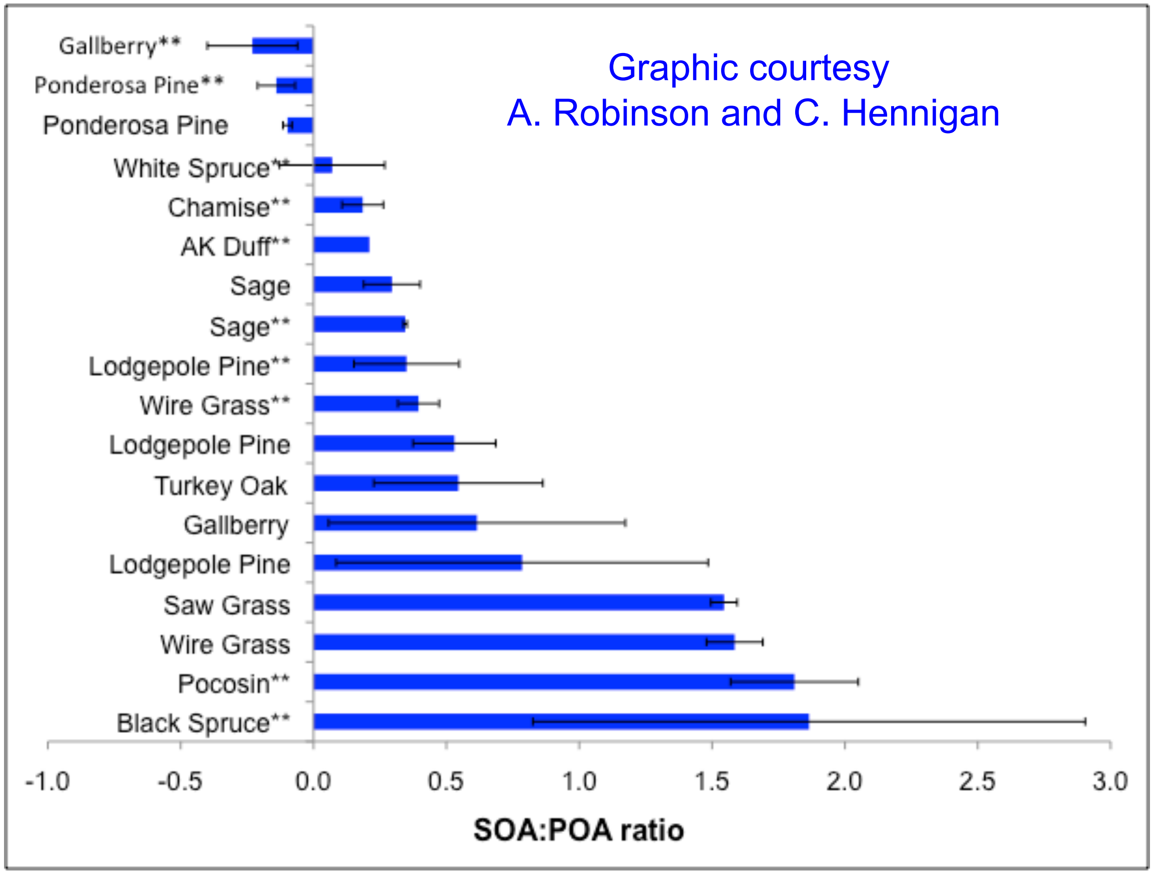
SP-AMS and SP-2 intercomparisons

SP-2 coincidence errors at high concentrations



SP-2 data courtesy
G. McMeeking and H. Coe

Add-on experiments: SOA from BB



CMU Mobile Lab sampled from the main combustion chamber into an outdoor smog chamber

Studied SOA formation from the BB emissions

← Wide range in behavior observed (net OA loss to significant net OA gain)

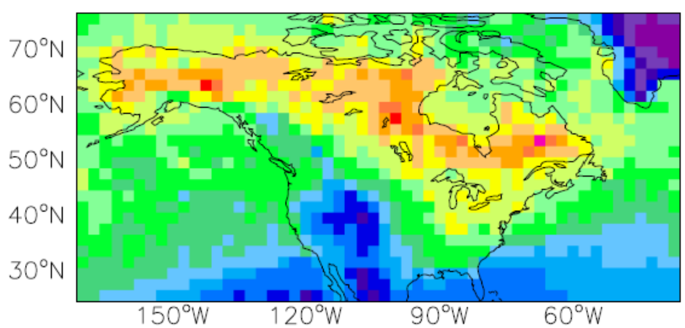
Plans for model development

- GEOS-Chem global 3-D CTM at 2°x2.5° resolution
  - Apply observed emission factors to GFED v2 (van der Werf, 2005) year-specific 8-day resolved biomass burning emission inventory for primary organics (lump to 3 fuel classes with similar partitioning characteristics) and SOA precursors (terpenes, aromatics)
  - Implement partitioning coefficients for each emission category following 2-product model SOA scheme in GEOS-Chem (3 new semi-volatile POA tracers, 2-3 new SOA from BB source tracers)
  - Implement oxidation rates and loss rates (wet/dry deposition) for new organics

Model applications

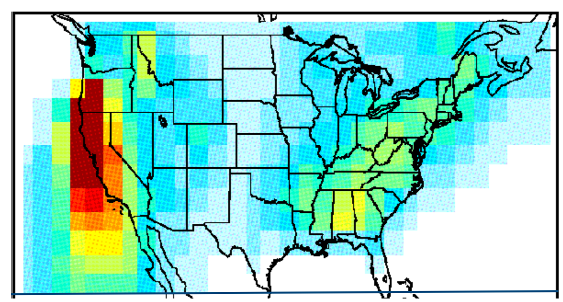
- Investigate OC aerosol loading over North America during wildfire (summer) season and compare to IMPROVE observations over the US (comparison to “standard” simulation) for 2002-2004
- Investigate particularly large events:

MOPITT CO – summer 2004



Alaskan fires of 2004: transported to East Coast and across Atlantic [Turquety et al., 2007; Lewis et al., 2007]

Surface Simulated OC: Aug 2002



Larges fires in Oregon responsible for haze throughout California, Washington and Oregon in summer 2002 [McMeeking et al., 2006]

Summary

- Our data for smoke from a wide variety of U.S-relevant fuels present a unique opportunity to study gas-aerosol partitioning of emissions from open biomass burning
  - Some of first available real-time data for BB [OC]
  - Isothermal dilution + thermal processing provide strong constraints on the volatility distribution fits
  - HR-ToF-AMS enables examination of degree of oxygenation and molecular markers
- Modules to be developed and tested in GEOS-Chem will provide insights into implications of our findings for regional air quality
  - Heavily-used and validated model for the US: good test bed
  - Coordinate with other EPA STAR studies on SOA formation from BB emissions