Contribution of Smoke to PM2.5 and Haze: Development of Smoke Source Profiles and Routine Smoke Source Apportionment Tools

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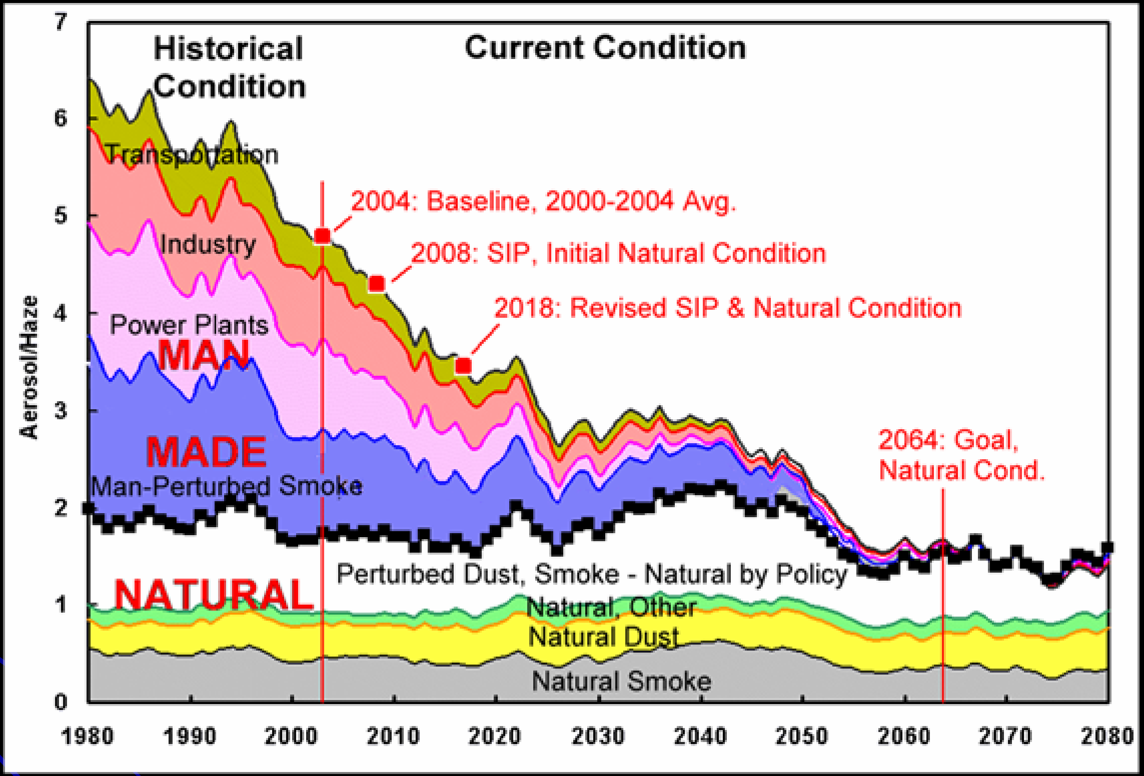
The Regional Haze Rule:

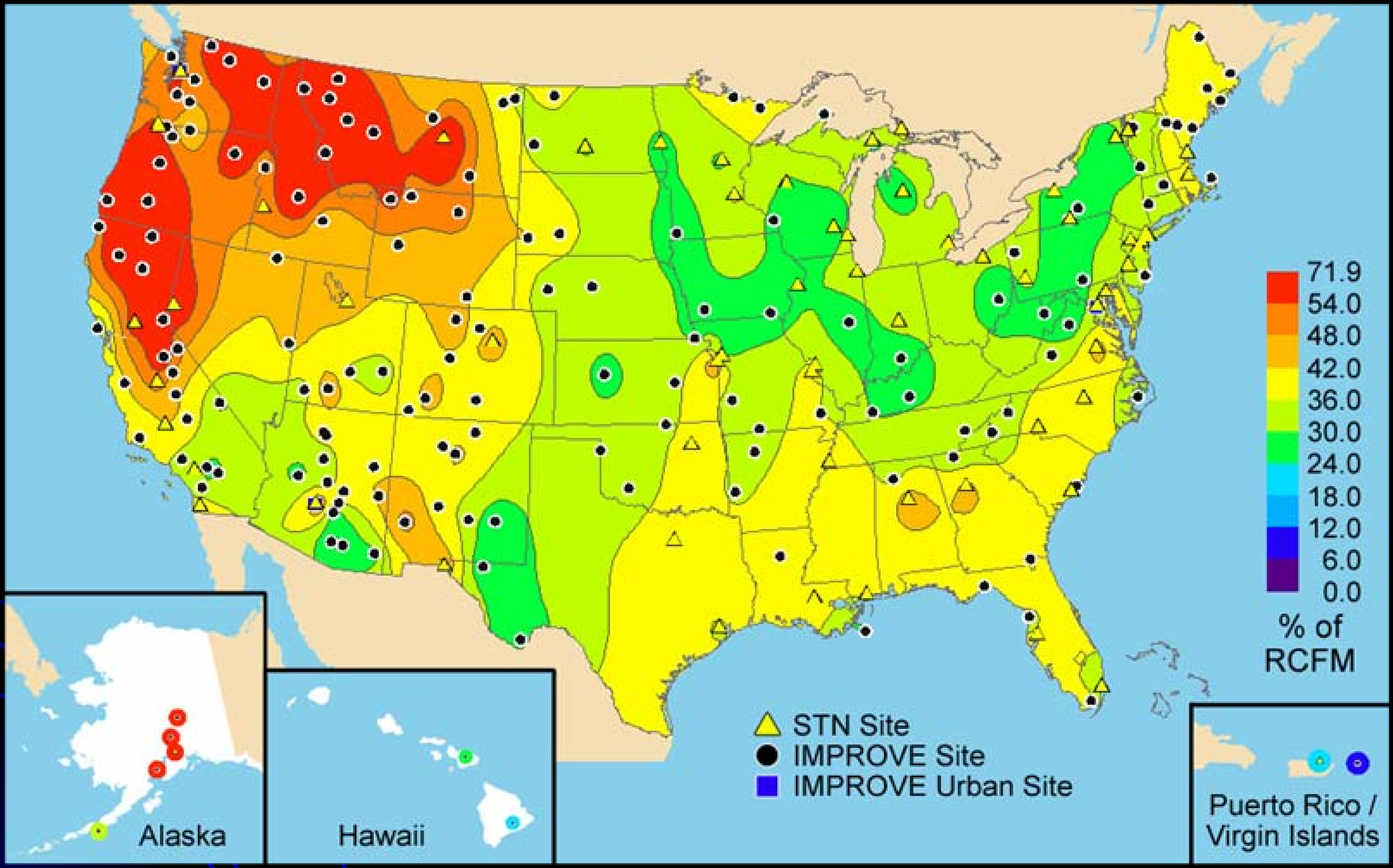
Return visibility in national parks and wilderness areas to "natural visibility" conditions by 2064



Husar, 2002

- Progress is tracked using the 20% worst haze days
- Natural haze: natural windblown dust, biomass smoke and other natural processes

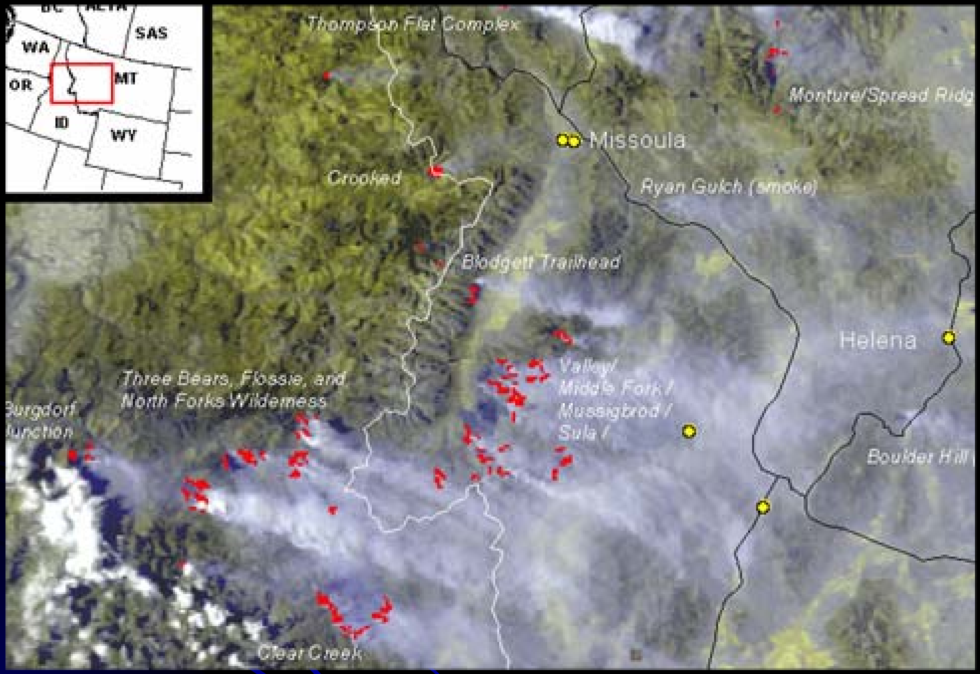
Urban & Rural Annual Organic Carbon

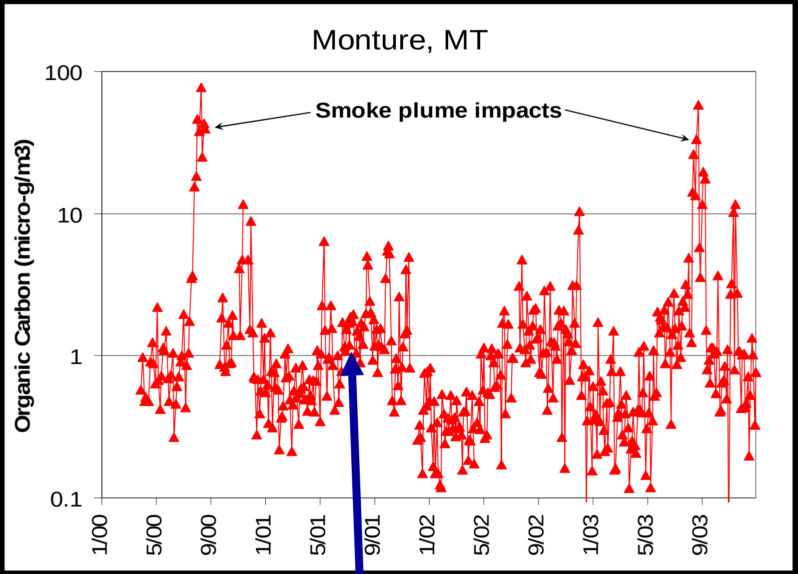


Sources

- Smoke from wild, prescribed, agricultural and residential fires
- Mobile sources, Cooking, SOA from vegetation

Smoke's Contribution?





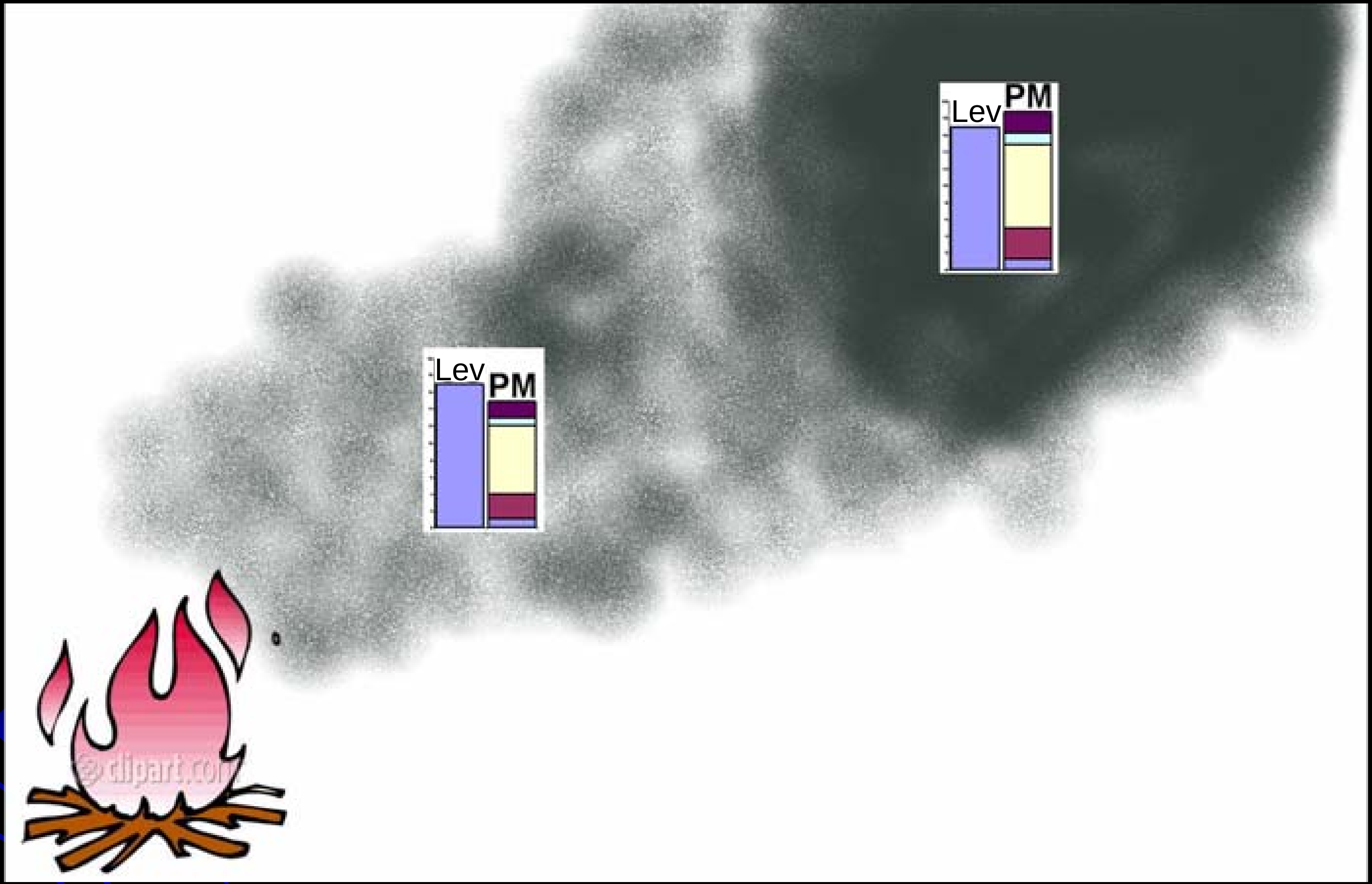
Wildfire? Fossil sources?
Agricultural fire?

Smoke Management Need for Air Quality Regulations

- **Develop an unambiguous <u>routine</u> and <u>cost effective</u> methodology for apportioning primary and secondary carbonaceous compounds in PM2.5 to prescribed, wildfire, agricultural fire, and residential wood burning activities**
  - Daily contributions needed for Haze Rule to properly estimate natural contribution and contribution to worst 20% haze days
  - Annual and daily contributions needed for PM2.5 and PM10 NAAQS
  - Long term data needed to assess successes of smoke management policies

- What is smoke's contribution to this haze?

Receptor Modeling



Source Marker Species

- One or more compounds that are unique to the source, emitted at a constant fraction of PM2.5, and are stable in the atmosphere.

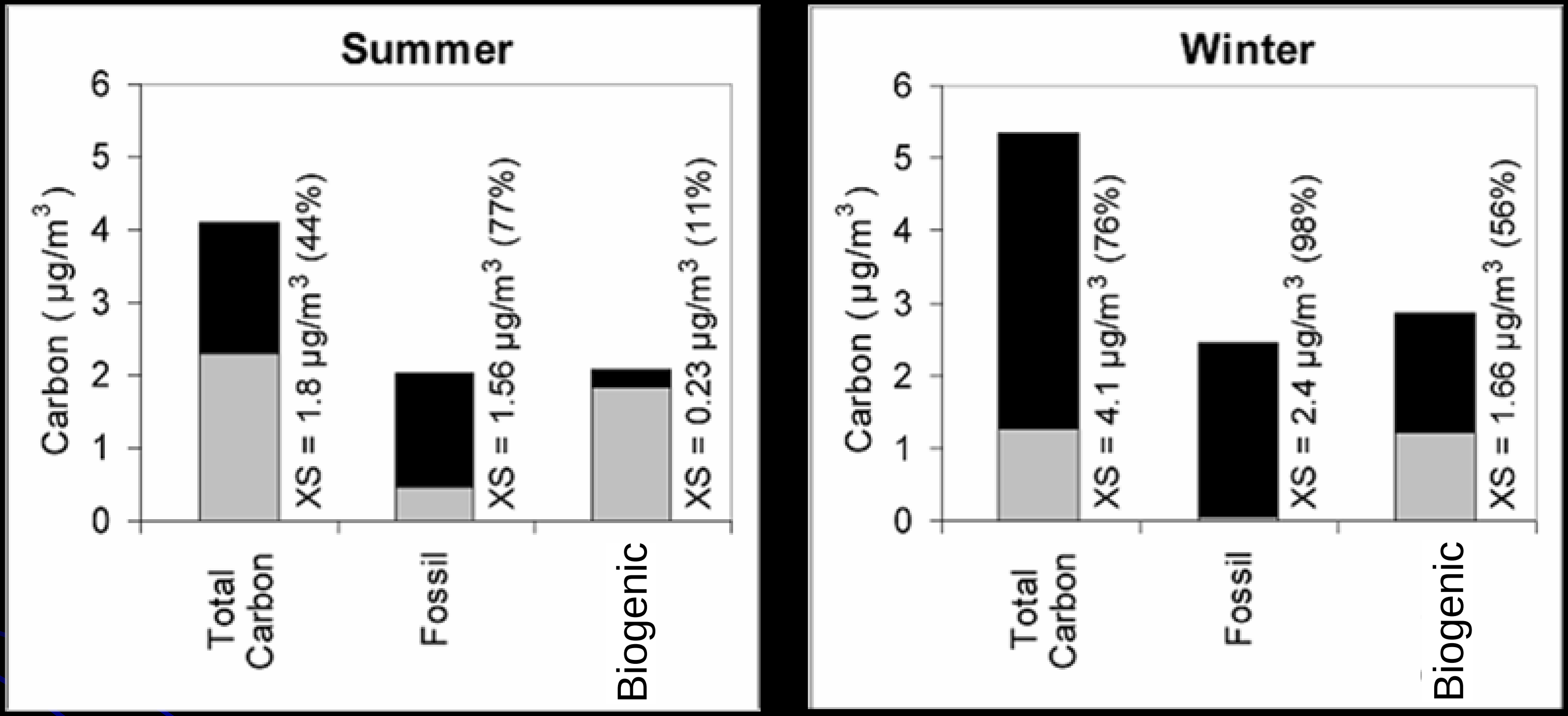
Radiocarbon Isotope (^{14}C)– Distinguishing Between Biogenic and Fossil Carbon

Fraction of biogenic carbon in PM2.5 carbon

Seasonal fraction of biogenic carbon The whiskers are the range in the fraction bigenic carbon in the 6-day samples

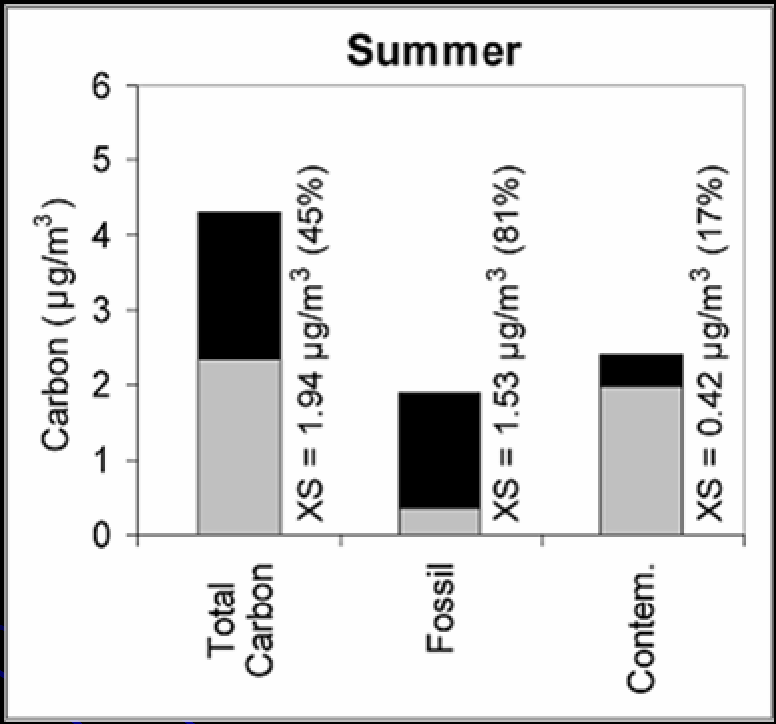
Urban Excess

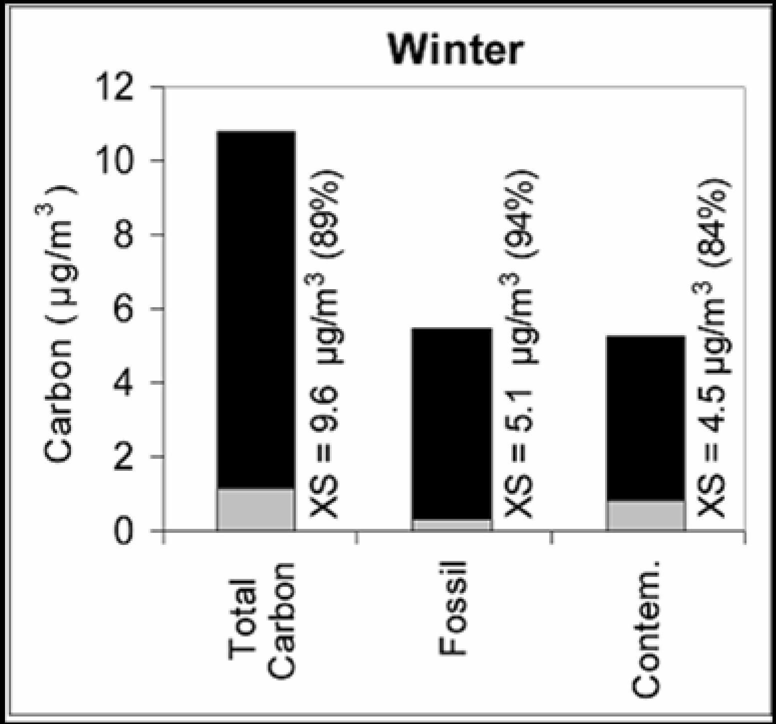
Puget Sound, WA (Blue) - Mount Rainier, WA (Red)



- Puget Sound fossil carbon is primarily due to local sources during winter and summer
- Summer biogenic carbon is regionally distributed
- ~40% of the winter urban excess is biogenic carbon– what anthropogenic sources?

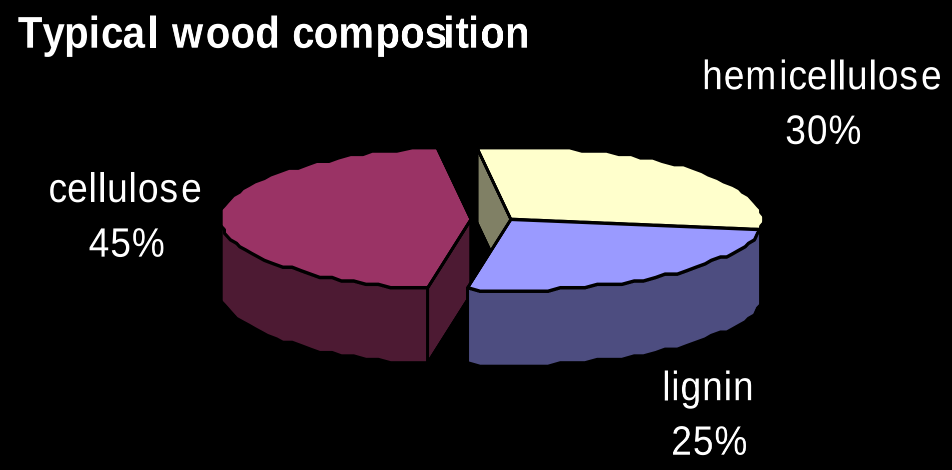
Urban Excess
Phoenix, AZ (Blue) – Tonto, AZ (Red)





- Phoenix fossil carbon is primarily due to local sources during winter and summer
- Summer biogenic carbon is regionally distributed
- About half of the winter urban excess is biogenic carbon
  - How important is residential wood burning in Phoenix Arizonia?

Smoke Markers Species



- Methoxylated phenols
  - Guaiacol and substituted guaiacols
  - vanillin, vanillic acid, eugenol, 2,6-dimethoxy phenol, ...
  - syringol and substituted syringols
- Resin Acids
  - abietic acid, pimaric acid, …
- Retene
- Monosaccharide Anhydrides (Sugar anhydrides)
  - **Levoglucosan**
    - Cellulose thermal decomposition product
    - Major component of wood smoke
  - Galactosan, mannosan

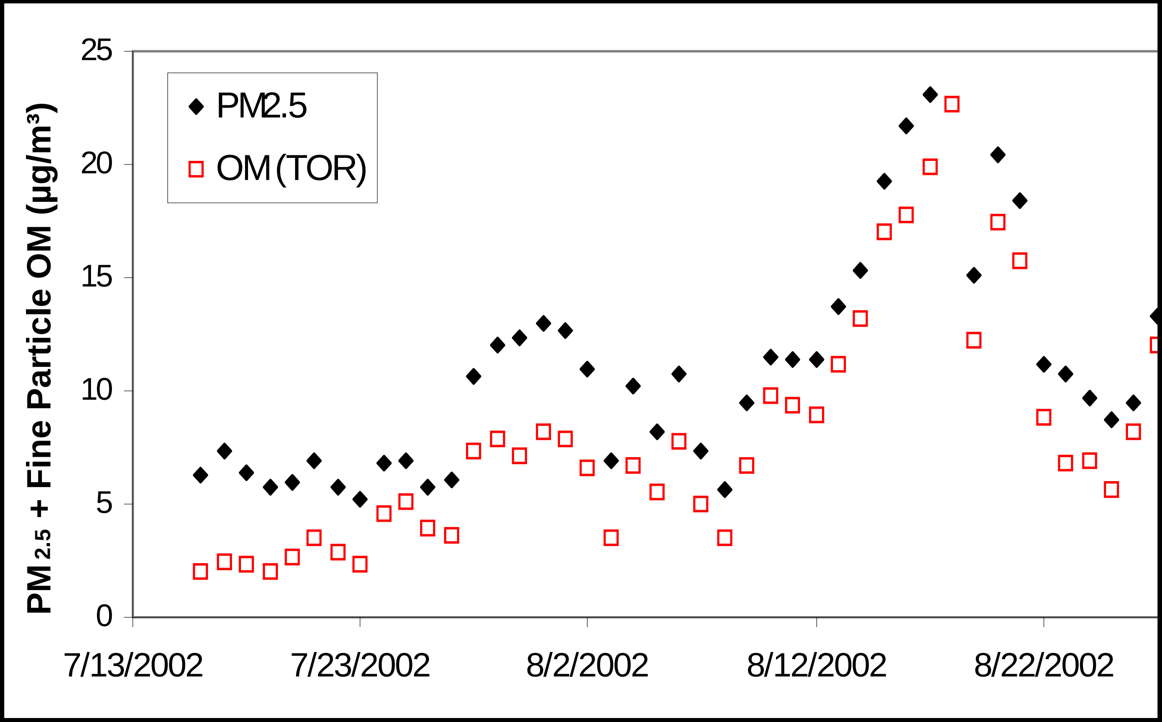
Smoke Marker Species Issues

- Resource intensive to measure
  - Multiple extraction of filters with organic solvents
  - Chemical derivatization of extracts
  - Analysis of extracts with GC/MS
- Requires large samples
- Few studies generating source profiles for wildland fuel types
- Marker species account only for primary fine particulate matter

Yosemite National Park Smoke Assessment Study Summer 2002

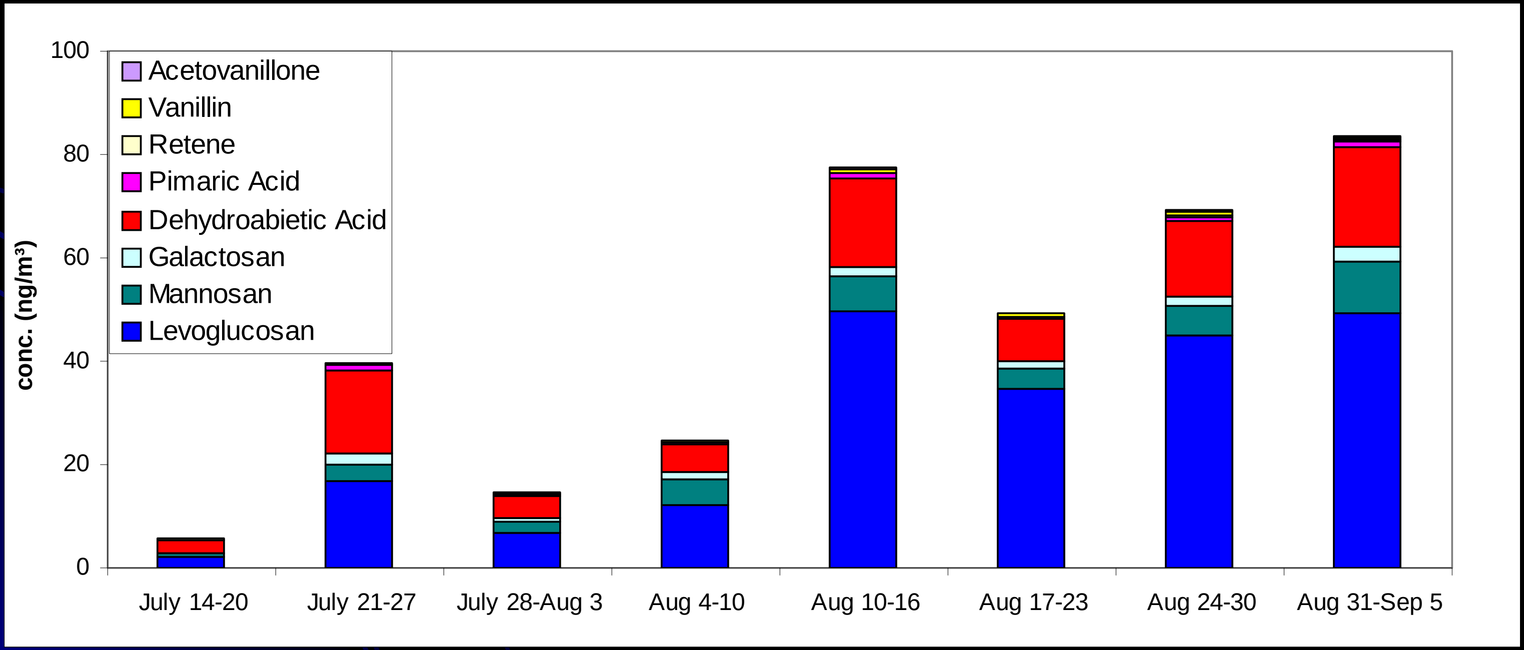
- Air quality in Yosemite National Park
  - IMPROVE shows high summer-time fine aerosol concentrations
  - Large carbonaceous PM content (> 40%) + high seasonal variability in OC
- Study Objectives
  - Estimation of wildland fire contributions to ambient aerosol and regional haze

Fires Impacting Yosemite NP Summer 2002



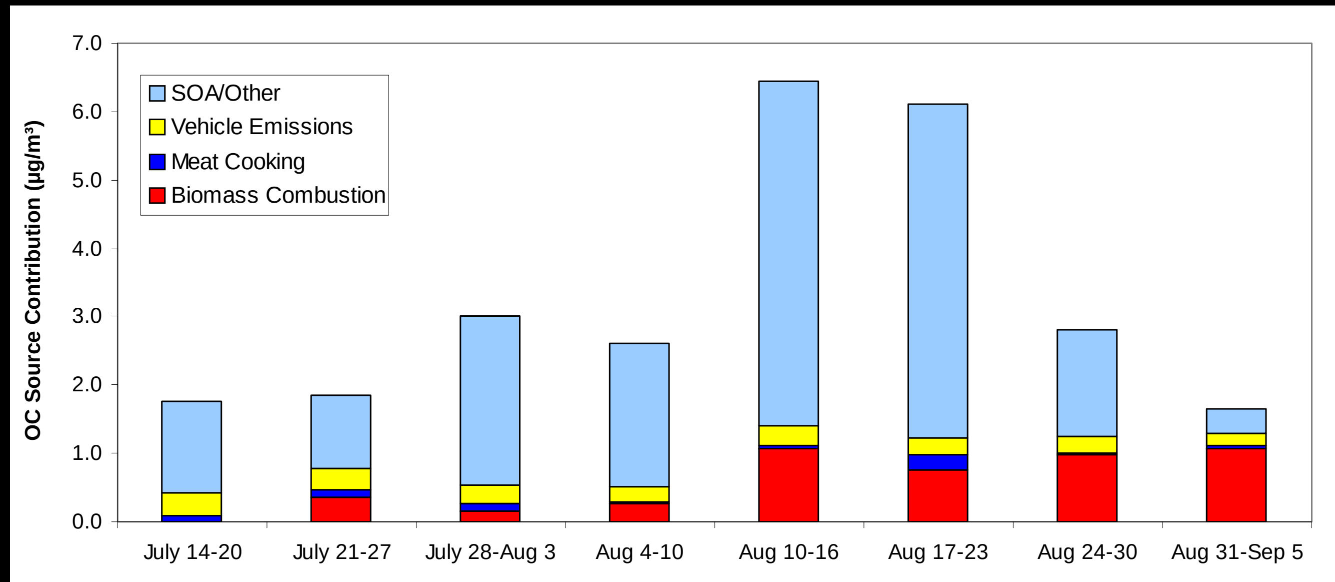
Yosemite smoke markers timeline

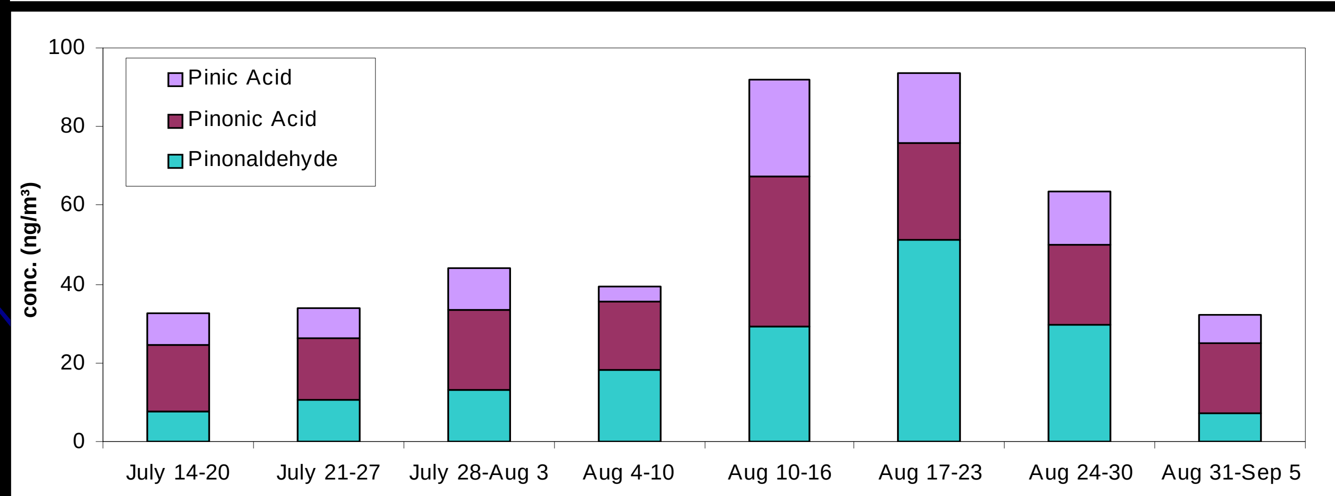
- Smoke markers also rise in mid-August
  - High concentrations in early Sept ←→ local fire



Overall apportionment

- Vehicle and cooking small sources
- SOA appears important
  - Biogenic source
  - Enhanced in smoke plume





Engling et al (2006) Atmos. Environ. 40, 2959-2972

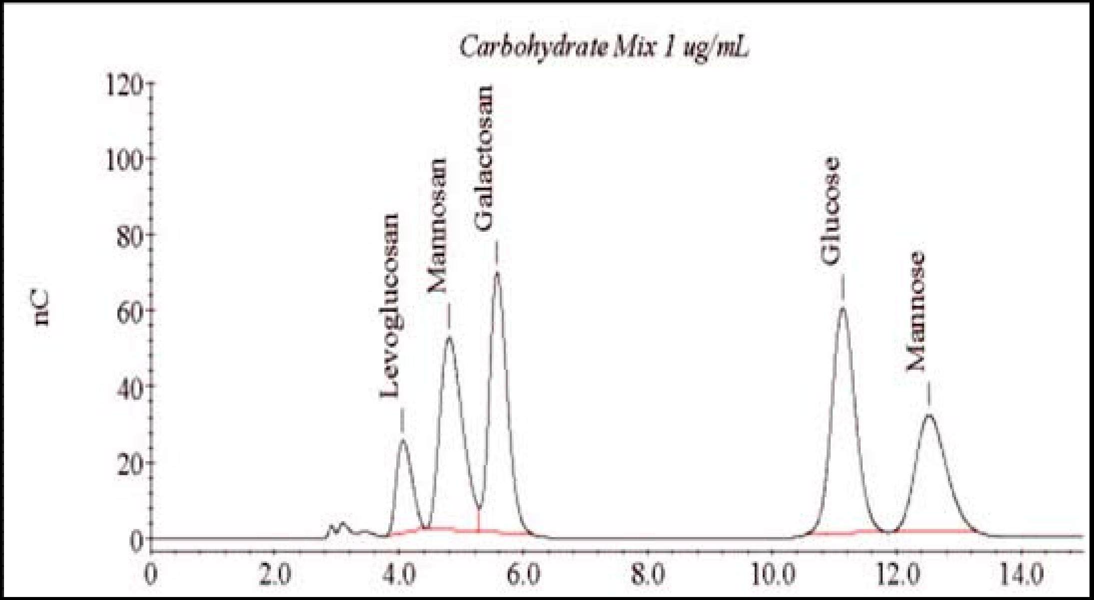
Developing Smoke Apportionment System

- Source apportionment system to estimate the contribution of primary and secondary smoke from different types of fire
  - Primary Smoke
    - Cheap and easy smoke markers species (Levoglucosan) measurements methods applicable in routine monitoring programs
    - Smoke source profiles for wildland fuel types
  - Secondary Smoke and Smoke Types
    - Hybrid source apportionment model - Statistical model for integrating deterministic modeling results and measured data

Anion exchange with electrochemical detection – Cheap and Easy

Filter Sample → Water extraction → Inject into IC

- H_2O extraction
  - no derivatization
- Carbohydrates separated on anion exchange column
  - can resolve levoglucosan, mannosan, galactosan, glucose,…
  - similar to IC but different detection



Engling et al. (2006) Atmos. Environ. 40, S299–S311

The FLAME Experiment

- USDA Forest Service Fire Science Lab at Missoula
- Characterization of primary smoke emissions
  - Hundreds of burns
  - Fuel components and complexes
  - NW, SW, and SE fuel emphasis
  - Chemistry, optical properties, hygroscopicity

Objectives

(1) development and validation of promising new, **inexpensive methods suitable for quantitative measurement of smoke marker (levoglucosan and K+) concentrations** in aerosol filter samples, such as those routinely collected by the IMPROVE or EPA STN networks;

Collett group, ongoing

(2) **laboratory measurements of smoke emission composition profiles** from several important fuel types burned under a variety of conditions to provide urgently-needed source profiles for classes of fires believed to severely impact air quality in the western and southeastern U.S.;

(3) concurrent with smoke emission profile measurements, **measurement of key physical and optical properties and emission rates in the laboratory**; and

Years 1 and 2

FLAME I, 2006

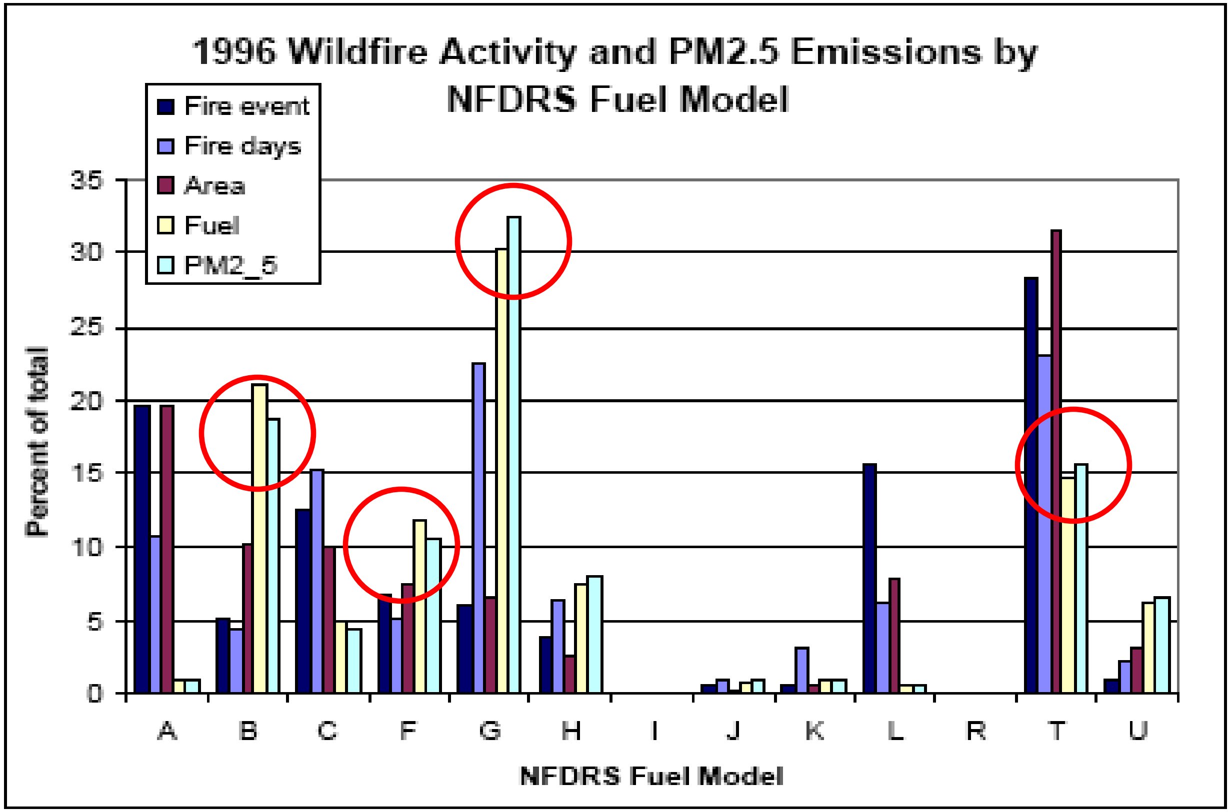
FLAME II, 2007

(4) **field measurements of fresh smoke plumes** to validate whether laboratory smoke studies, conducted under well controlled conditions, can simulate $PM_{2.5}$ mass, composition, and optical property emissions characteristics of more complex, actual prescribed and wild fires.

Year 3

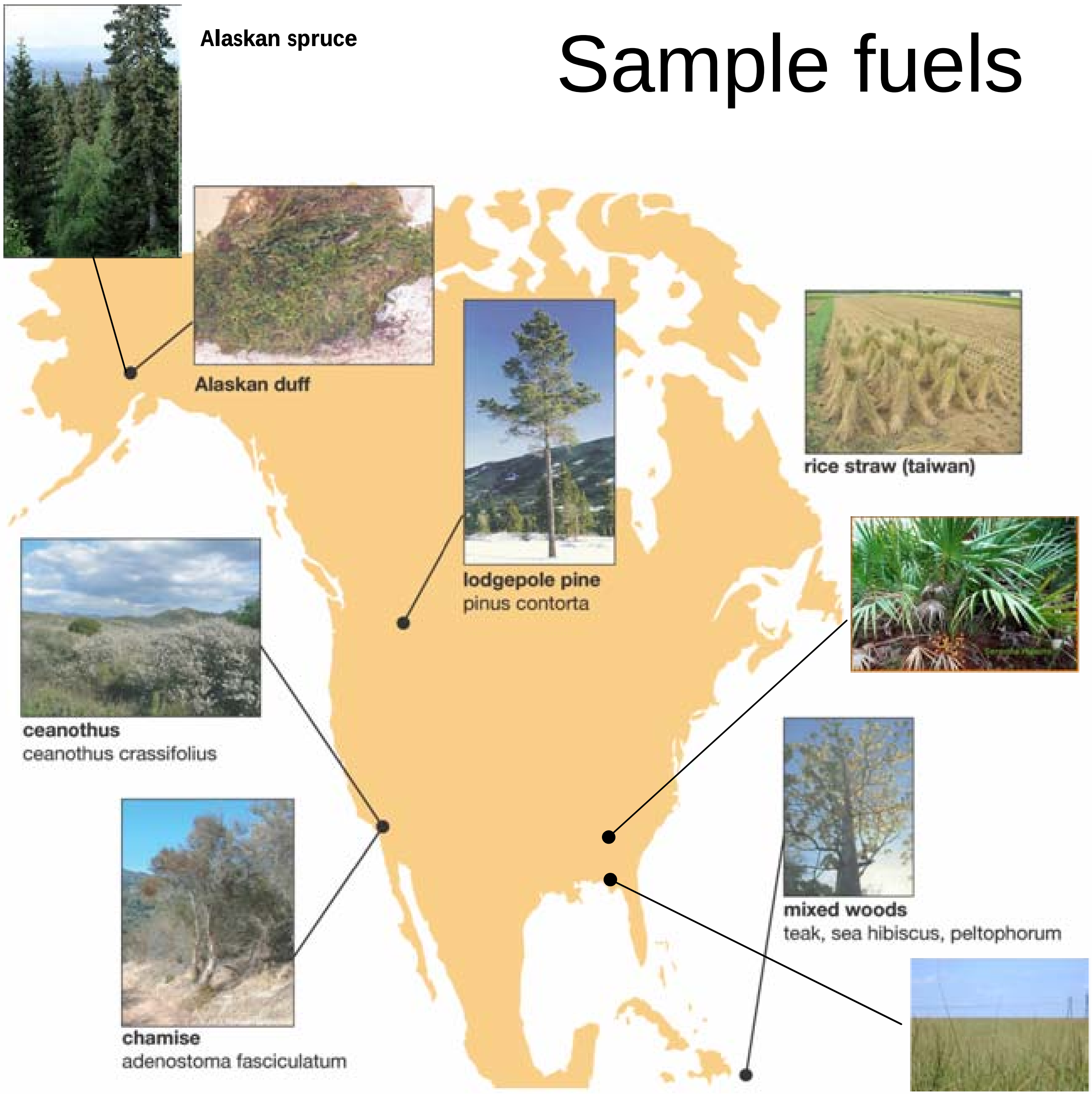
Which fuels are of interest?

(**Western US** only represented here – by FUEL MODEL)



B = mature CA mixed chapparal
F = CA mixed chapparal; AZ, UT & CO chamise stands
G = dense conifer stands w heavy accum of litter, duff (H = healthy)
T = sagebrush-grass + shrubs of Great Basin & intermountain West
U = western long-needled pine

Sample 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

Choices of **Southeastern U.S.** fuels guided by Dennis Haddow and colleagues (primarily 2007 burns)

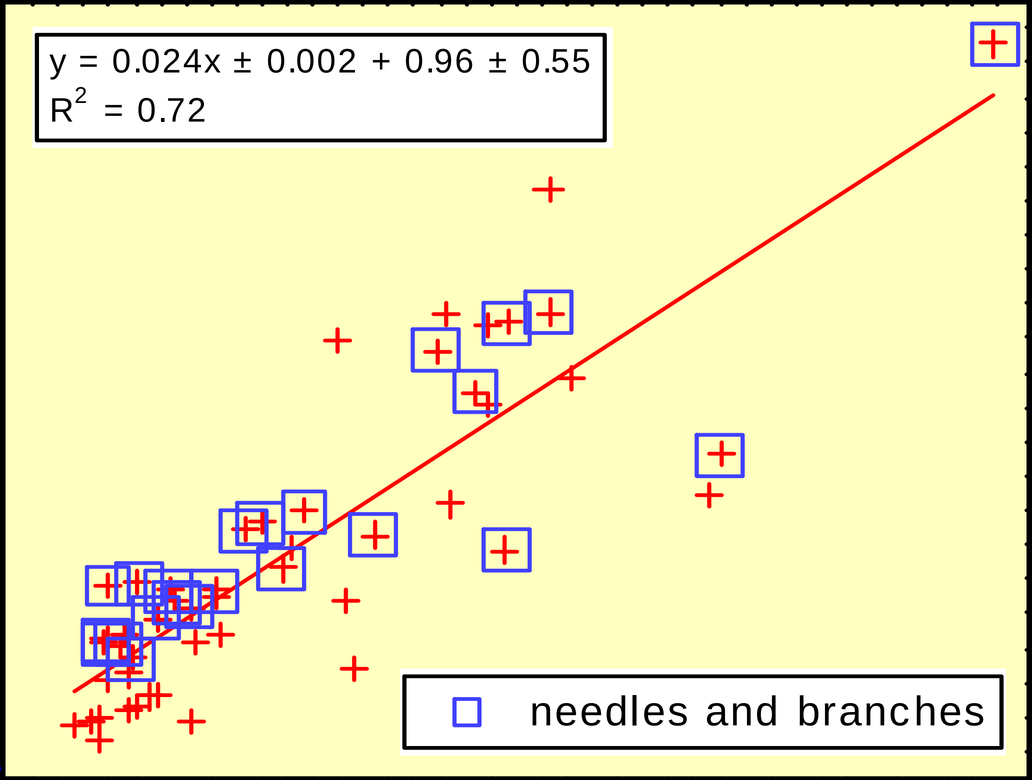
Included marsh plants (grasses), oak+hickory leaves, gallberry, and wax myrtle in addition to those shown here

Levoglucosan from Ponderosa Pine

	FLAME 2006	Hays et al., 2002 (burn enclosure)	Schauer et al., 2001 (residential fireplace)
Branches (dead, large)	0.057	0.019	0.115
Branches (dead, small)	0.034		
Branches (fresh, large)	0.040		
Branches (fresh, small)	0.039		
Needle Litter	0.030, 0.027, 0.037, 0.033, 0.031		
Needles (fresh)	0.016		
Complex	0.032, 0.016		
Duff	0.027, 0.034		

*all units µg C/µg C

Levoglucosan vs. OC from multiple fuel types (On Carbon Mass Basis)



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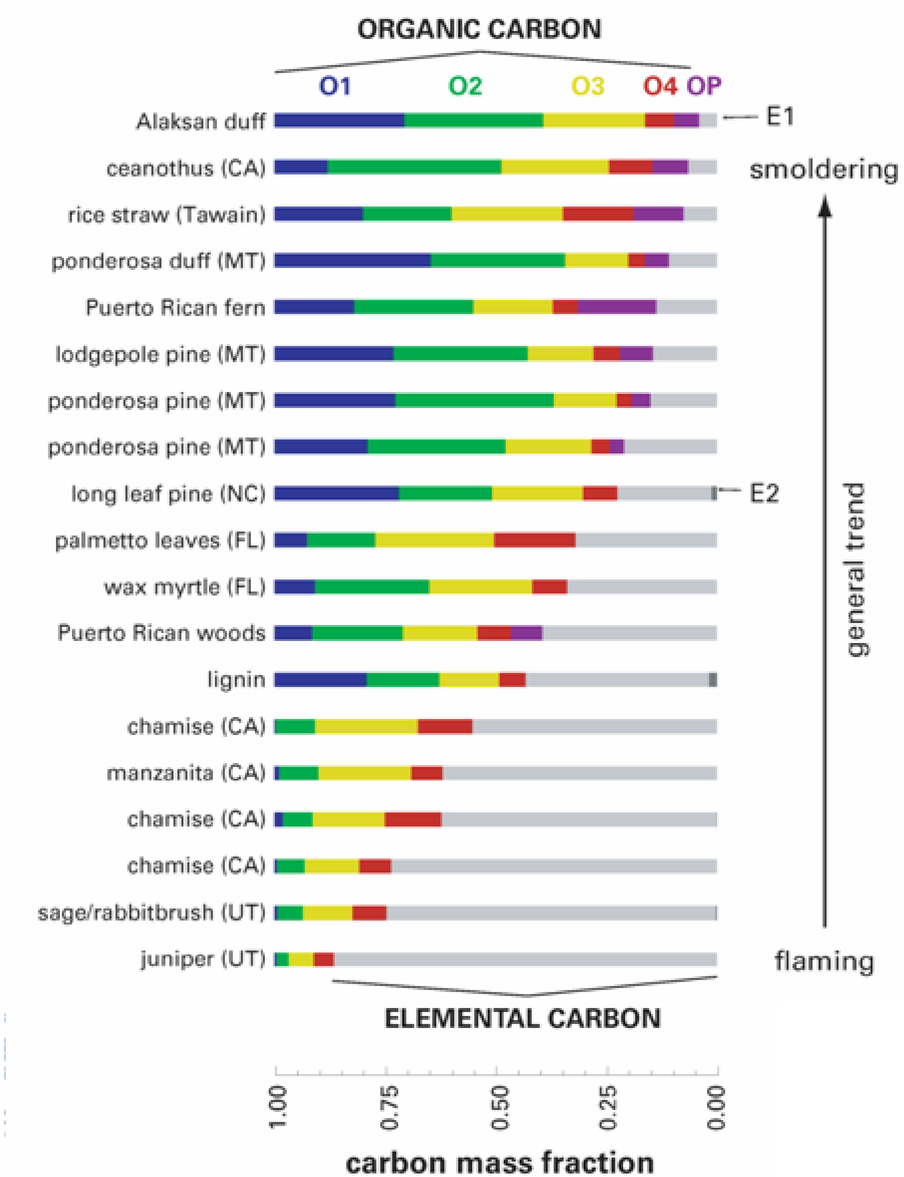
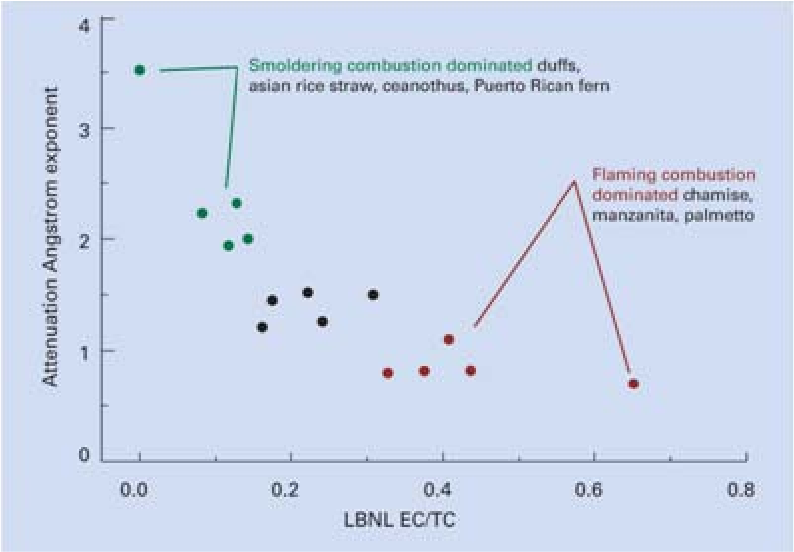
Carbon content and extinction



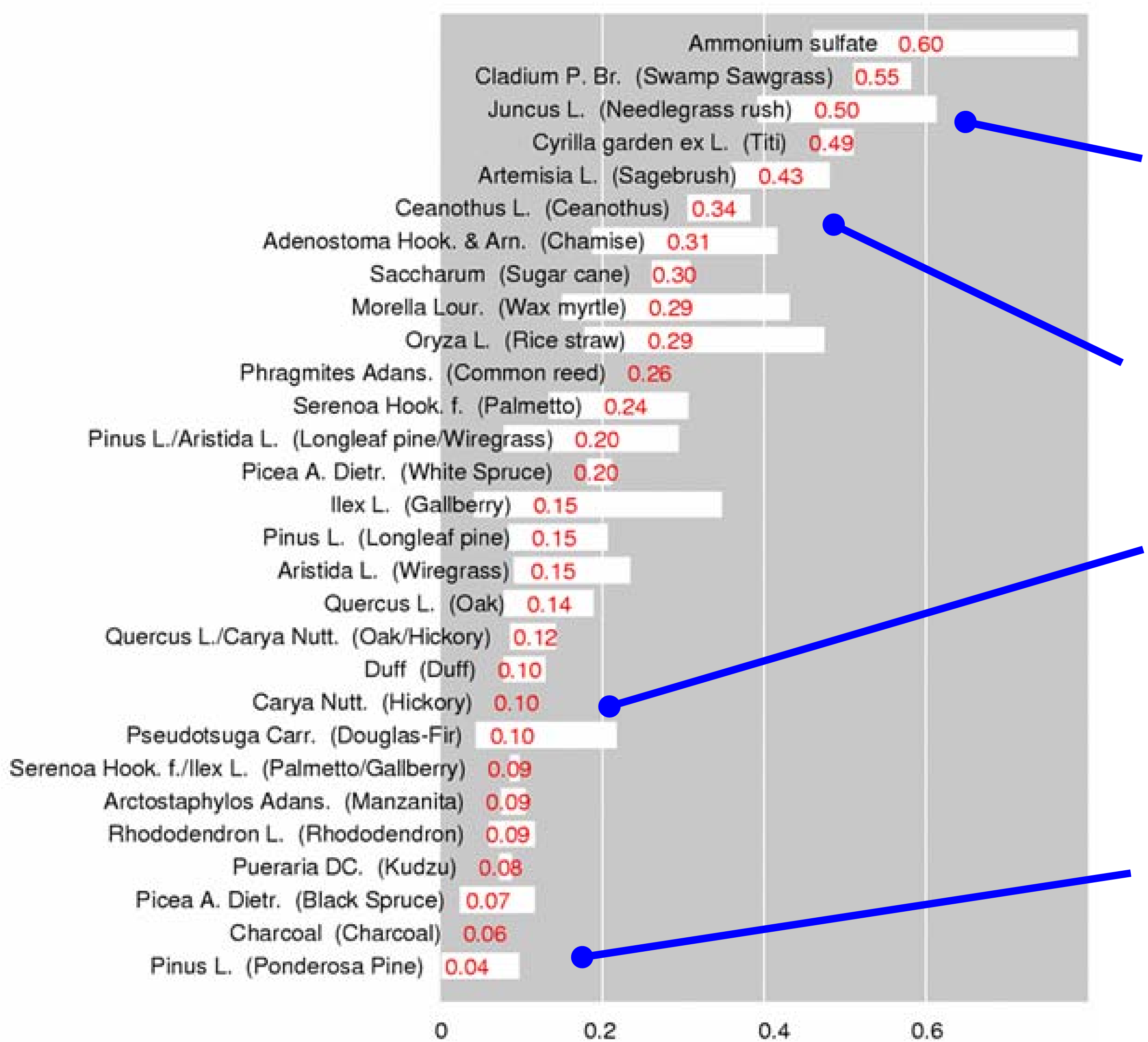


Light attenuation Angstrom exponent (wavelength-dependence of extinction, 400 nm to 1000 nm):

expect values ~1 for "soot"

Find higher values for smoldering-dominated smokes (low EC/TC ratios)
- OC component(s) light-absorbing

Hygroscopic growth rankings



Some smokes were nearly as hygroscopic as pure ammonium sulfate

Many in this group had low single-scattering albedo and high EC content

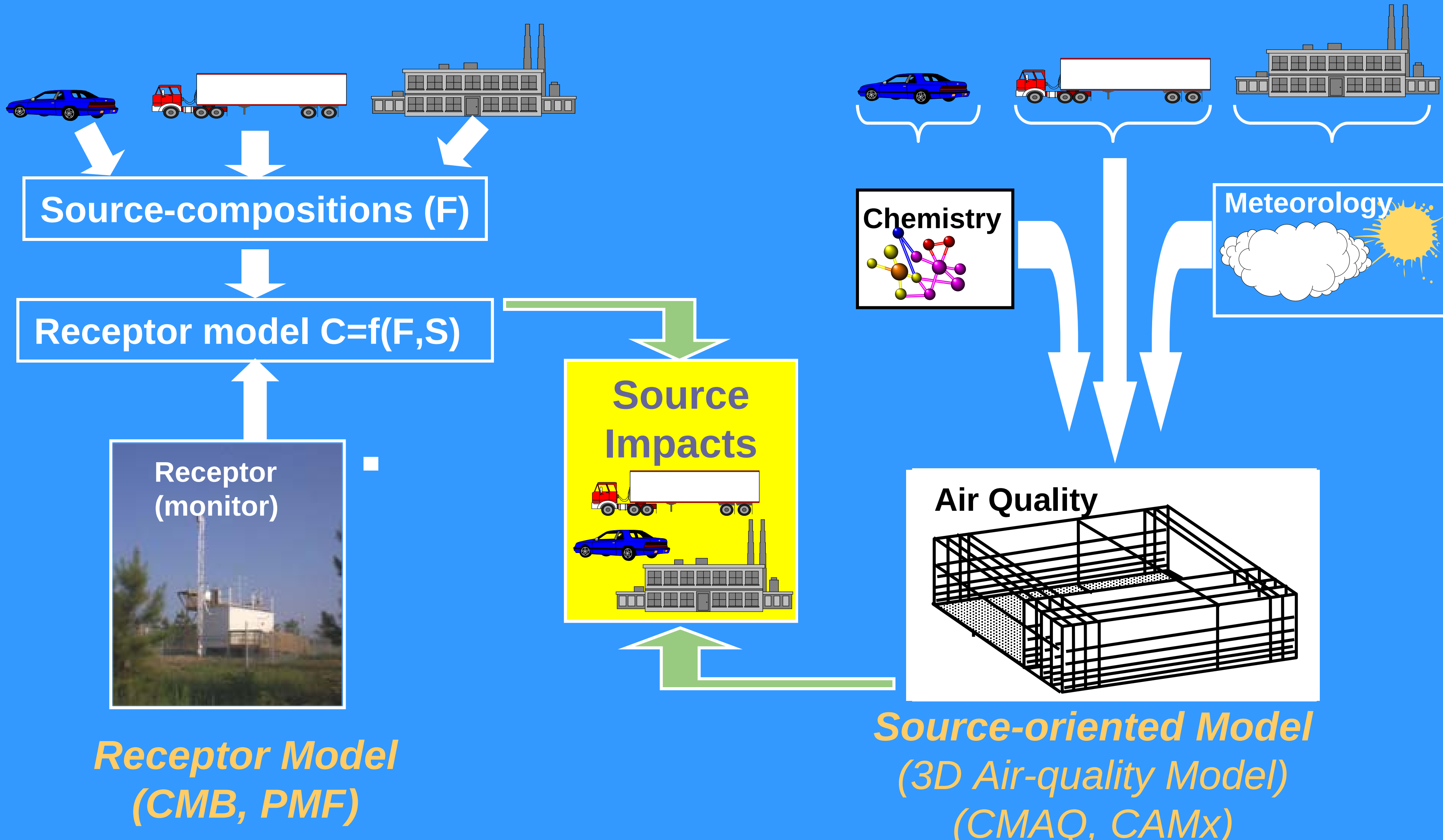
A ranking of 0.1 represents “typical” secondary organic aerosol

This group represents low water uptake at subsaturated conditions

What's next

- **Remaining Year 3 phase calls for field study to test composition profiles, ability to estimate optical properties from lab data**
  - Will be conducted in conjunction with USFS Missoula in a prescribed-burn region, most probably western / southwestern US
    - Early summer planned (not finalized)
  - CSU will deploy Mobile Laboratory with subset of aerosol characterization instrumentation
- We have a NUMBER of papers in the works, from both 2006 and 2007
  - Several should be submitted by year-end

Hybrid Source Apportionment Model



Proposed Hybrid Receptor model

CMB framework:

$$c_{ki} = \sum_j S_{kj} a_{ji} + \varepsilon_{ki}$$

where

k = 1 ... m, the number of observations,

I = 1 ... n, the number of marker species,

j = 1 ... N, the number of sources,

c_{ki} = concentrations of aerosol species (including marker species) i for time period k,

S_{kj} = relative contribution of source type j to observation k at the receptor

a_{ij} = source profiles. The relative concentration of species i in source type j

ε_{ki} = model residual

Solve for Source Contribution Matrix S

Three measures of quality of fit :

1) Model to measured data fit:

$$Qc = \sum \frac{(c - \hat{c})^2}{uc^2}$$

2) Fit to *a-priori* air quality model source apportionment results

$$Qs = \sum \frac{(S_m - \hat{S})^2}{uS_m^2}$$

S_m air quality model estimate for an element of ***S***;

$\hat{S}$ is the corresponding fitted value

3) Allow the source profiles ***a*** to vary within a predetermined range

$$Qa = \sum \frac{(a - \hat{a})^2}{ua^2}$$

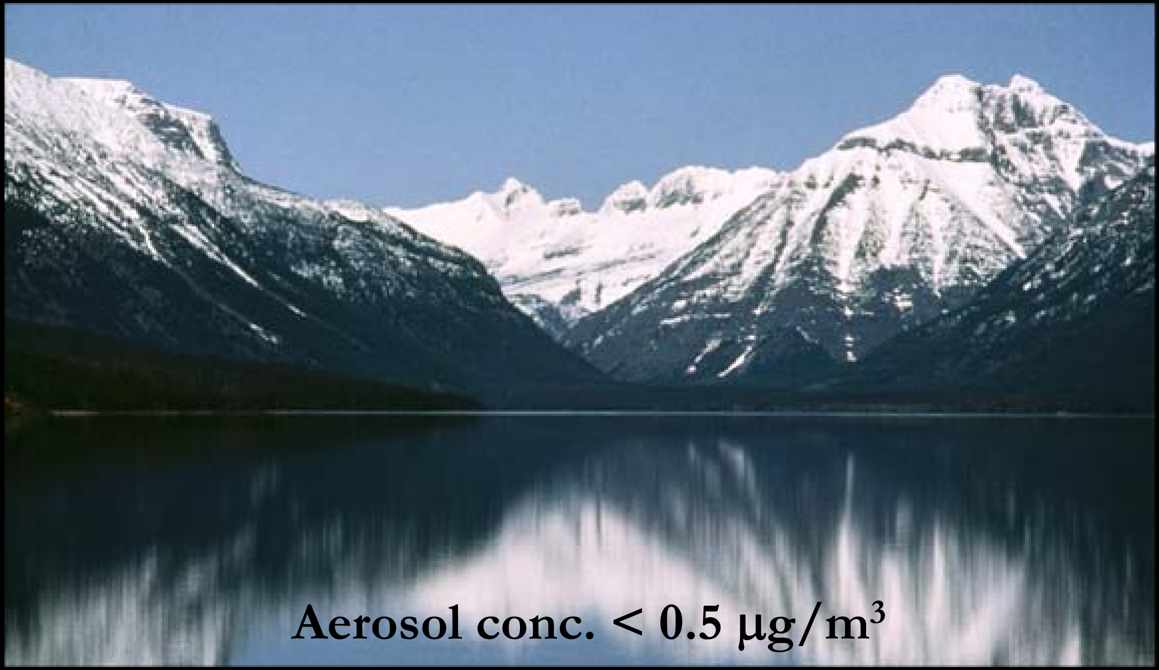
a = f(primary, secondary); e.g. a 2 component mixing model

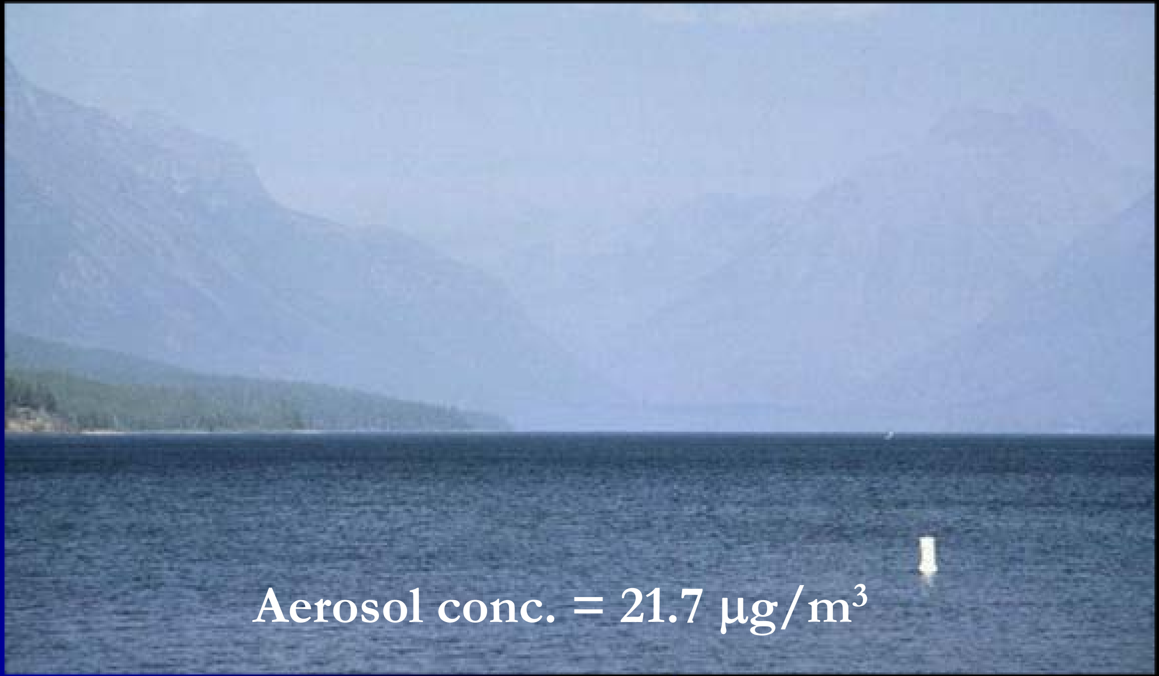
a represents an *a-priori* source profile value, $\hat{a}$ the corresponding fitted value

Next Steps and Needs

- Source Profiles
  - Develop source profiles from actual prescribe and wildfires
    - Do lab tests translate to real world fires?
  - Flaming vs. smoldering?
- Test the smoke marker measurement method in a routine monitoring network, e.g. IMPROVE
- Routine deterministic modeling source apportionment results
  - or at least emission inventories with complete smoke emissions
- Need better understanding of production of SOA in smoke plumes

Questions





Glacier NP