$PM_{2.5}$ chemical speciation data without a speciation monitor???

EPA and Idaho's experience with Pinehurst Idaho.

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NW-AIRQUEST, Portland OR, 2015

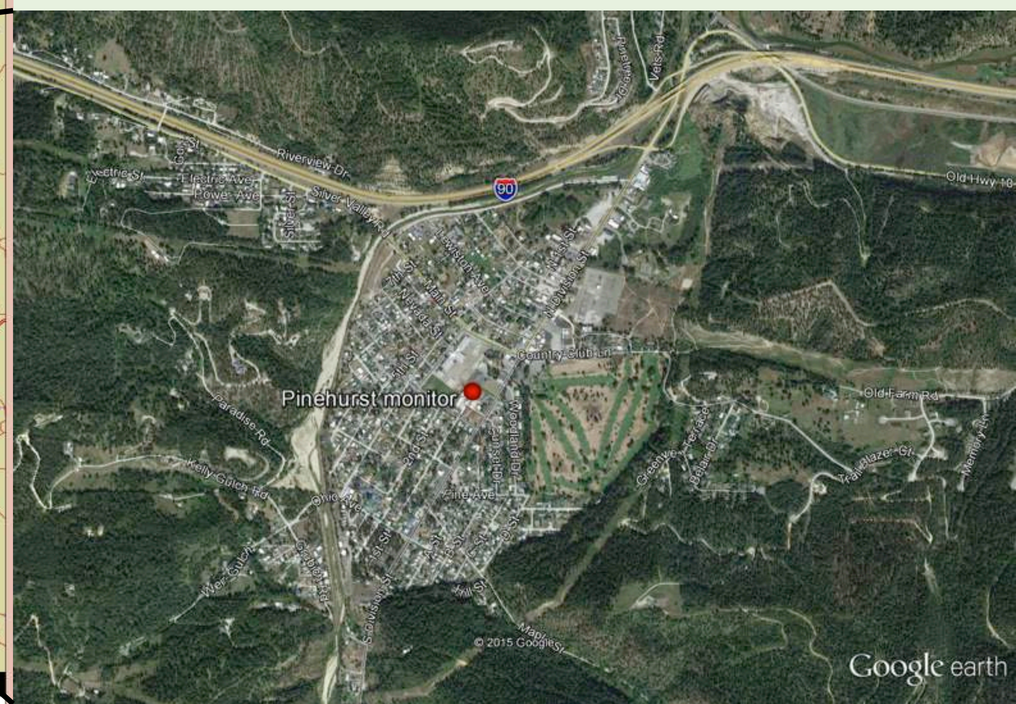
Why is $PM_{2.5}$ speciation data needed for Pinehurst?

Pinehurst is a new $PM_{2.5}$ nonattainment area based on the 12 μg/m3 annual standard.

$PM_{2.5}$ chemical speciation data is needed for

(a) attainment demonstration in the SIP and

(b) to better understand what sources are impacting the monitor.



Pinehurst, ID

(population ~1600)

Problem:

- Pinehurst does not have a $PM_{2.5}$ chemical speciation monitor.

Typical solution:

- Install a chemical speciation network (CSN) monitor and run for at least 1 year.

However, Idaho and EPA were aware of a possible alternate solution:

- Perform chemical analyses on archived filters from the regulatory (FRM) $PM_{2.5}$ monitor.

There are several examples of FRM monitor filters being used for chemical speciation analyses, but not many:

- In 2008, Neil Frank (EPA, OAQPS) documented a proof of concept analysis that used chemical analysis on archived Teflon FRM filters to construct a chemical speciation of $PM_{2.5}$ for 15 urban areas.
- Subsequent to that, Zhang et al. (2010)* used this methodology to analyze biomass burning impacts to $PM_{2.5}$ in the southeastern US.
- While there have been limited examples, the methodology seems sound.

*Zhang et al., Atmos. Chem. Phys., 10, 6839–6853, 2010

What kind of chemical data can we get from a FRM Teflon filter?

… surprisingly, a lot …

x-ray fluorescence (XRF) -> elemental analysis

- Soil impact estimation (Al, Si, Ca, Fe, Ti)
- Sea salt estimation (Na, Cl)
- Biomass burning tracer (K)
- Trace metals/elements associated with mobile sources, industry, etc.

ion chromatography (IC)

- major inorganic secondary PM2.5 (NO3-, SO4--, NH4+)
- Na+, Cl-, K+
- levoglucosan (biomass burning tracer)

optical light absorption (transmission densitometer, 'Babs')

- indirect measure of EC

… but not organic carbon (Teflon media is carbon containing)

- However, Neil Frank has shown that adding up all the above measurements and subtracting from total PM2.5 is a good estimate for total organic mass. I.e, <u>one can estimate total organic mass by difference</u>.

Comparing the typical CSN monitor data with FRM chemical analysis (with respect to the kinds of data obtained).

FRM chemical speciation	Typical CSN sampler chemical speciation	Usefulness
x-ray fluorescence (XRF)	**x-ray fluorescence (XRF)**	**- Soil estimation (Al, Si, Ca, Fe, Ti)** **- Sea salt estimation (Na, Cl)** **- Biomass burning tracer (K)** **- Trace metals/elements associated with mobile sources, industry, etc.**
ion chromatography (IC)	**ion chromatography (IC)**	**- major inorganic secondary PM2.5 (NO3-, SO4--, NH4+)** **- Na+, Cl-, K+**
Elemental carbon (**EC, indirectly** by light absorption; 2 methods; Babs & Magee IR)	- Elemental carbon (**EC, directly** by thermal evolution) **- 3 thermal EC fractions**	**- Combustions sources (biomass, fossil fuel)** **- For CSN, thermal fractions help with source apportionment.**
Organic mass (**OM, by difference**, bulk PM2.5 minus quantified chemical constituents)	- Organic carbon (**OC, directly** by thermal evolution) **- 5 thermal OC fractions**	**- Primary combustions sources (biomass, fossil fuel)** **- Secondary (SOA) anthropogenic and biogenic VOC sources.** **- For CSN, thermal fractions help with source apportionment.**

Why not just install the typical CSN monitor in Pinehurst?

Time and money

Chemical speciation with FRM filters is faster and cheaper.

Method	Timescale to obtain needed data	Cost for ~60-70 samples	Benefits
Typical 1-in-6 CSN monitoring for 1 year	16-20 months	~$90,000	Direct & more detailed OC and EC analyses
FRM archived filter analyses	~4 months	$25,000 (includes levoglucosan!)	Faster and cheaper

Benefits of FRM-based analysis:

- **about 4x faster at about 1/4 the cost**
- **FRM filter analysis included levoglucosan**

Drawbacks:

- **Data for OC and EC are indirect, and less detailed**
- **FRM monitors are known to be subject to NO3 losses**

Idaho and EPA chose to do FRM filter analysis for Pinehurst. For $25,000 we got …

73 FRM filters (66 primary samples + 7 QA duplicates)
+7 field blanks filters

Comparable to ~1 year 1-in-6 sampling, here spread over 3 years 2011-2013.

The 66 primary samples were chosen based on:

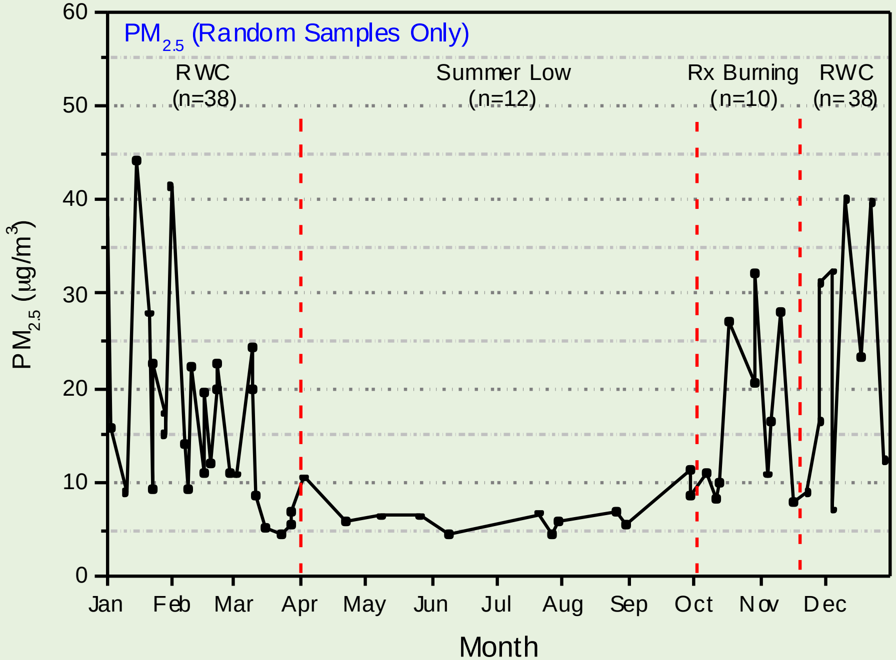
1) **SIP attainment demonstration needs and**
2) **source apportionment analysis**

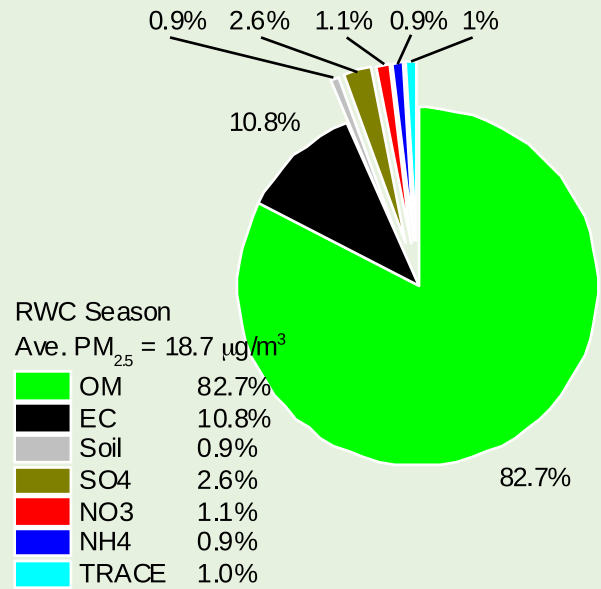
Of the 66 samples, 60 randomly selected from 3 defined seasons.

(38 filters) Winter	Jan – Mar &	Nov 20 – Dec
(12 filters) Prescribed burning		Oct – Nov 19
(10 filters) Summer		Apr – Sept

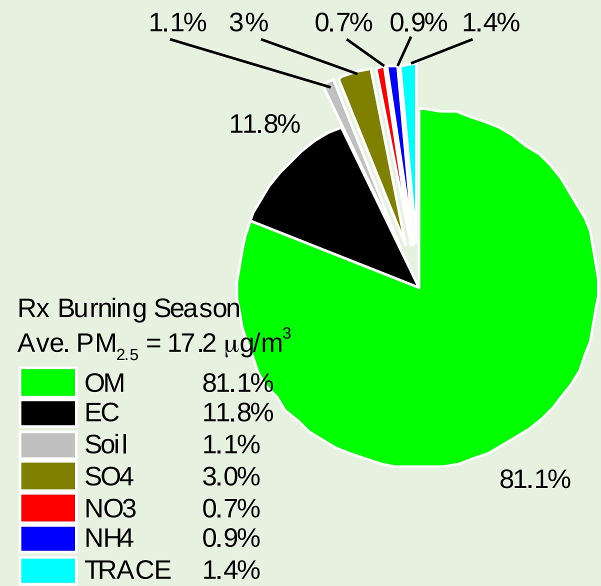
+6 non-random filters selected from high PM2.5 days

Results: Pinehurst composition distribution by season

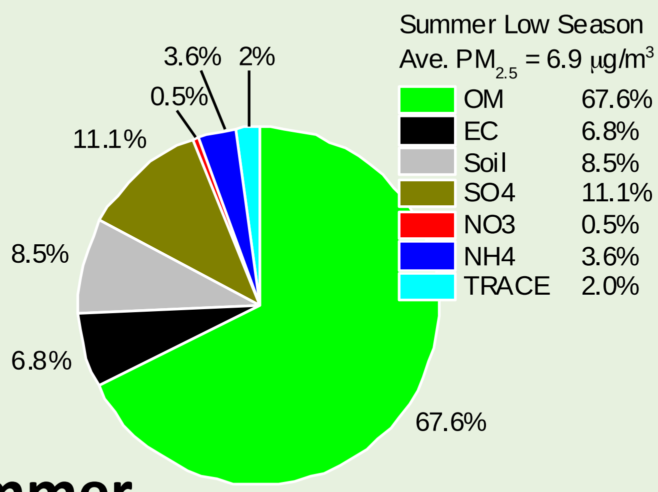




Winter (RWC)



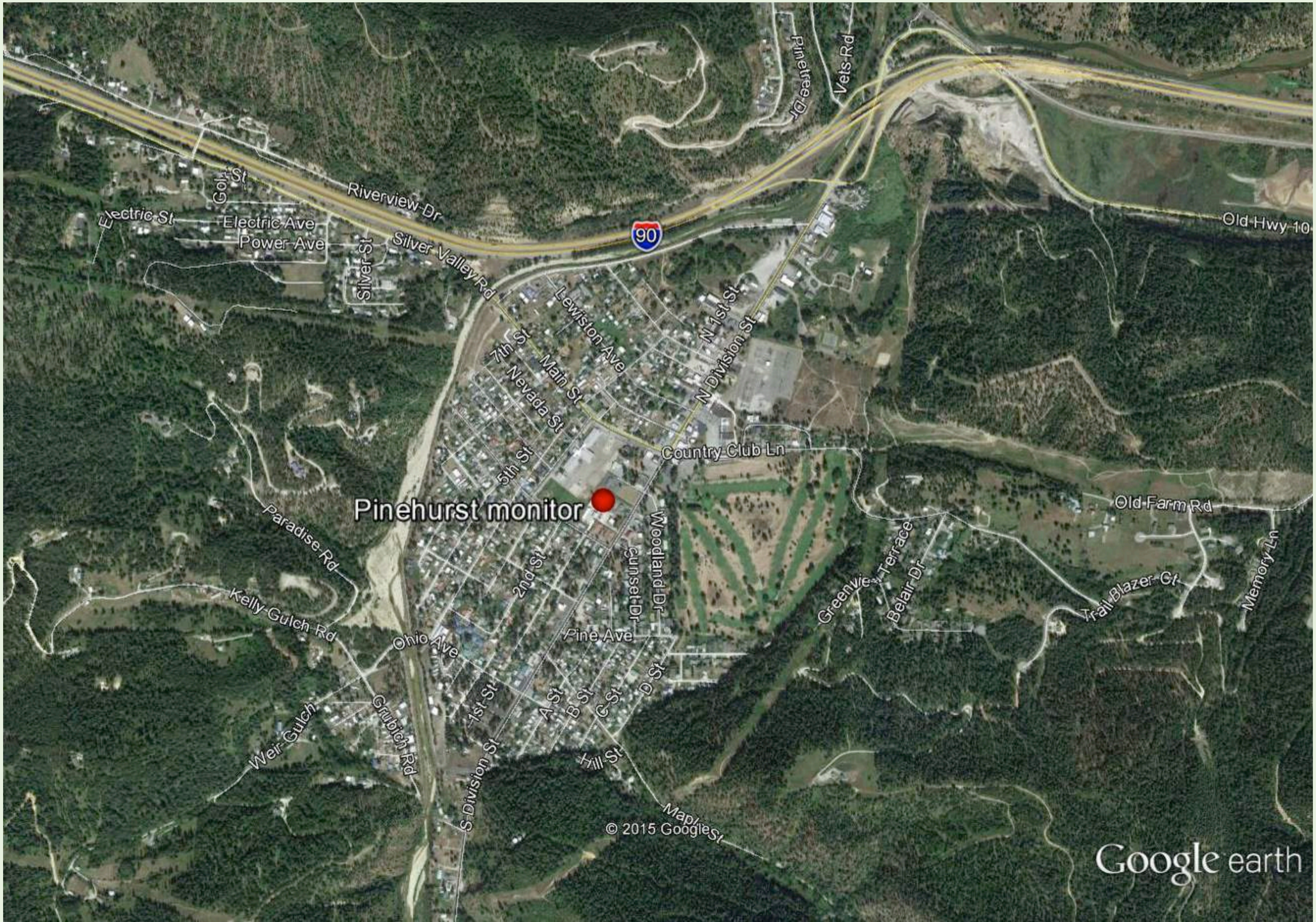
Rx



Summer

Source Apportionment Modeling

Pinehurst, ID Preliminary Results



How is source apportionment performed?

Traditionally, 'Receptor' models (aka 'source apportionment' models) have been used to estimate source contributions.

The Receptor Model used here was the Positive Matrix Factorization (PMF) model.

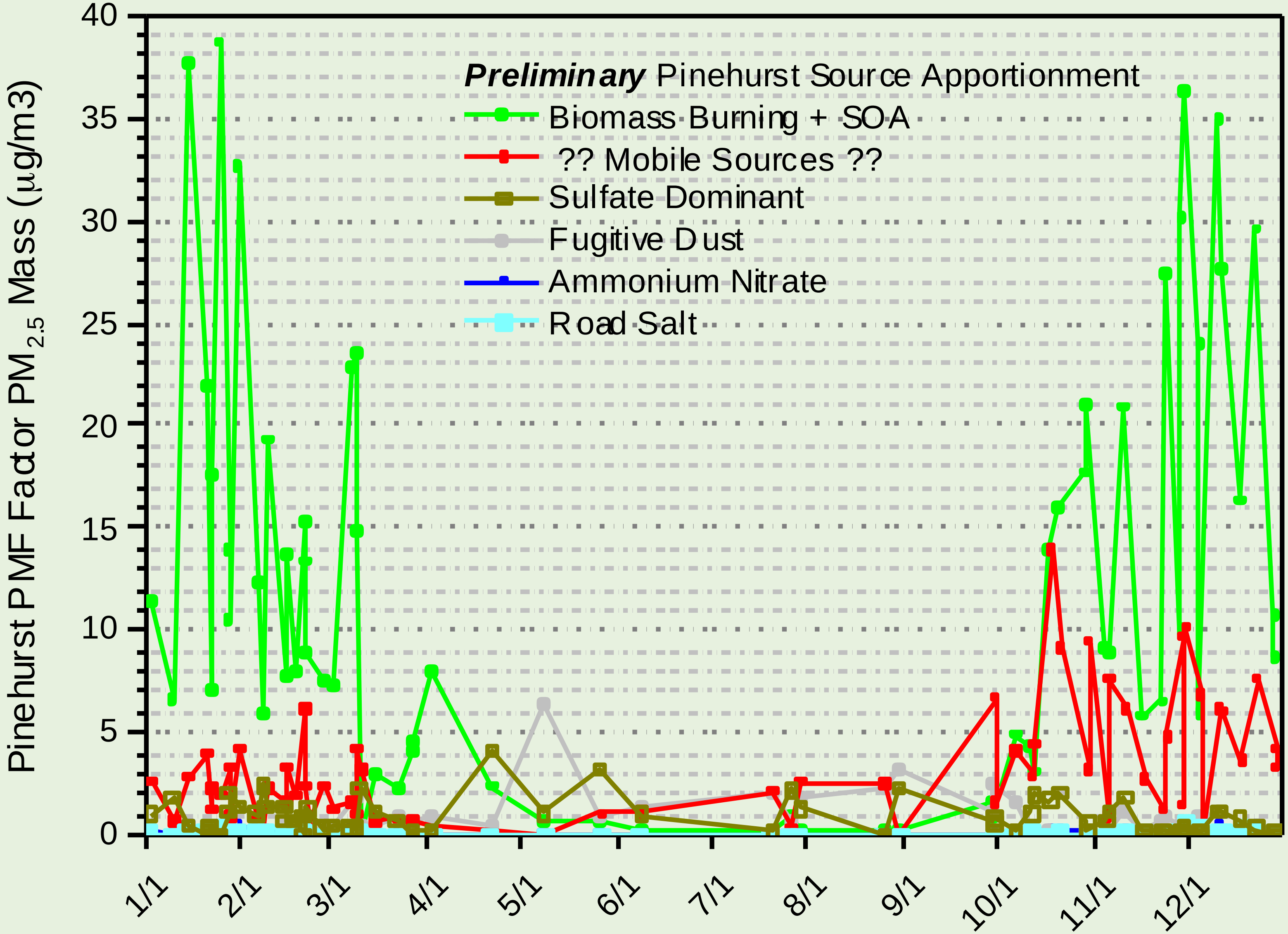
PMF uses a mathematical/statistical approach and is a form of 'Factor Analysis' (also related to Principal Component Analysis [PCA]).

How the model works:

The model looks for systematic patterns in the day-to-day chemical variations and quantifies a smaller set of 'factors' that can explain the overall data variability.

These model 'factors' can often be associated with aerosol sources (or source categories) by comparing the model factors to known source chemical emissions profiles.

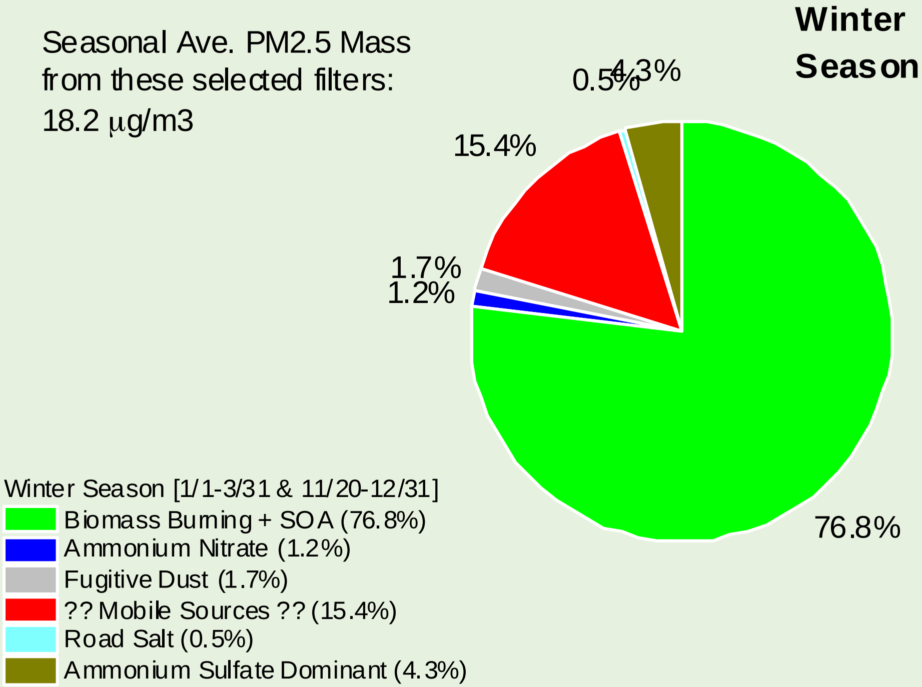
Preliminary Pinehurst Source Apportionment Results: **mass impacts time series plot**

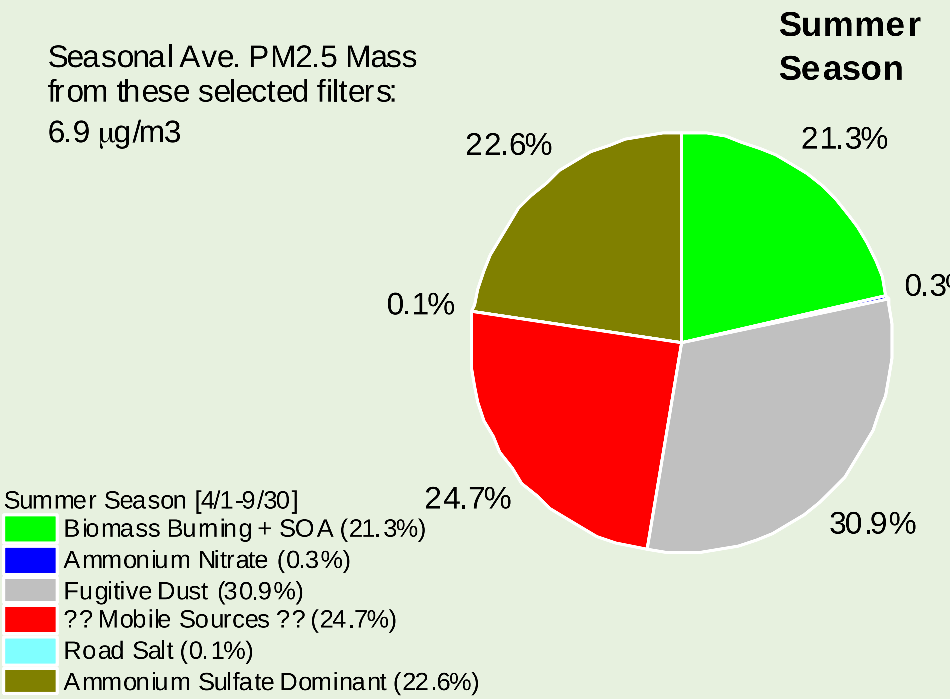


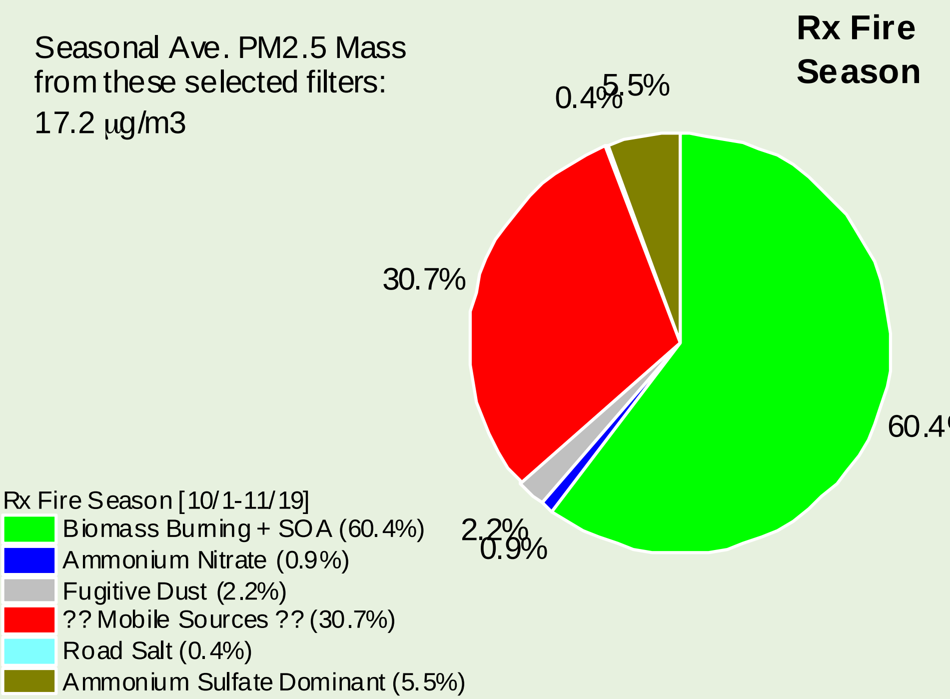
Note: While the data above represent dates in 2011 – 2013, the specific year was removed and only month & day plotted to better show the seasonal cycle.

Preliminary Pinehurst Source Apportionment Results: **seasonal pie charts**

(note: this data for randomly selected samples only)







Summary:

- Idaho and EPA used archived FRM PM2.5 filters to obtain chemically speciated PM2.5.
- Data is sufficient for SIP attainment demonstration analysis
- Filter data was used for source apportionment analysis

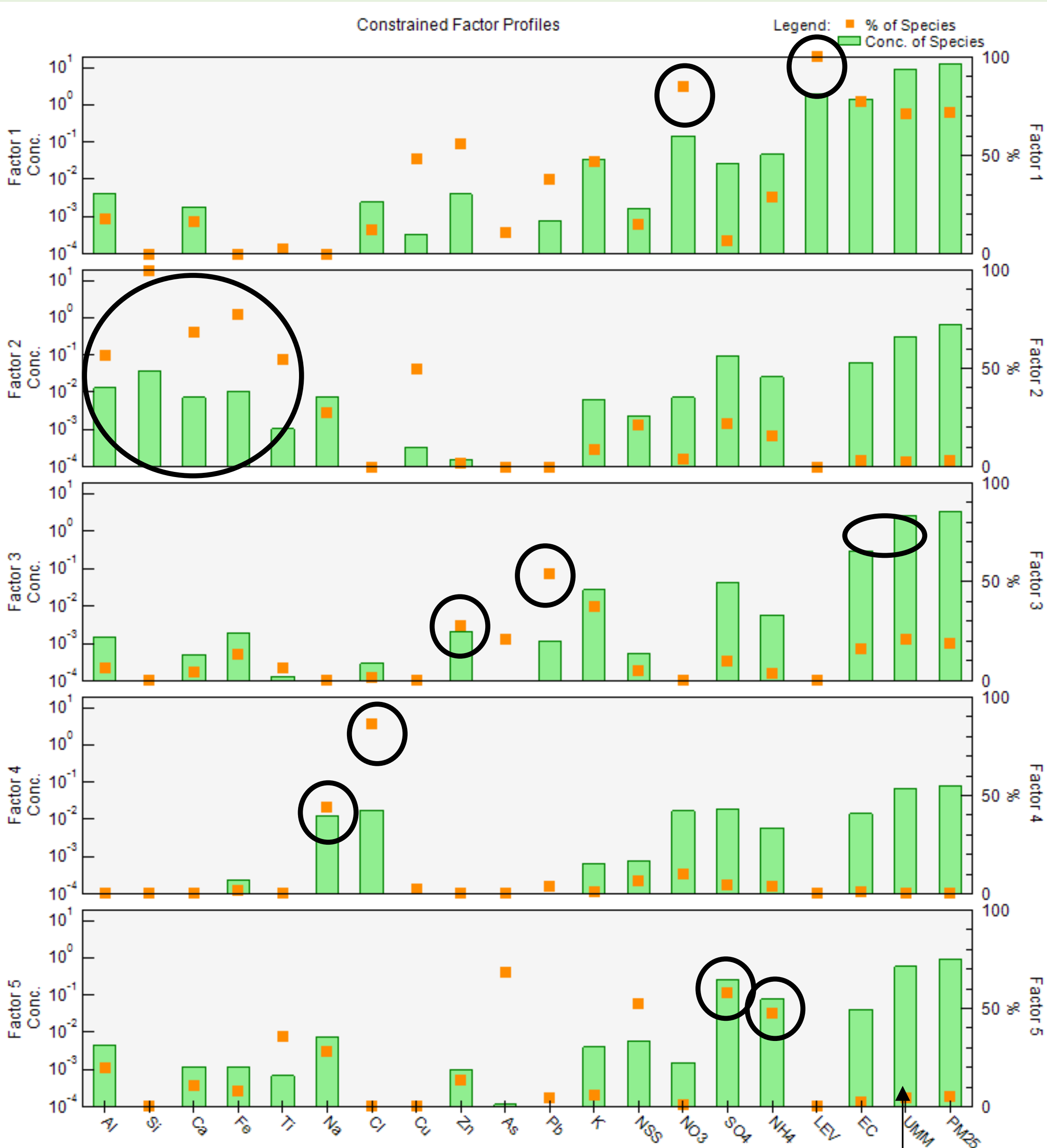
Further work:

- The possible ‘mobile source’ factor in the source apportionment analysis needs more scrutiny.
  - Weekend vs. weekday statistical analysis
  - Wind direction analysis
  - Look at hourly PM traces with wind diretction

Thank you!

Questions and Discussion …

Pinehurst PMF Factor Chemical Profiles



UMM = Unmeasured mass (assumed organic mass)

Factor notes	Factor association
• All Levoglucosan In this factor. • Could not separate NO3	**Biomass burning + SOA + Nitrate**
• Main dust elements	**Fugitive Dust**
• Name assigned based on Pb, Zn, UMM & EC	**?? Mobile Sources ??**
• Na and Cl dominant	**Road Salt**
• SO4 and NH3 dominant	**Sulfate Dominant**