The Chemical Composition of PM2.5
to support PM Implementation

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For Presentation at
EPA State / Local / Tribal Training Workshop: PM 2.5 Final Rule Implementation and 2006 PM 2.5 Designation Process
June20-21

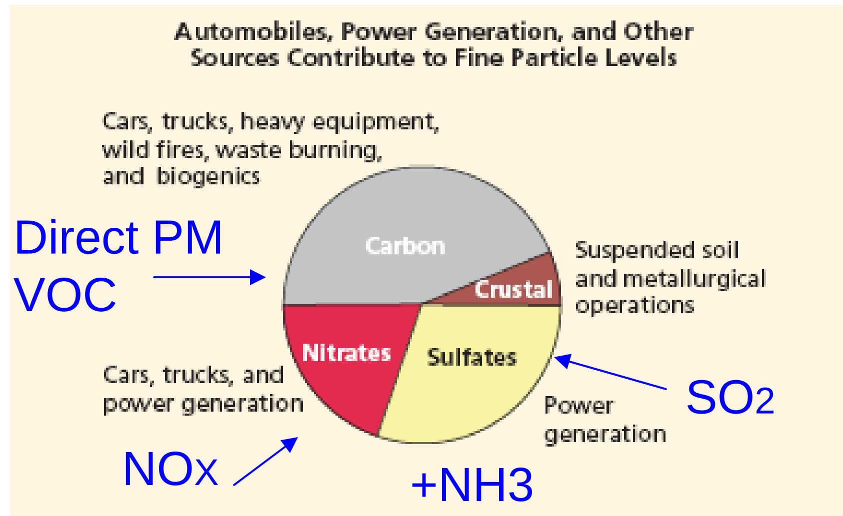
Topics

- How do we derive FRM $PM_{2.5}$ composition
- How does avg composition vary by region, by season and over time
- Variation within urban areas
- What are the local vs regional components and how does this relate to potential emission sources
- Differences between peak day and average composition

What is the composition of PM2.5 and where does it come from?

Major components

- Ammonium Sulfate
- Ammonium Nitrate
- Organic Carbonaceous Mass
- Elemental Carbon
- Crustal Material



Note: Ammonia from sources such as fertilizer and animal feed operations contributes to the formation of sulfates and nitrates that exist in the atmosphere as ammonium sulfate and ammonium nitrate.

From: ***The Particle Pollution Report: Current Understanding of Air Quality and Emissions through 2003***

The chemistry is complicated and particle formation is dependent on other pollutants and atmospheric conditions

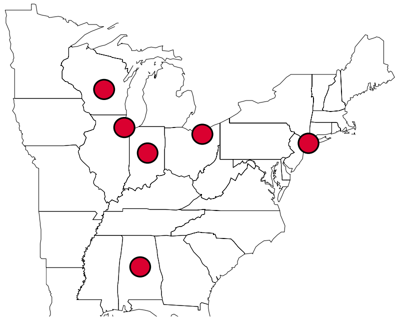
To estimate urban PM2.5 composition

- Use measurements from routine monitoring networks
  - STN, SLAMS (=CSN)
- Make adjustments to represent FRM mass
- *FRM mass does <u>not</u> equal the simple sum of the measured components*

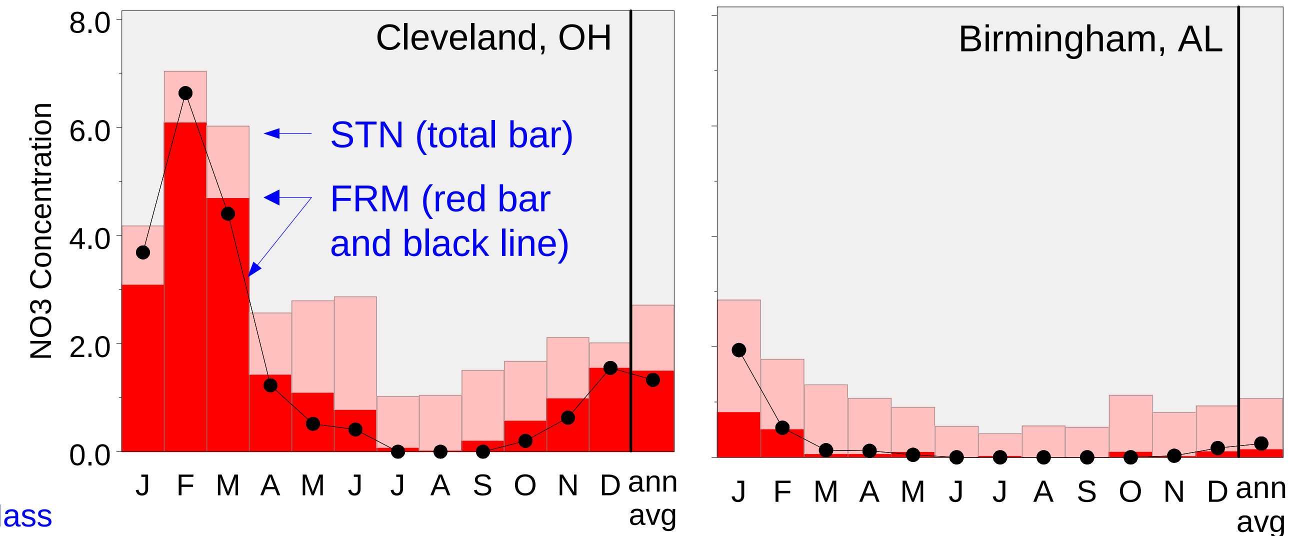
  [i.e. PM2.5 ≠ AmmSul + AmmNitr + OCM +EC + Crustal]

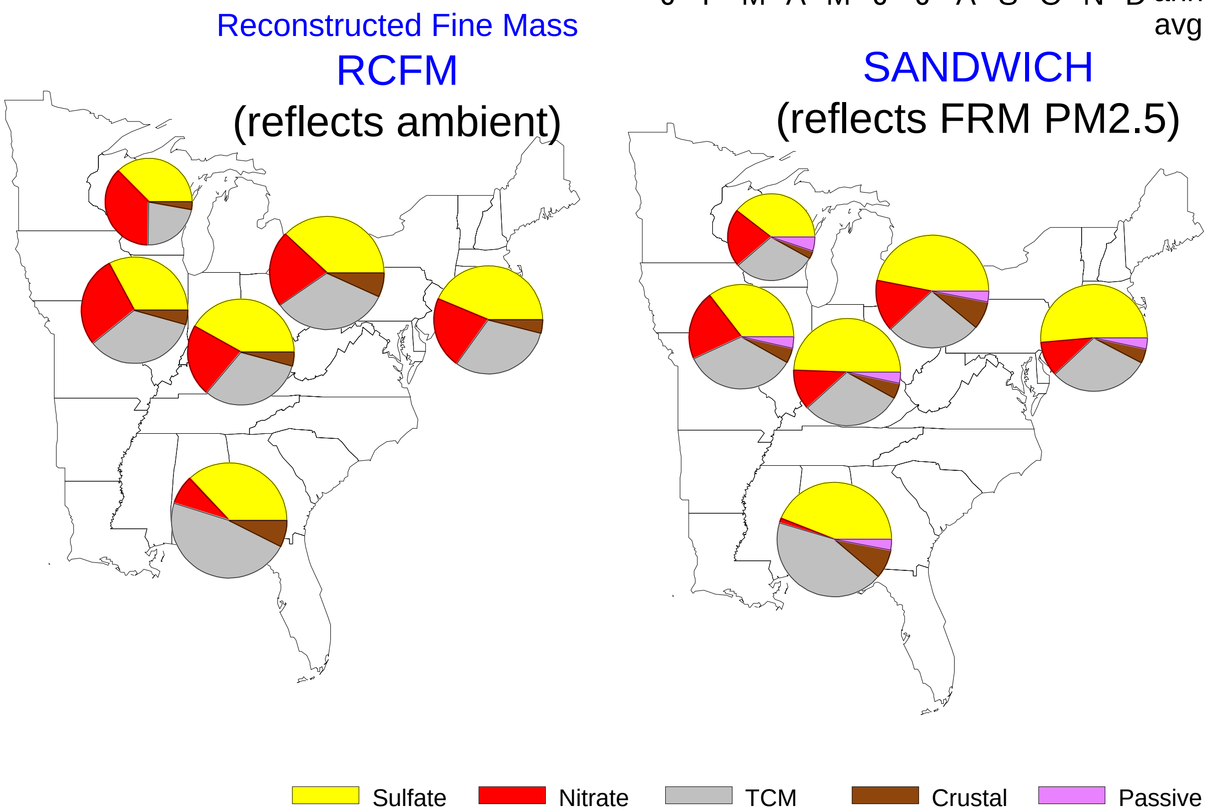
FRM doesn't retain all ambient nitrates

6 Nitrate Study Sites, 2003



Monthly and Annual Average NO3, 2003





PM2.5 mass <u>also</u> includes particle bound water
(at mass weighing conditions)

FRM Compared to Speciation <u>Network Measurements</u>

- Less Nitrate
- Includes particle bound water
- Carbon achieves mass balance and reflects all needed adjustments

SANDWICH

more than a cute acronym

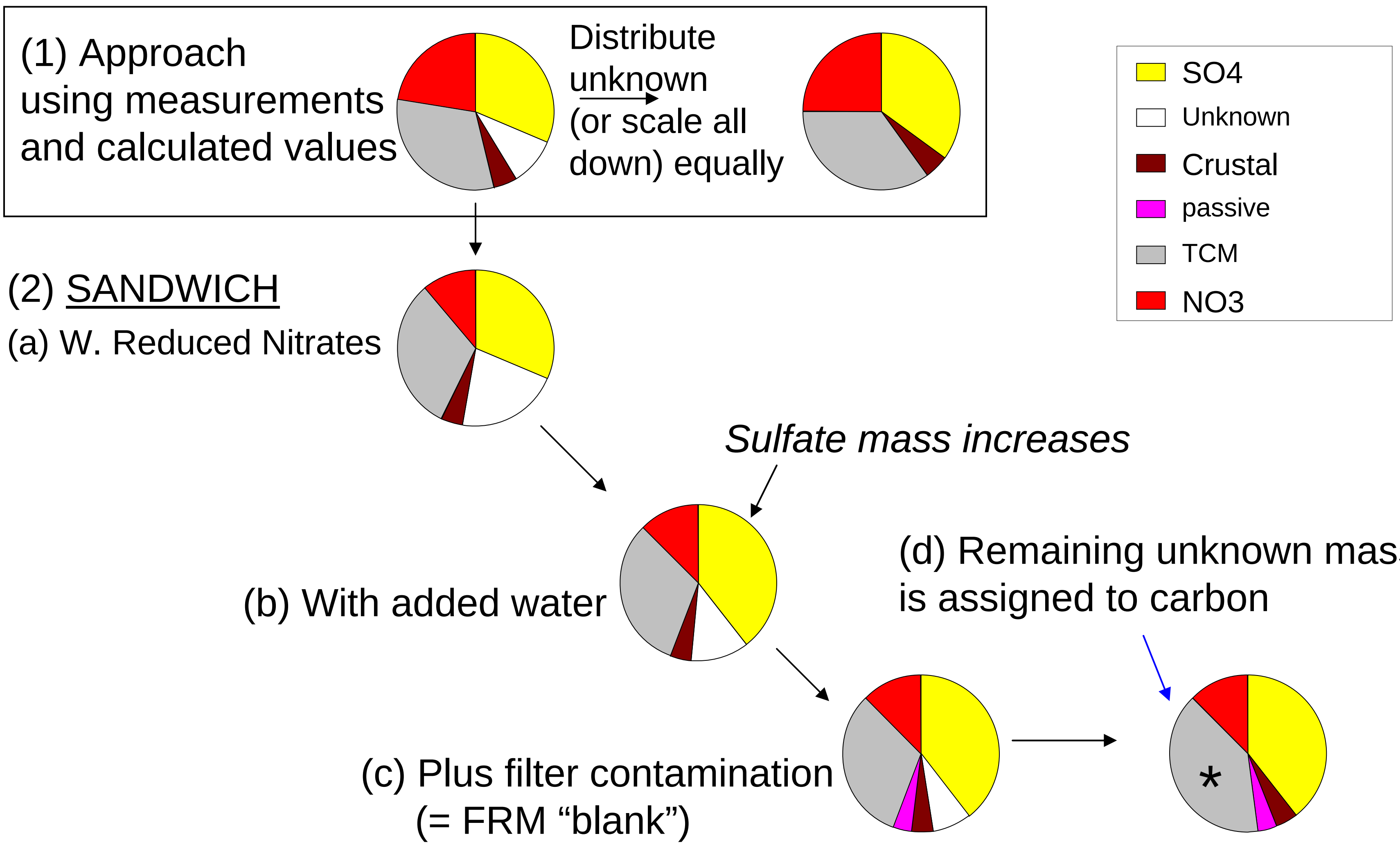
- What is the **SANDWICH** Approach?
  - **S**ulfate, **A**djusted **N**itrate, **D**erived **W**ater, **I**nferred **C**arbon **H**ybrid material balance approach
    - for estimating PM2.5 mass composition as if it was measured by the PM2.5 FRM.
  - The approach uses a combination of speciation measurements and modeled speciation estimates to represent FRM PM2.5.

- Why is it needed?
  - The FRM defines the regulatory indicator of PM2.5.
  - FRM mass may not retain all nitrate, and includes particle bound water and other components not estimated directly with STN measurements.
  - To estimate FRM PM2.5 composition including FRM carbonaceous mass without "fudge" factors.
  - To help QC speciation measurements

- SANDWICH is the default method in EPA modeling guidance to define baseline PM2.5
  - for SMAT (speciated modeled attainment test)
  - "FRM" composition with the p*eer-reviewed "SANDWICH" technique used in CAIR and PM2.5 RIA*

Frank, N. Retained Nitrate, Hydrated Sulfates, and Carbonaceous Mass in Federal Reference Method Fine Particulate Matter for Six Eastern U.S. Cities, *J. Air & Waste Manage. Assoc.* **56** :500–511

Conceptual Overview of Mass Balance Approaches

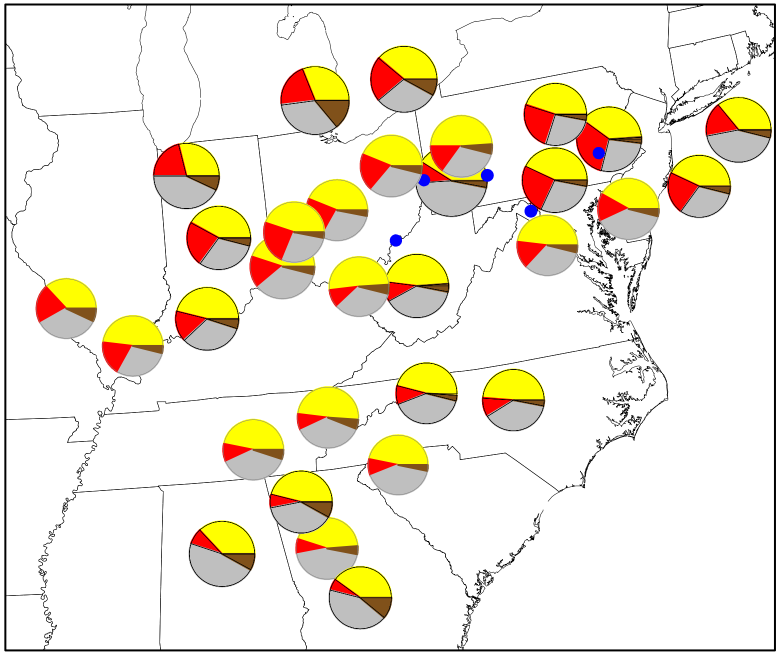


* Default SANDWICH can be modified to consider other components, like salt. This reduces estimate of TCM.

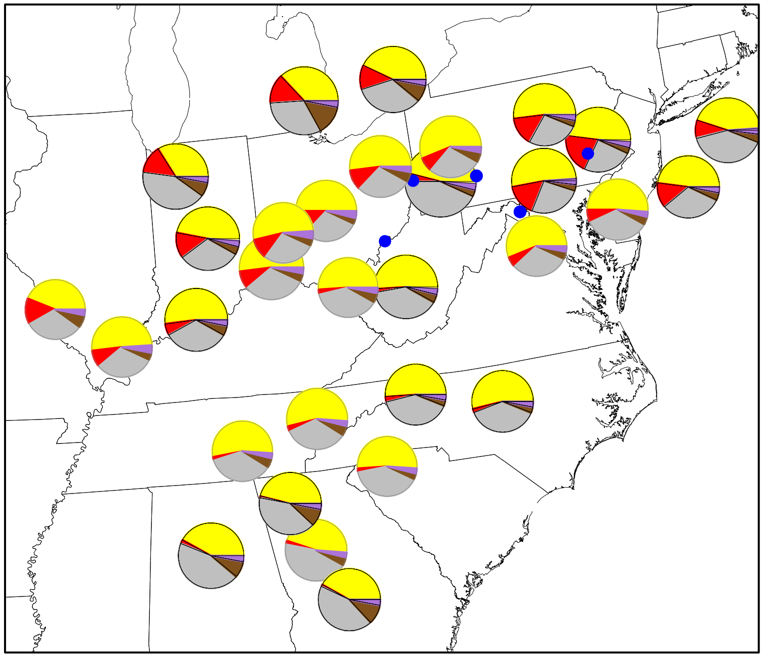
Annual Average Composition (2002-04) in East NA areas

Less nitrate and more sulfate mass with SANDWICH

RCFM



SANDWICH



area	area_annual_dv
NA area: Johnstown, PA	15.3
NA area: Martinsburg, WV-Hagerstown, MD	16.1
NA area: Parkersburg-Marietta, WV-OH	15.2
NA area: Reading, PA	16.1
NA area: Steubenville-Weirton, OH-WV	17
NA area: Wheeling, WV-OH	15.1

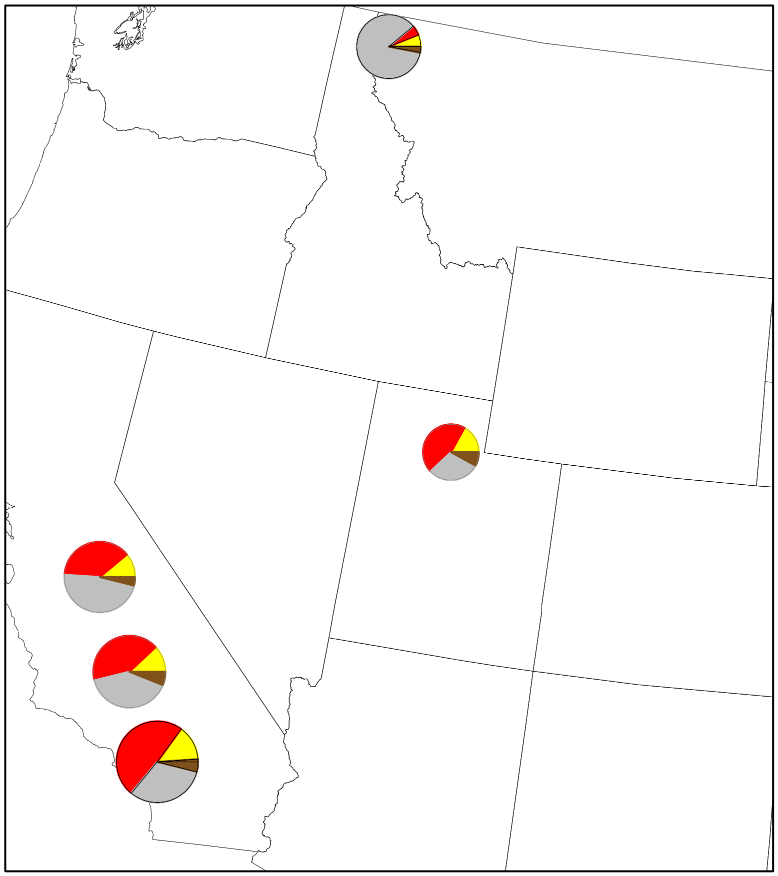
• NA area without STN data (02-04)

Black outlined pies had collocated FRM and speciation

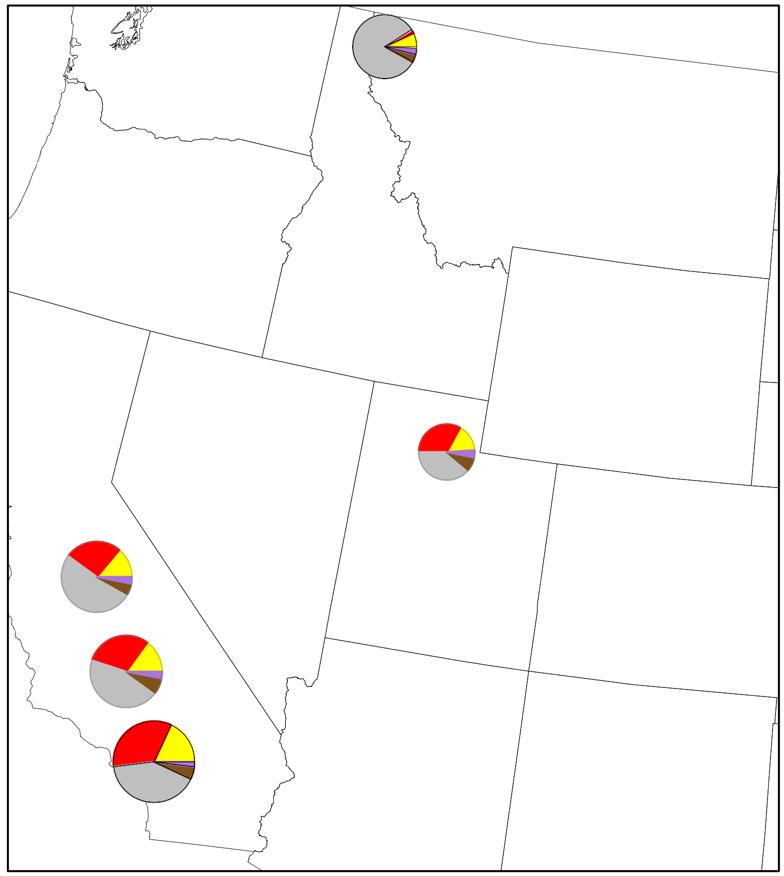
Annual Average Composition (2002-04) in West NA areas

Less nitrate and more carbon mass with SANDWICH

RCFM

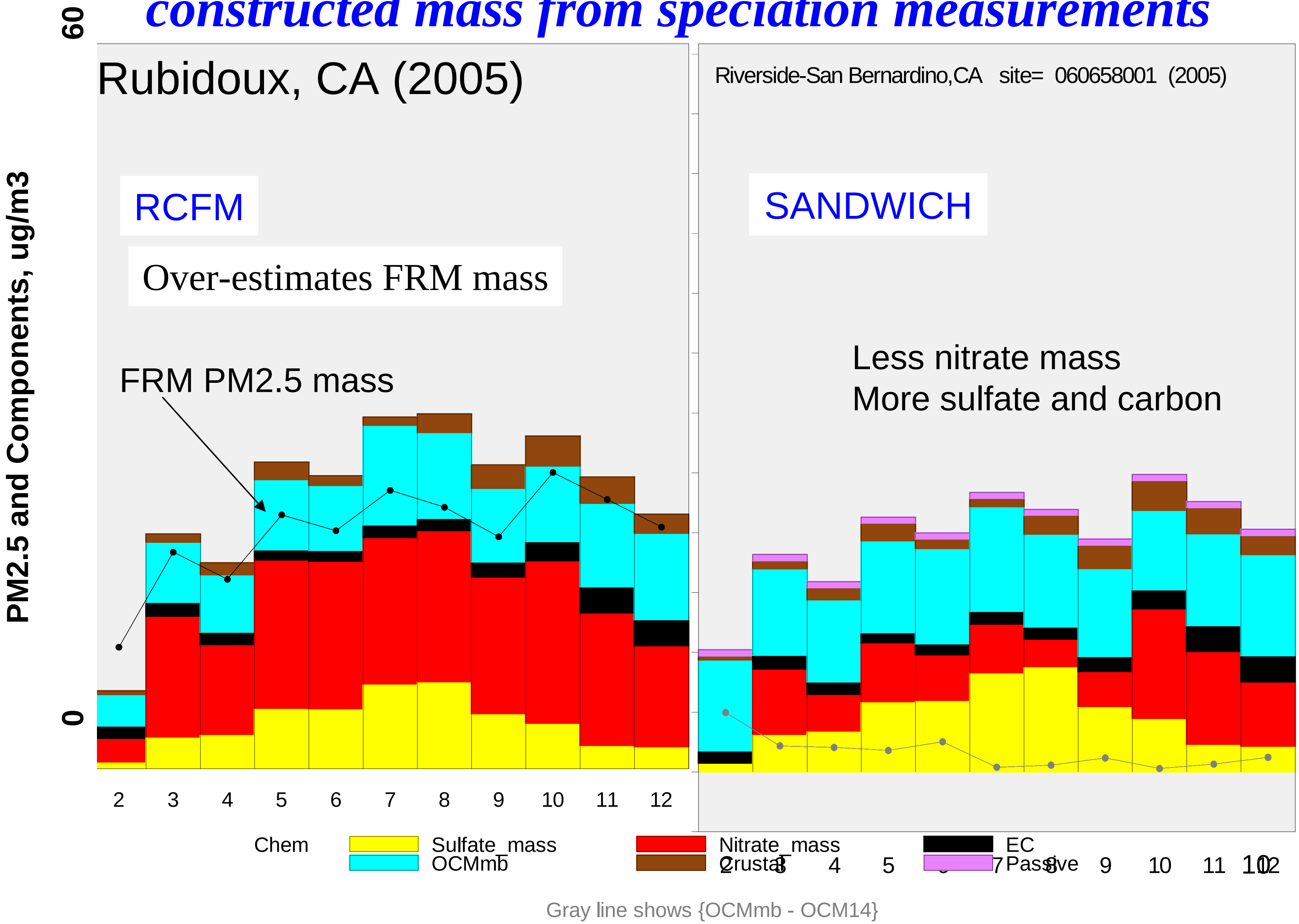


SANDWICH

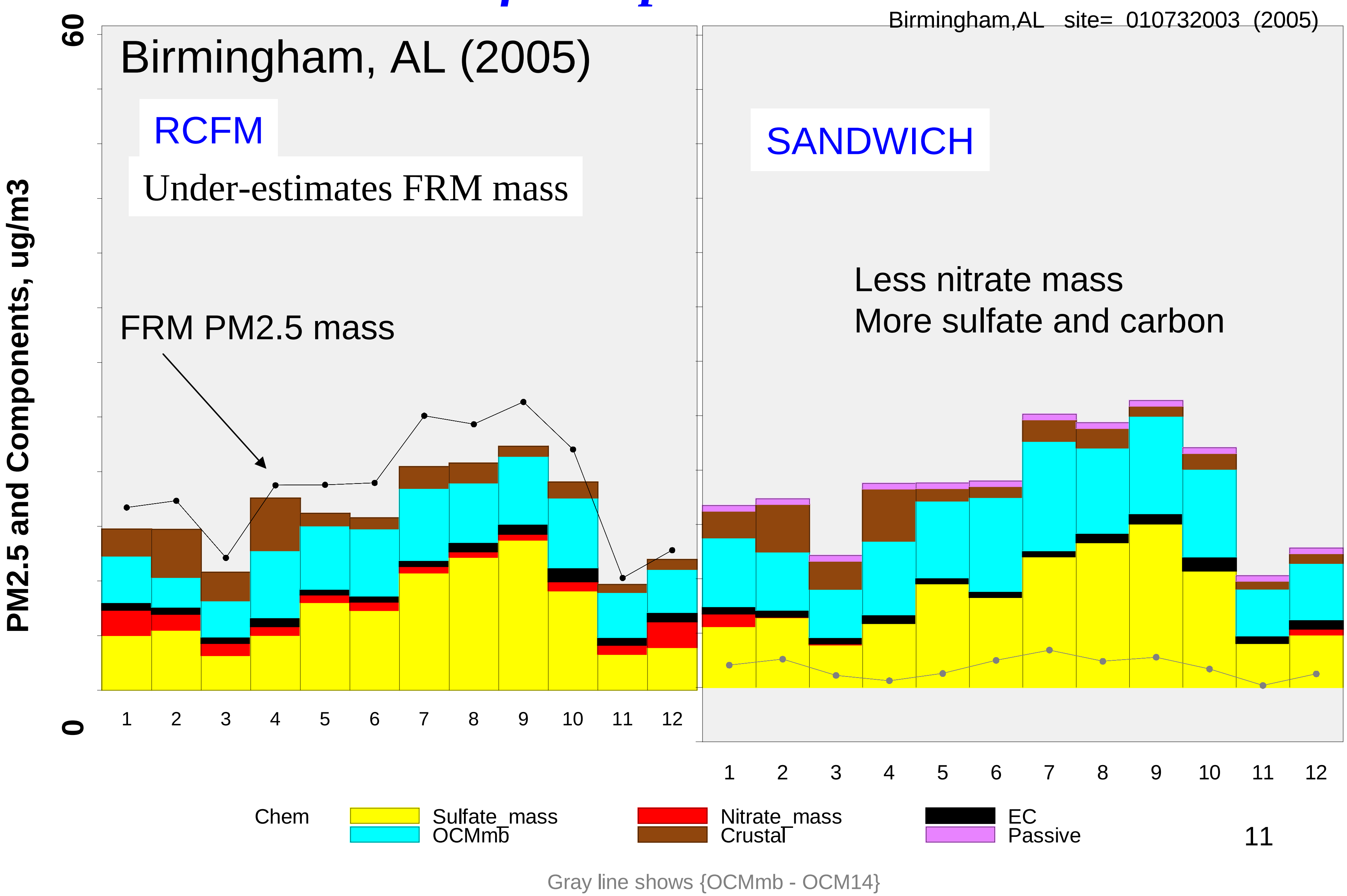


Black outlined pies have collocated FRM and speciation

FRM composition can be very different than constructed mass from speciation measurements



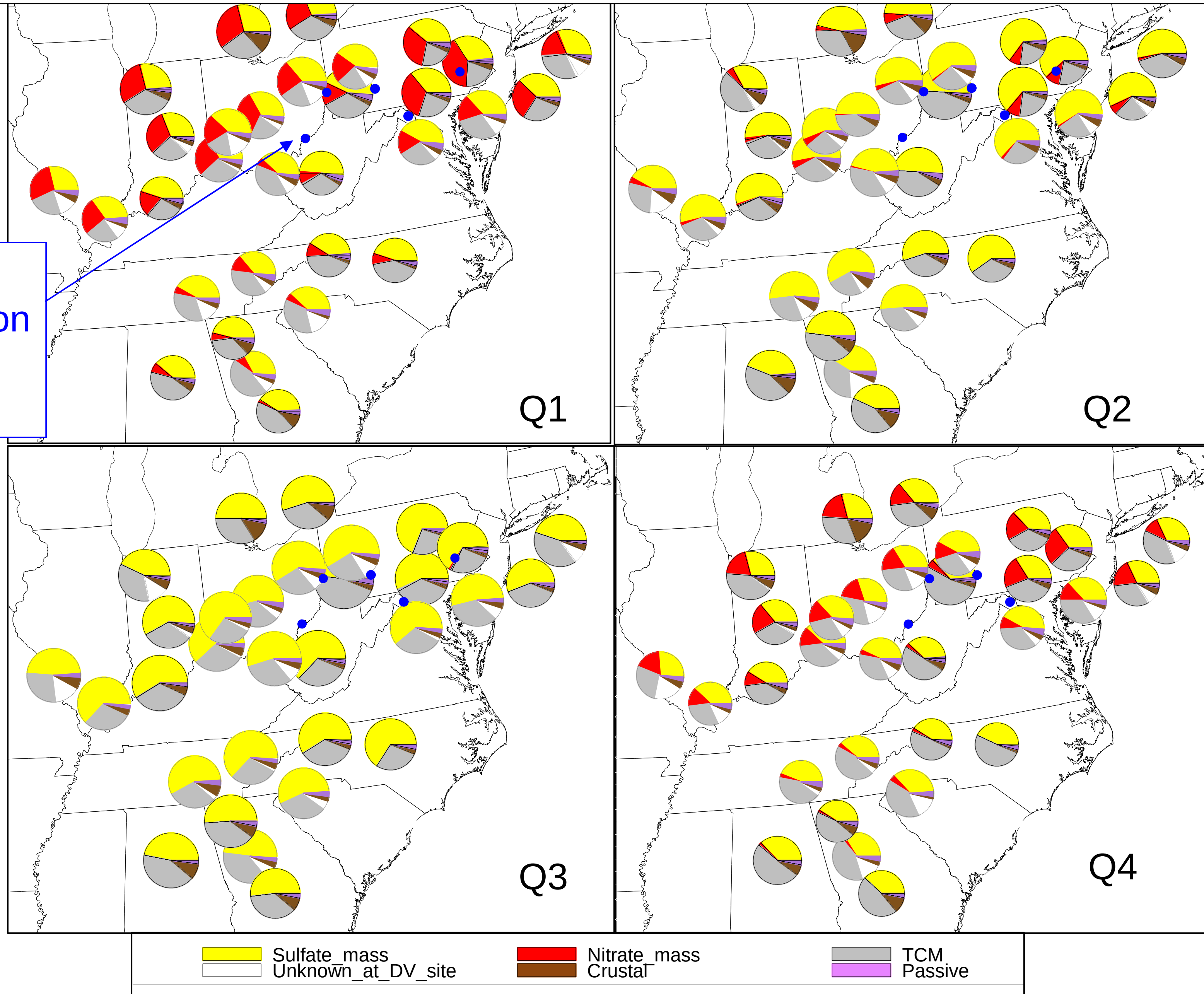
FRM composition can be very different than constructed mass from speciation measurements



Quarterly PM2.5 Composition in Eastern NA areas, 2002-04

Note: Many areas do not have speciation data and some at a different site

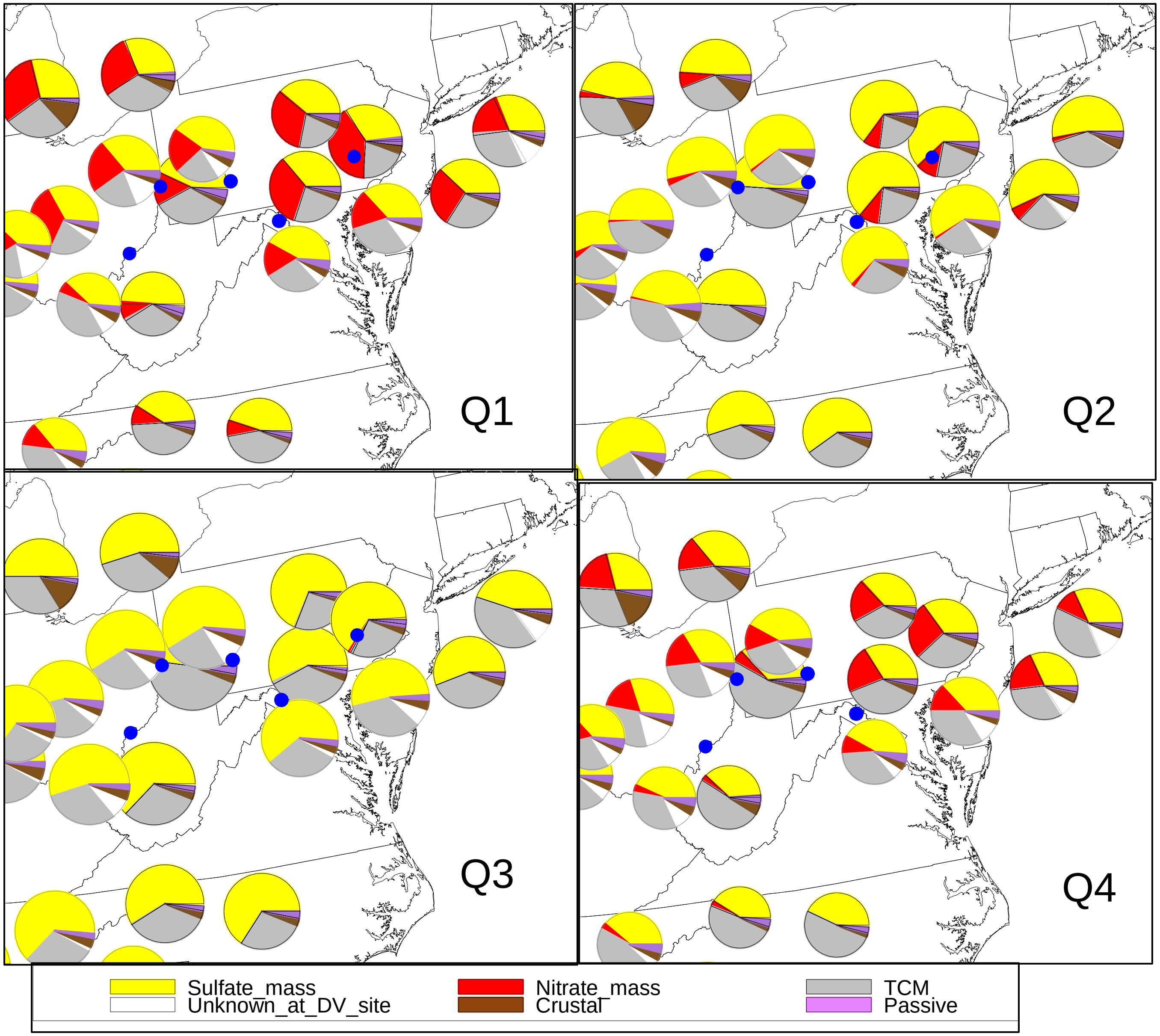
No speciation data in 2002-04



ZOOM

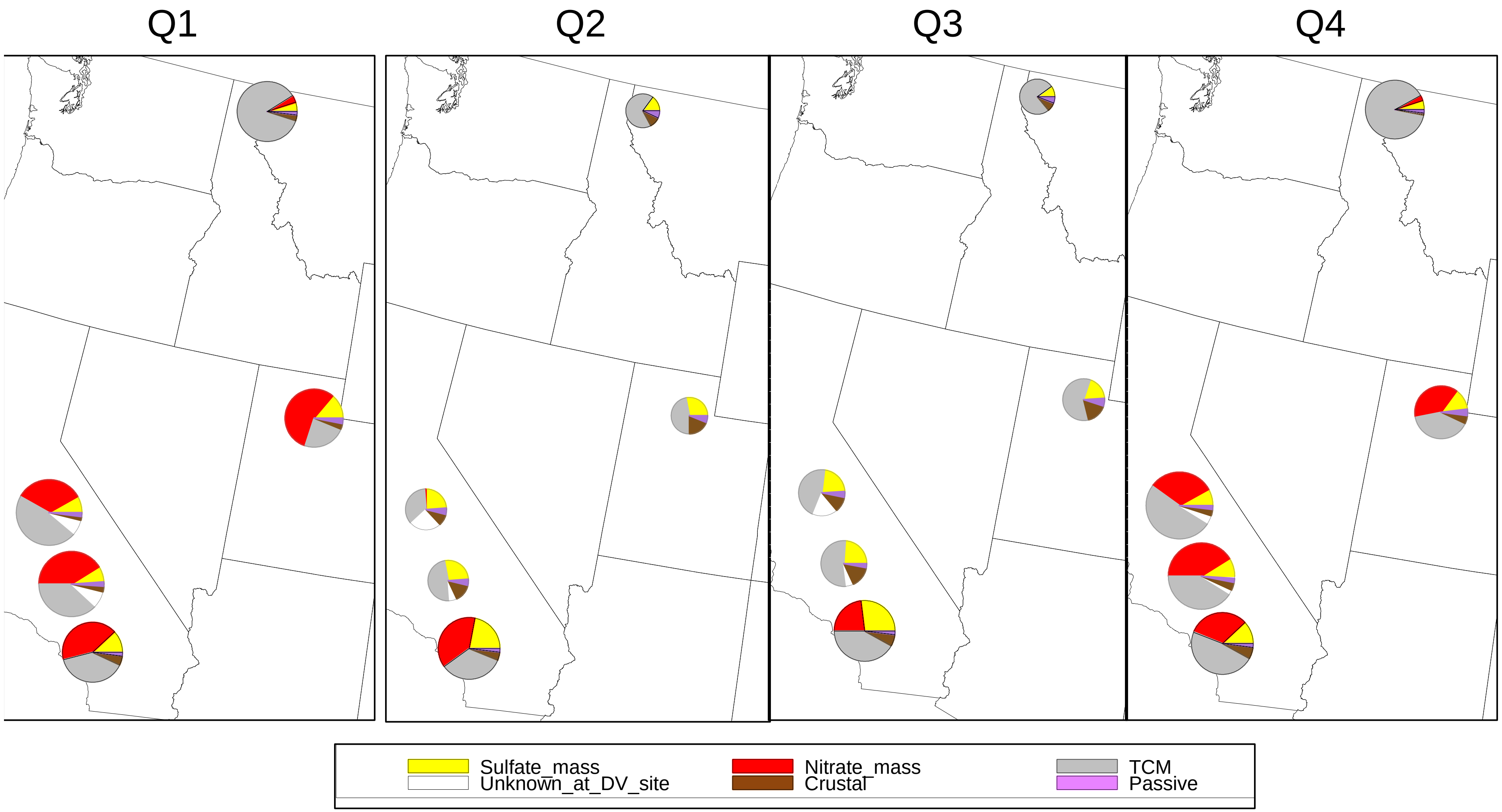
Quarterly PM2.5 Composition in NA areas, 2002-04

Many areas do not have speciation data and some at a different site



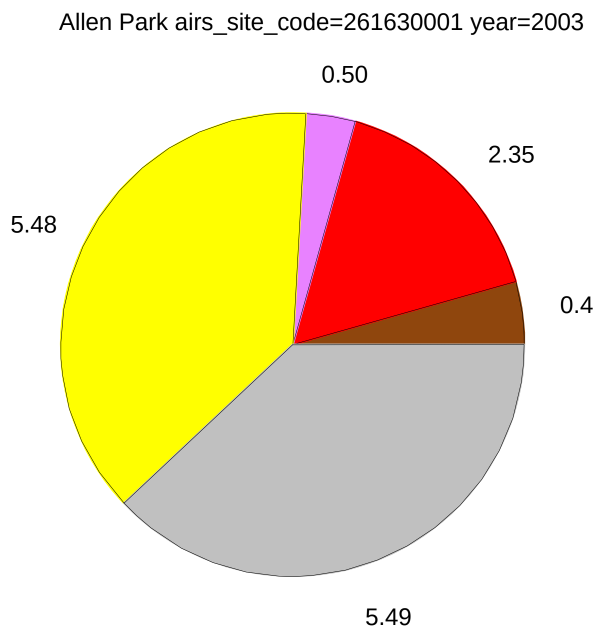
Quarterly PM2.5 Composition in Western NA areas, 2002-04

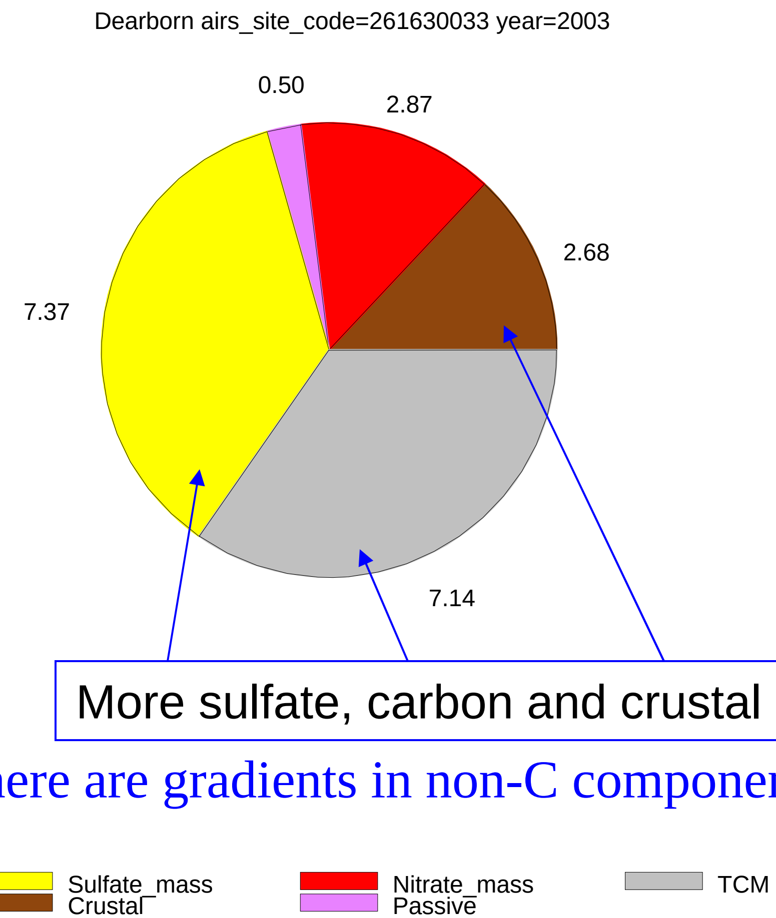
1st and 4th quarters have higher concentrations (except LA)



Composition Can Vary Within the NA Area

"Generally" the extra component is carbon





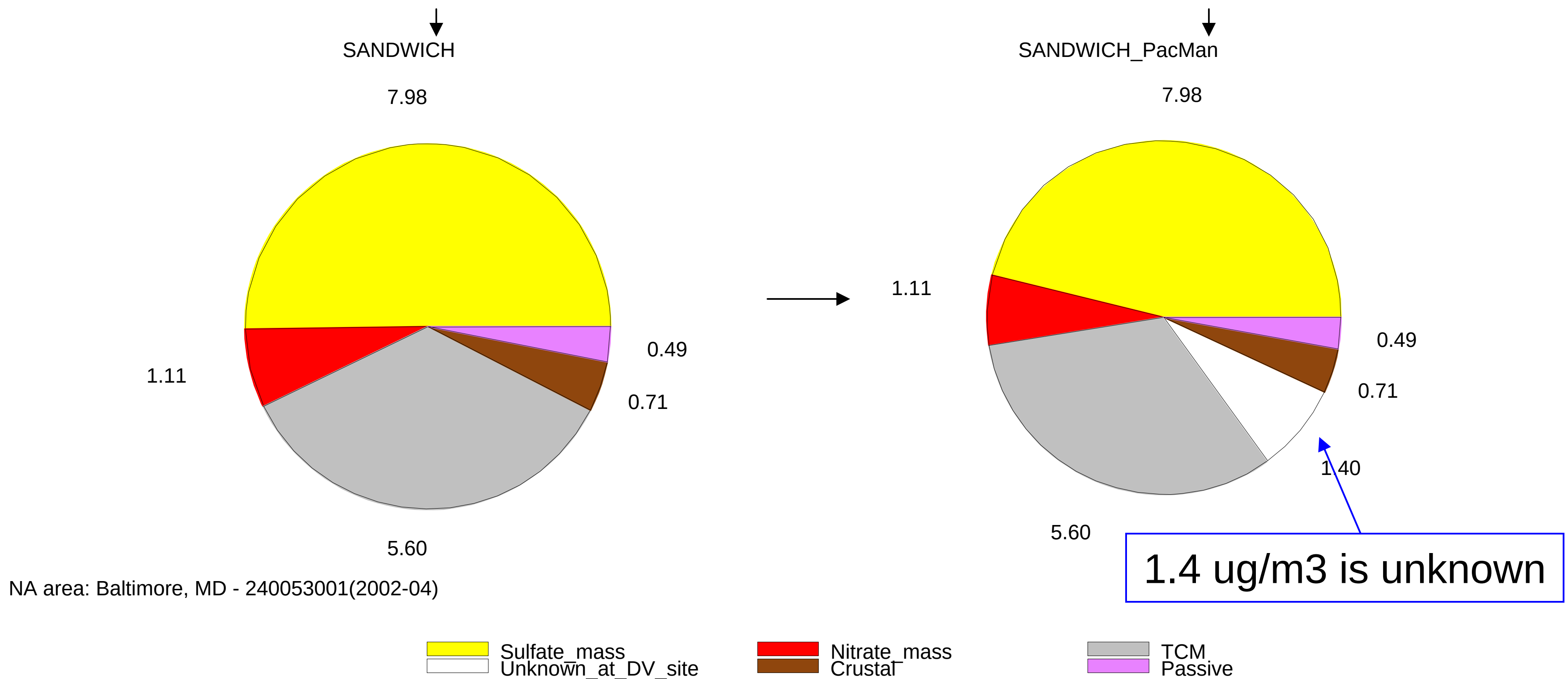
For some cities, there are gradients in non-C components

	Allen Pk	Dearborn
Sulfate Mass	5.5	7.4
Carbonaceous Mass	5.5	7.1
Nitrate	2.4	2.9
Crustal Material	0.4	2.7
PM2.5	14.22	20.56

What to do if speciation is not at the DV site?

Accounting for differences in within-area speciation profiles

Speciation location (Ann Avg=14.9 ug/m3) DV site (16.3 ug/m3)



Baltimore (Essex speciation site) is not at DV site, 2002 speciation data

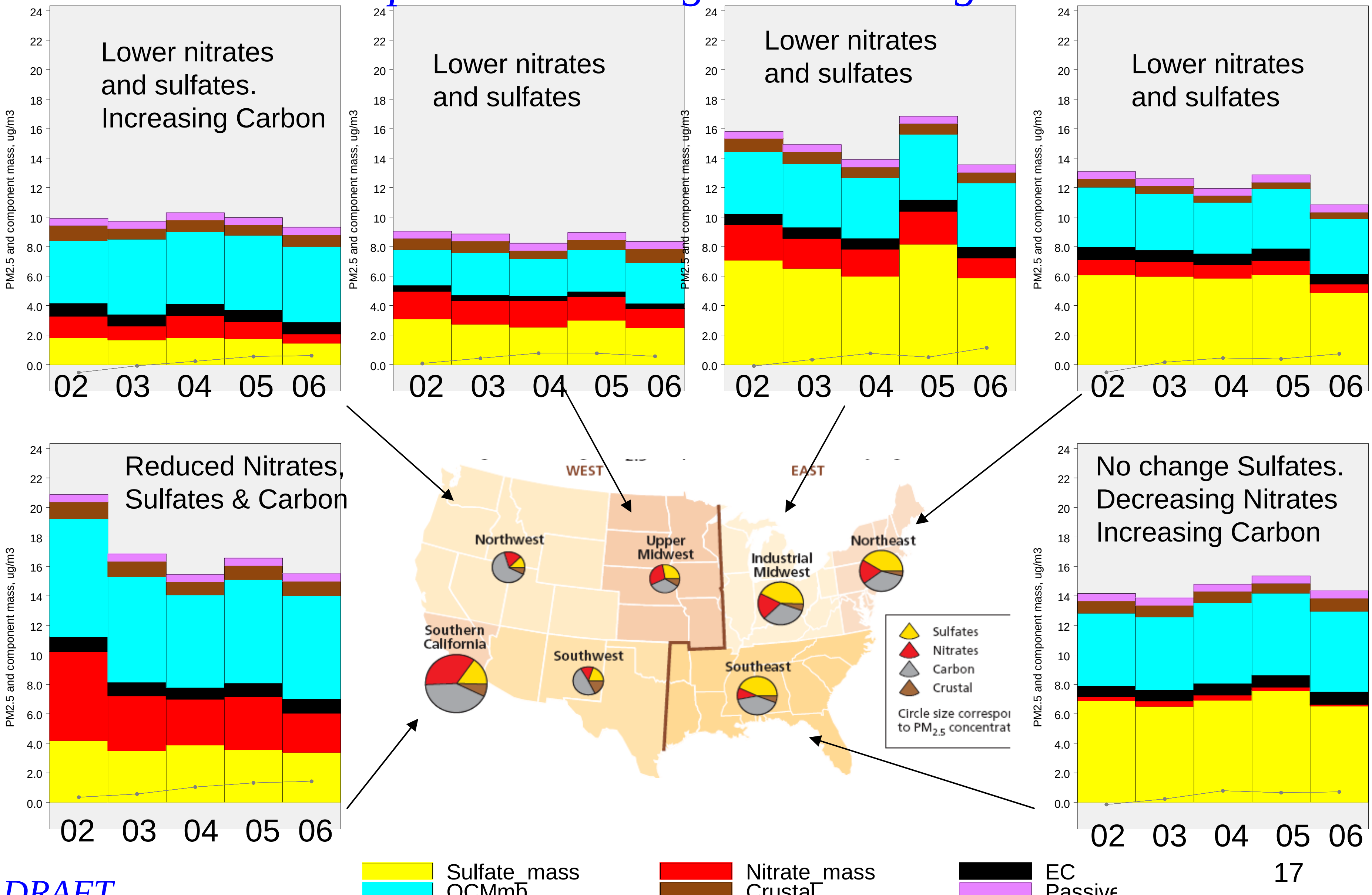
When DV site does not have speciation data, the unknown mass may or may not be TCM

It could be crustal material (as we observe in Birmingham and Detroit) or possibly Nitrate

Carbon, NO3 or Crustal?

Regional Trends in PM2.5 Composition, 2002-2006

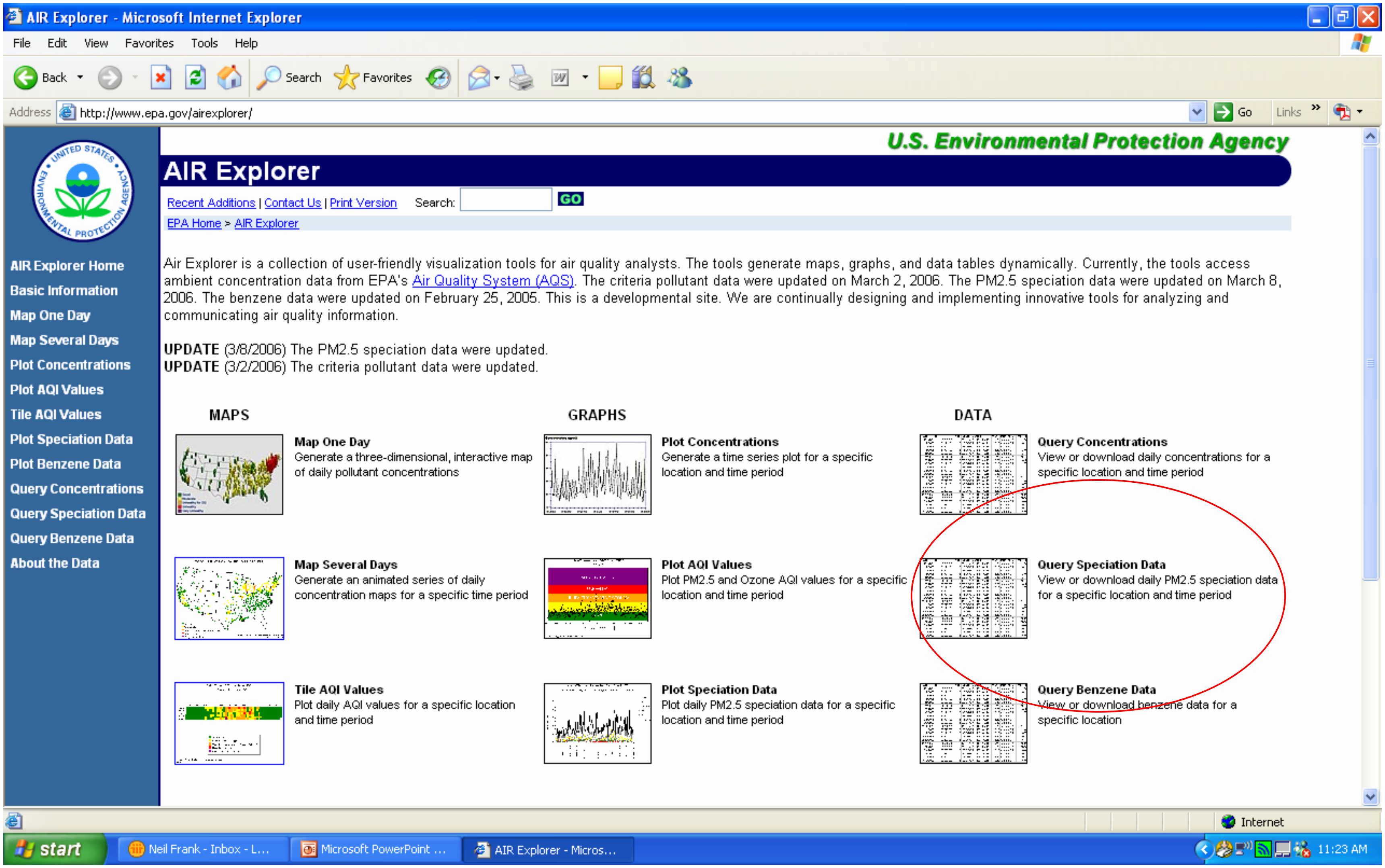
Compositional changes in some regions



DRAFT

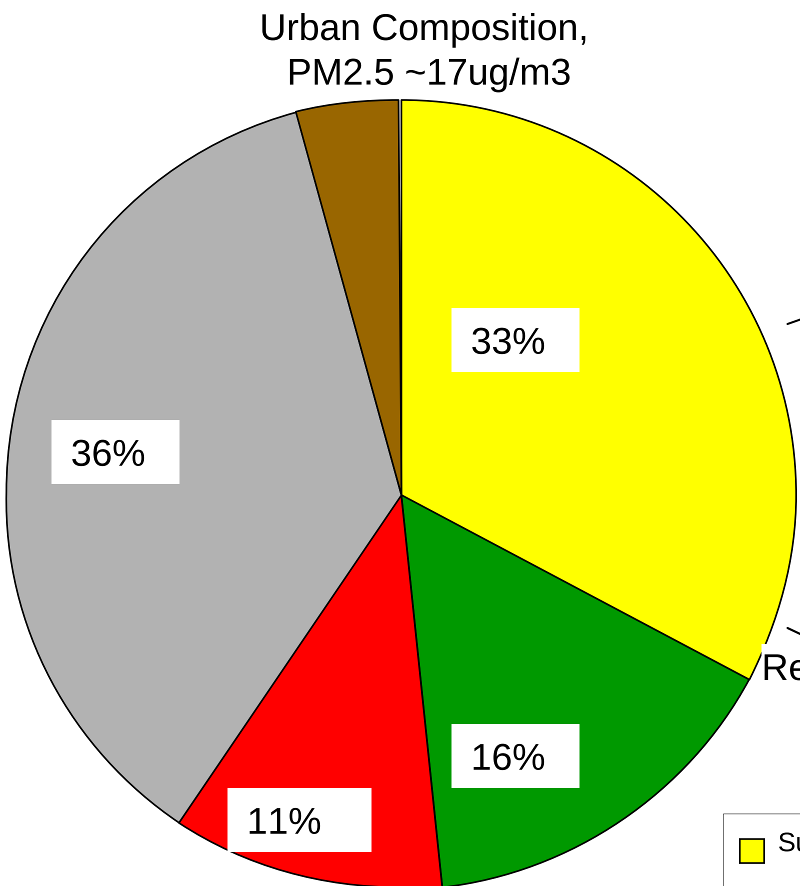
SANDWICH data are now available on Air Explorer

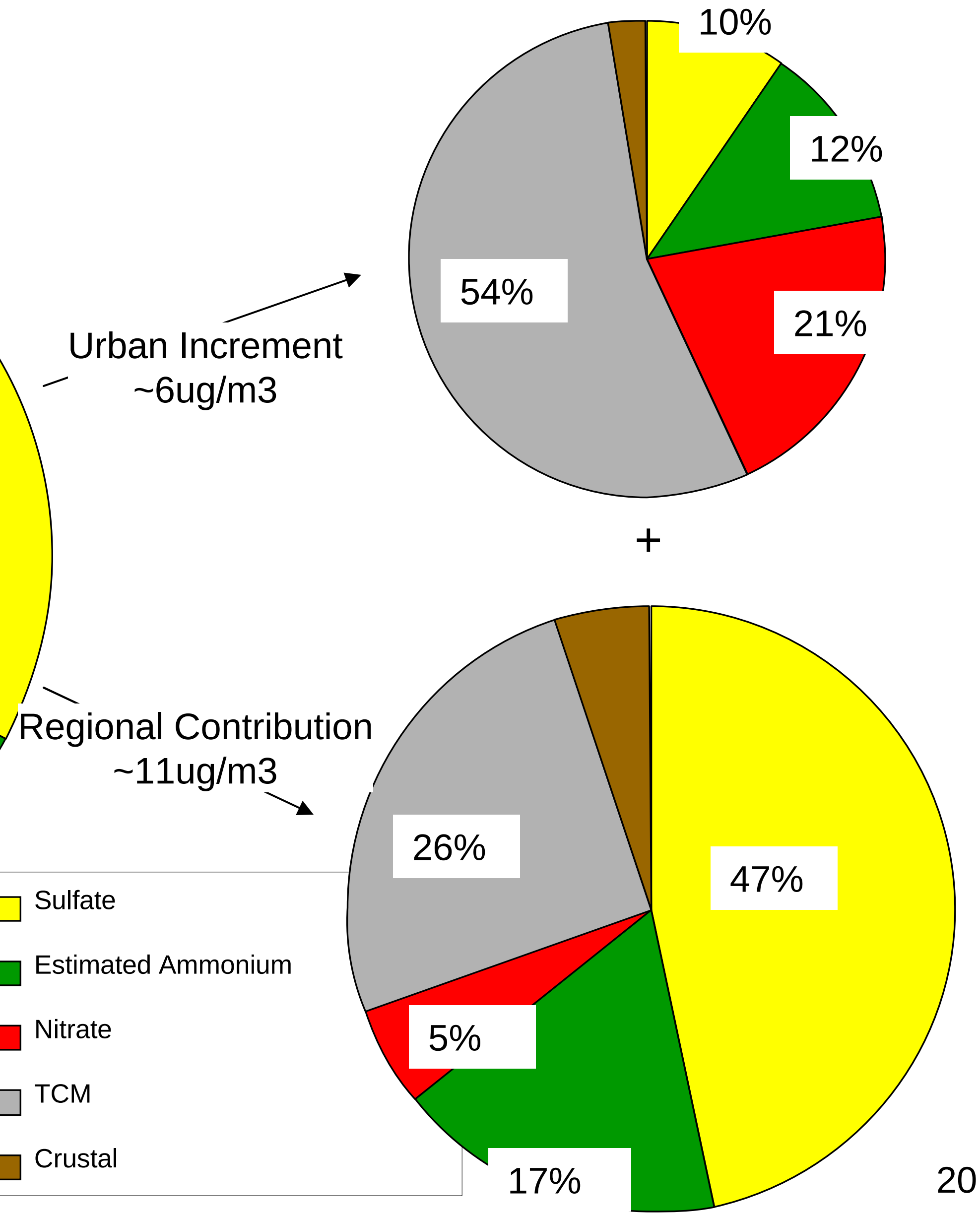
http://www.epa.gov/airexplorer/



The Urban Excess

Urban PM2.5 is Composed of Urban and Regional Components





Baltimore PM2.5 compared to Upwind rural site illustrates urban/rural contributions

Based on constructed mass (not SANDWICH), *March 01 – Feb 02*

Urban PM2.5 is Composed of Urban and Regional Components

Sulfates

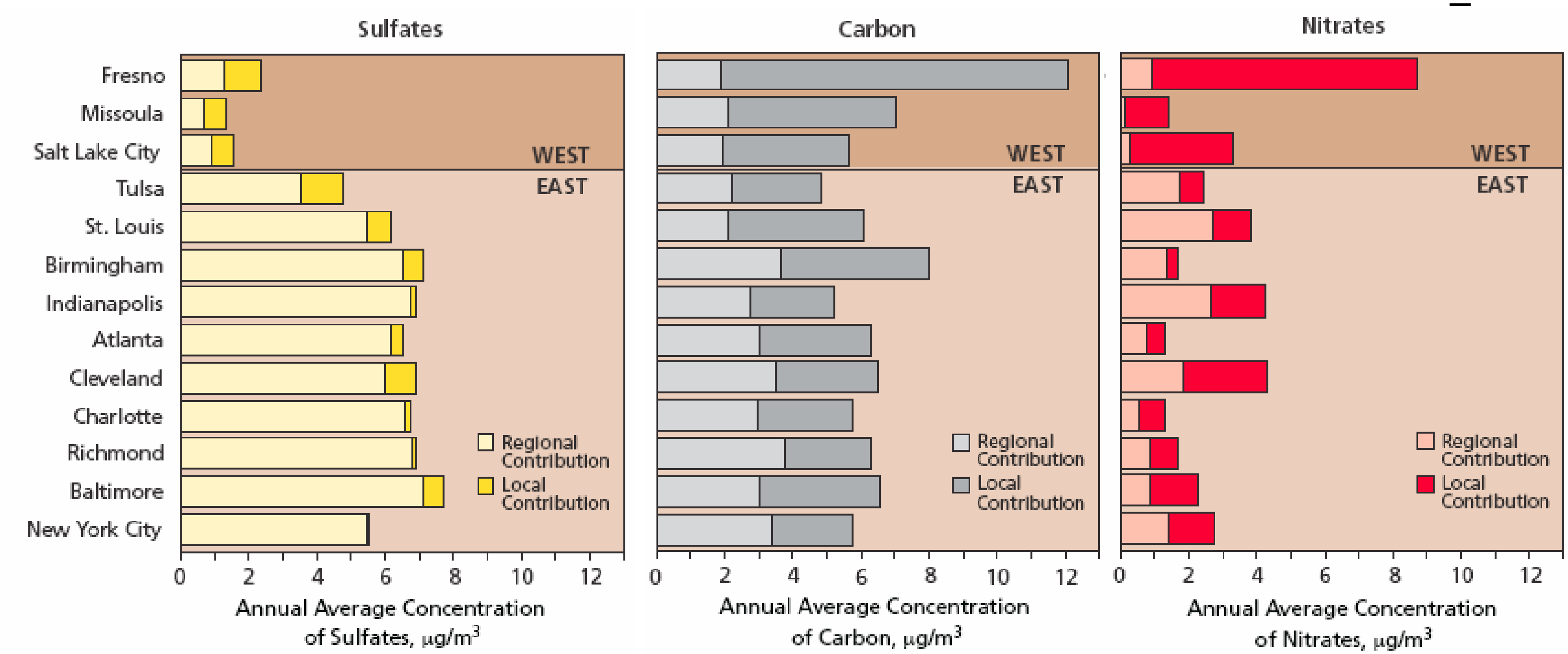
•Most from regional sources

Carbon

- Large PM2.5 component
- Local contribution (40-70%)

Nitrates

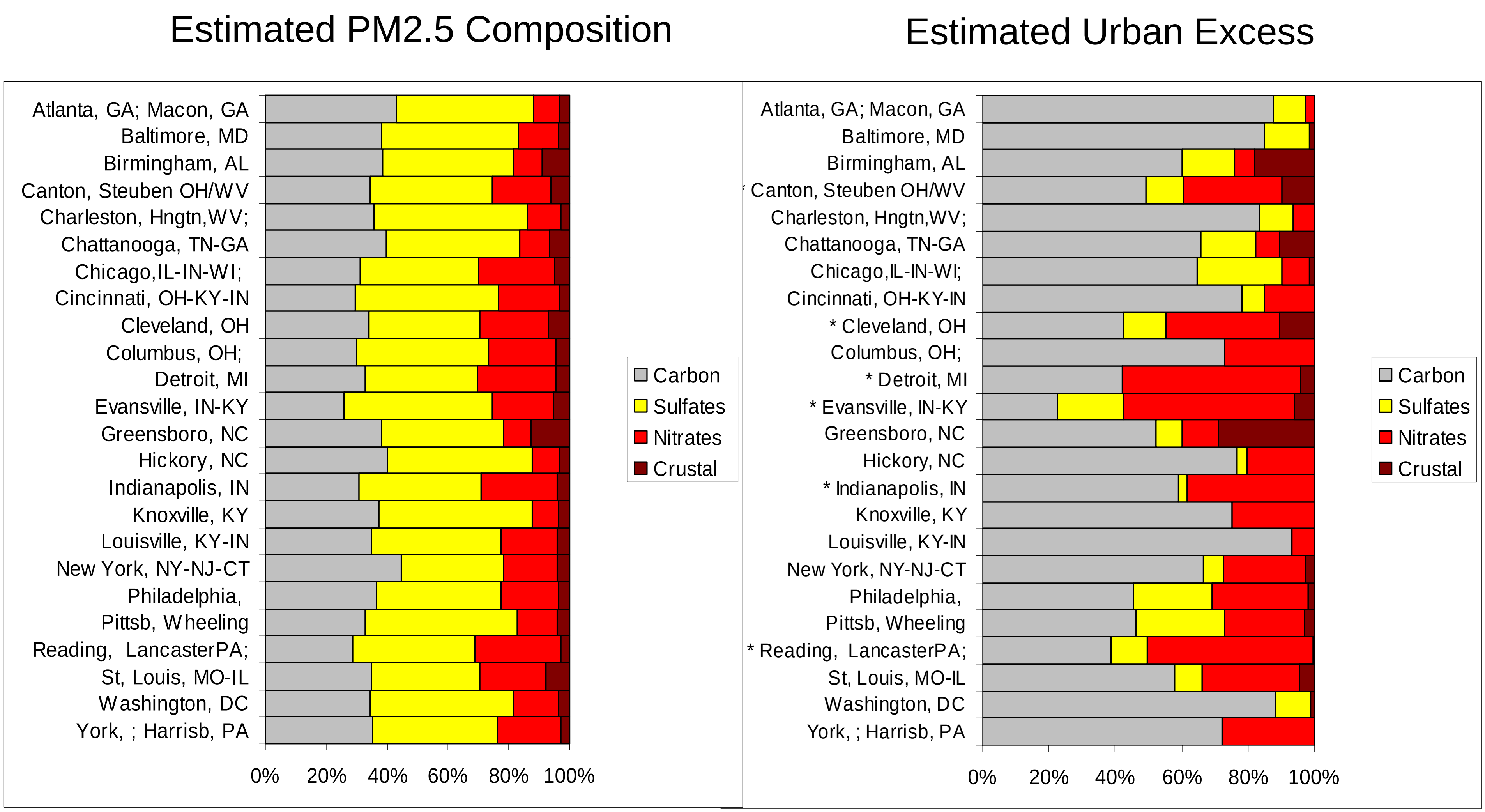
- 10-30% of PM2.5
- Some east avg. ambient nitrates ~4 ug/m3
- Local contribution $\geq$ 50%



From Particle Pollution Report, 2003
Comparing single urban and rural locations

Carbon and Nitrates dominate the average local urban excess

Composition of Eastern PM2.5 Non-Attainment Areas



* Indicates areas with > 30% UE nitrates

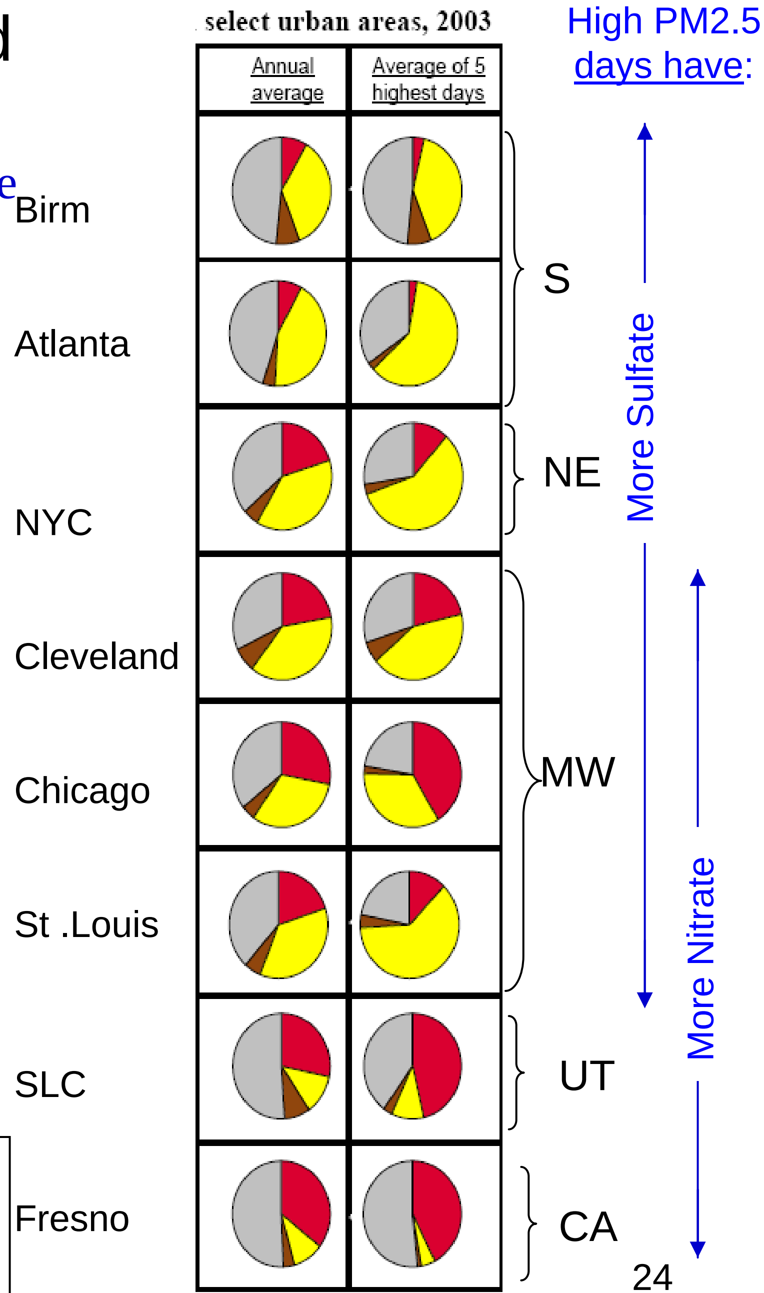
High Day vs. Average Composition

Average Concentration is based on all days but is strongly influenced by the highest concentration days

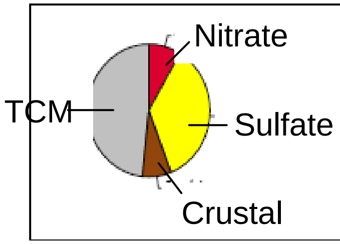
Composition on Annual Average and High PM2.5 Days

Some source categories and regional influences may be more important for high concentration days

- Comparing average of 5 highest days during 2003, regional sources of sulfates and nitrates are larger contributors to peak day concentrations than to annual average (selected city analysis)
- Composition can vary from high day to high day
- Carbon can be smaller as % -- but still larger in absolute concentration values -- compared to the average



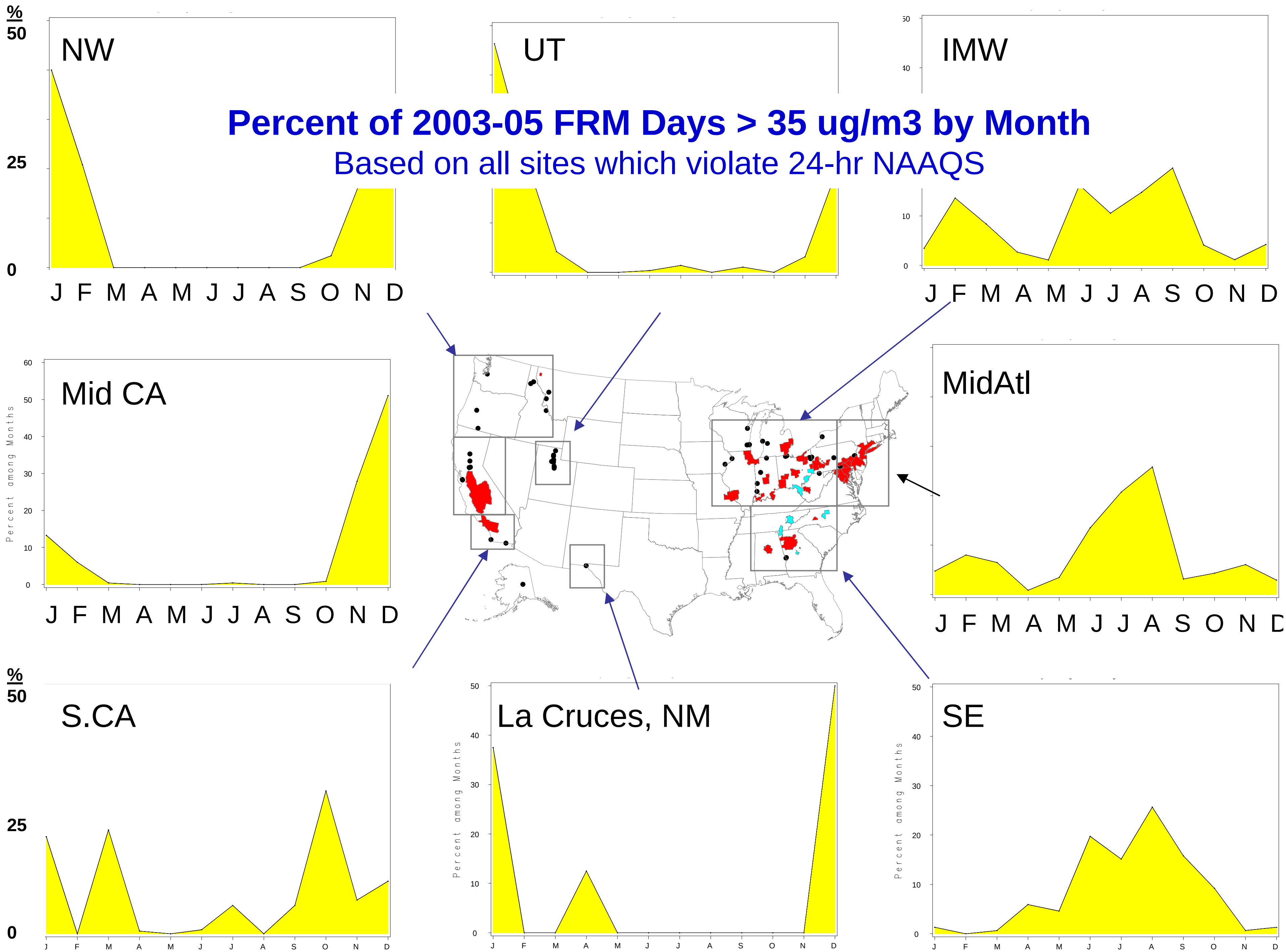
From PM Staff Paper (Rao et al)

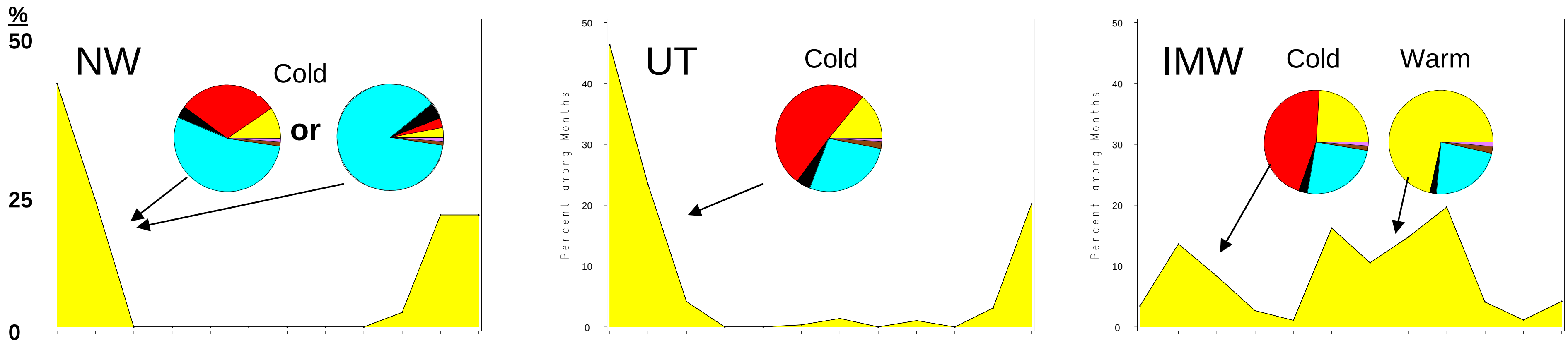


This analysis shows PM2.5 Composition of the ambient aerosol (not adjusted to represent FRM mass)

Percent of 2003-05 FRM Days > 35 ug/m3 by Month

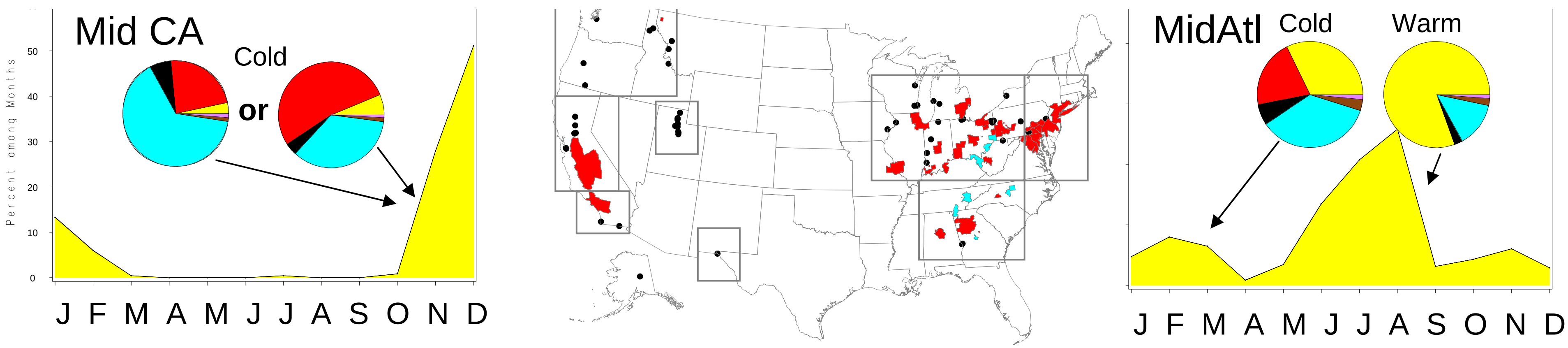
Based on all sites which violate 24-hr NAAQS



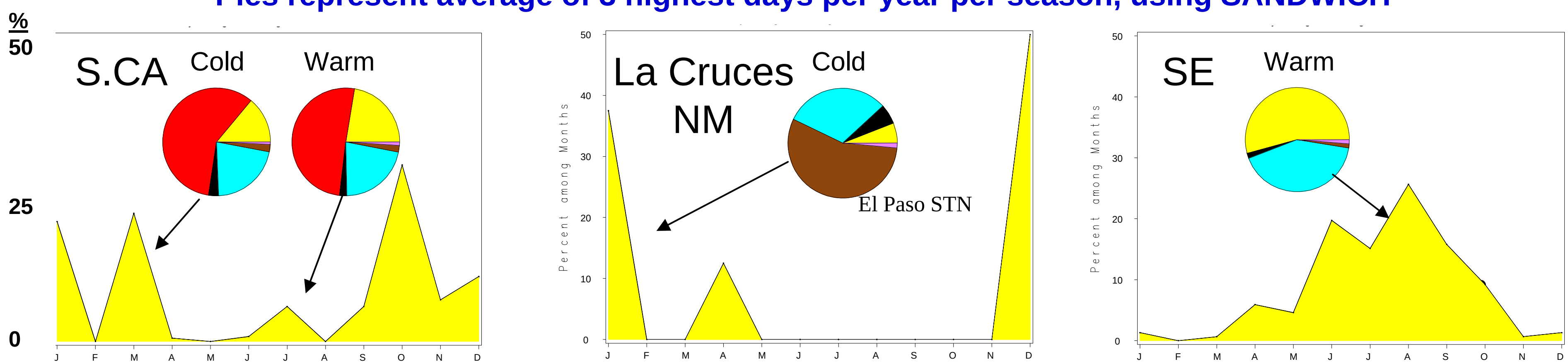


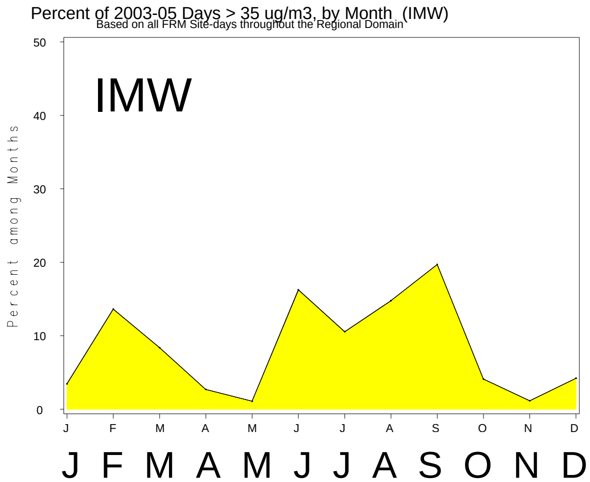
“Example” Composition for High Days ["Warm” Season (May-Sept) & “Cold”]

But sites can be different within each “domain”

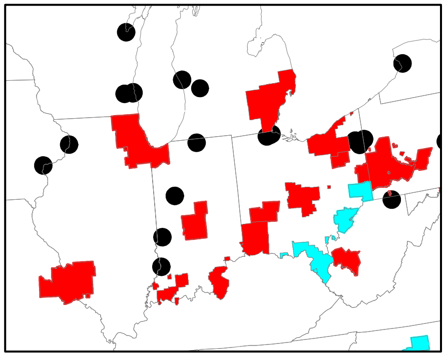


Pies represent average of 3 highest days per year per season, using SANDWICH



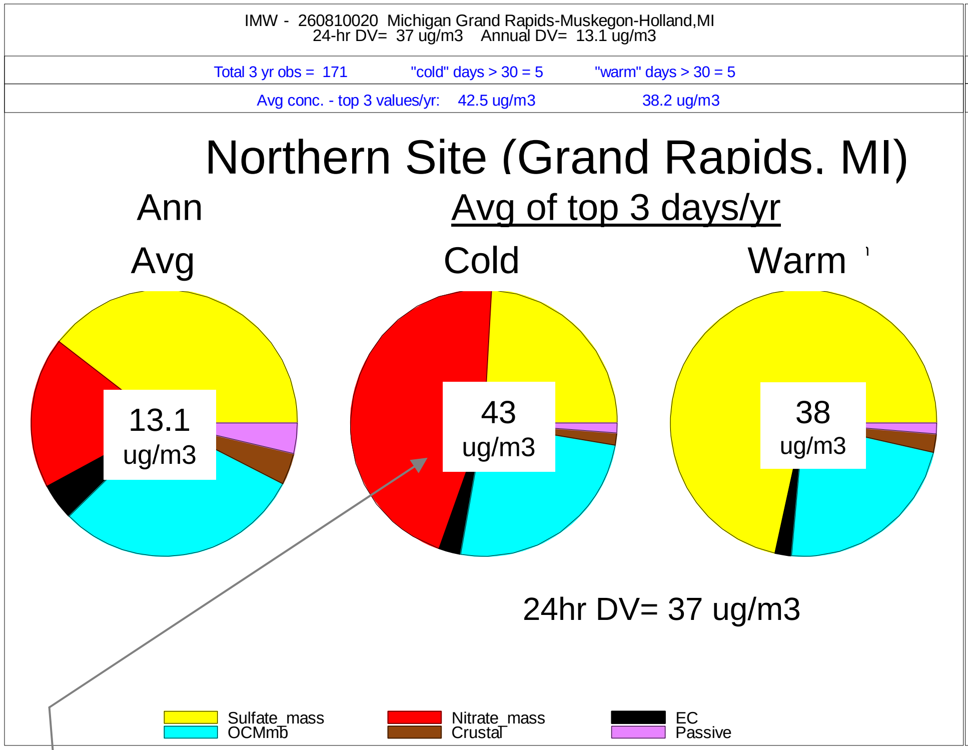


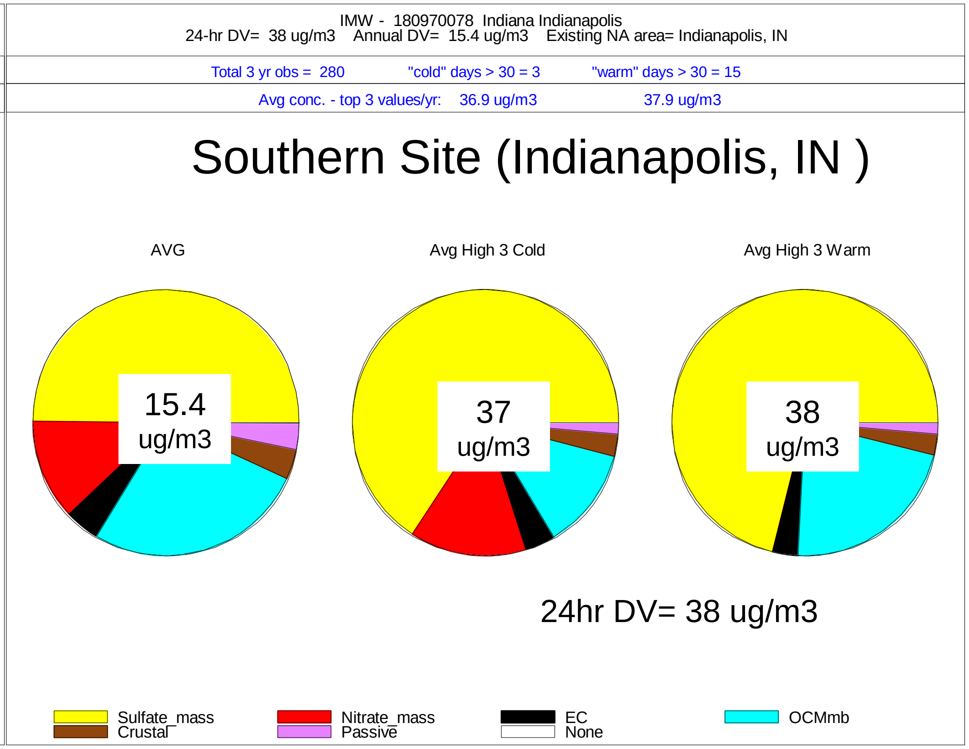
More Details about PM2.5 Chemical Composition for the IMW



Industrial Midwest

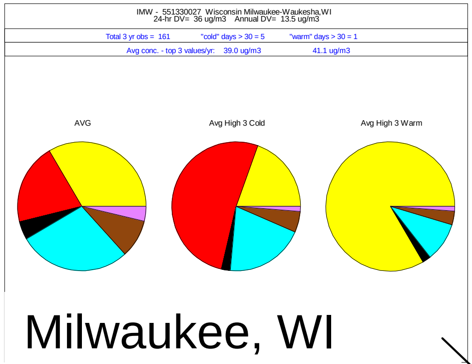
- Generally nitrate dominated winter-time values in northern areas
- Sulfate dominated episodes in summer (region-wide)

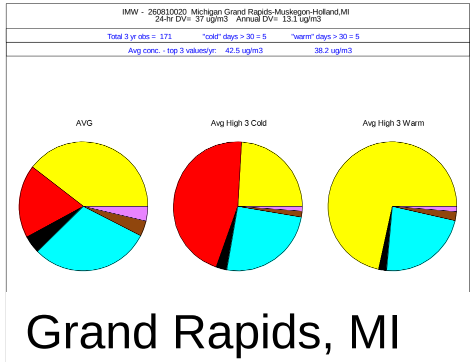


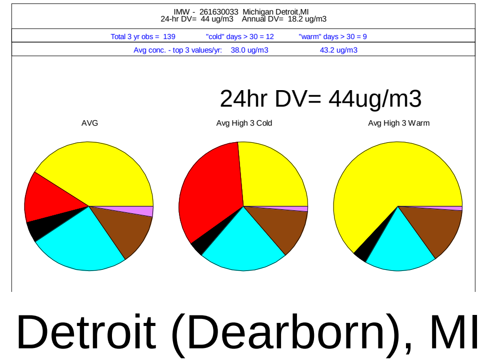


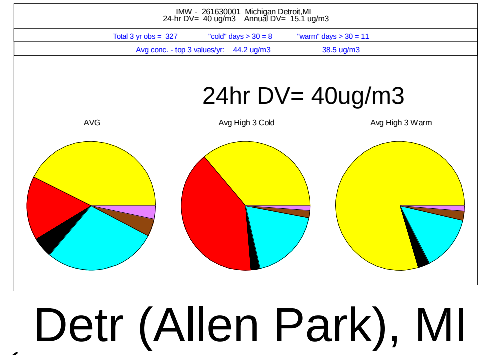
Note: Passive is PM2.5 unrelated to emissions

Number inside pie is the “top 3” average concentration, ug/m3

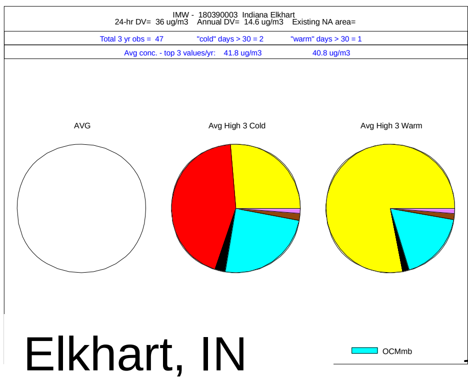


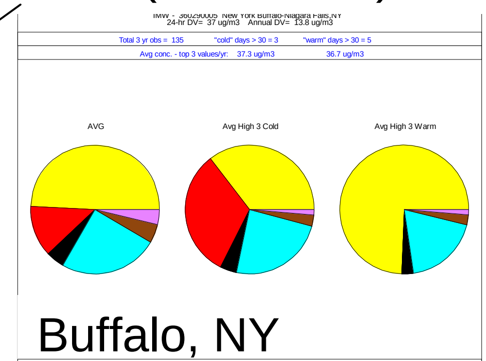


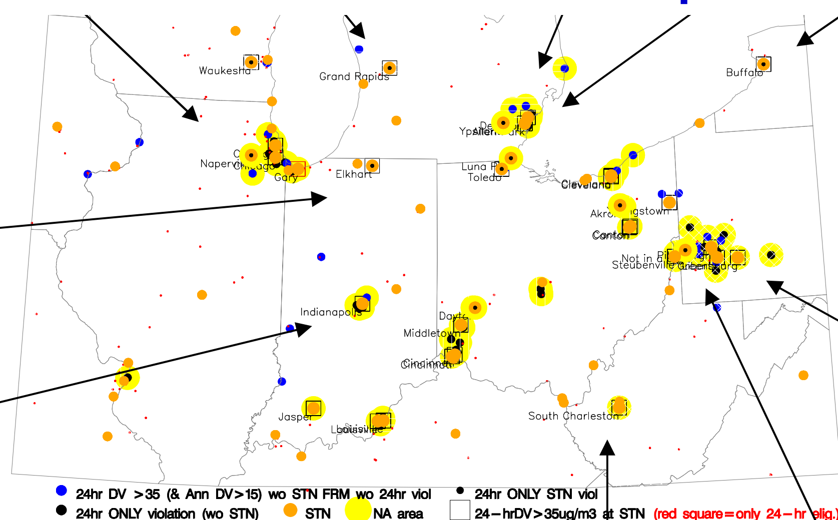


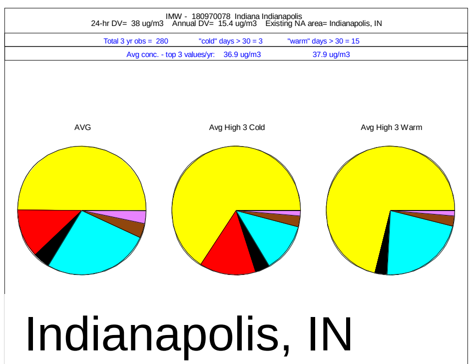


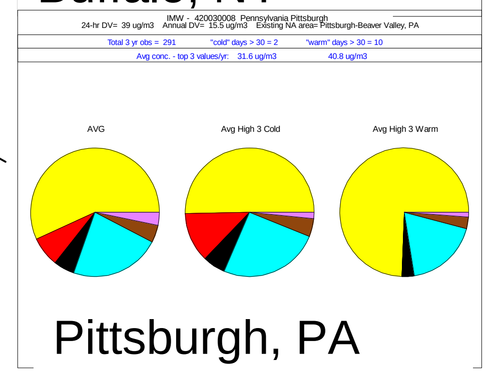
Nitrates - important in the N. sub-Region
Sulfates and warm season in S. portion





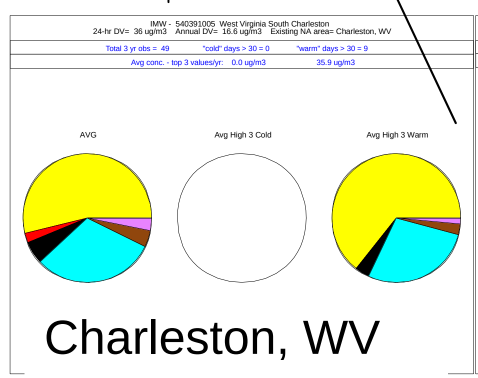


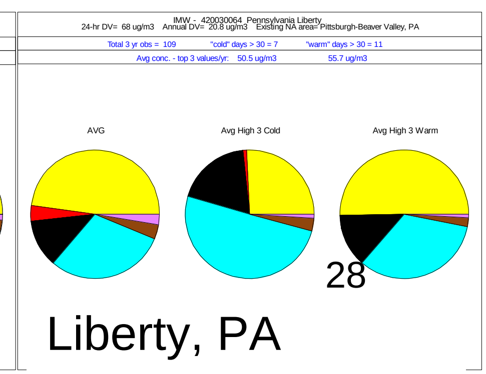


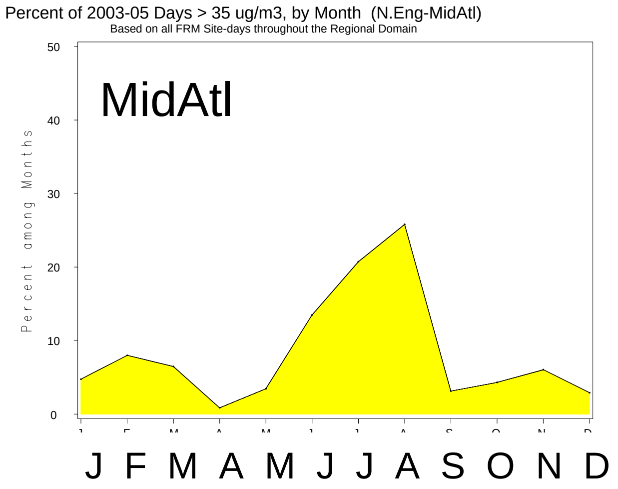


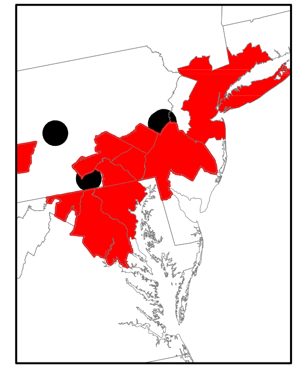
Note: Map show existing NA areas
& new violation sites

Sulfate_mass | OCMmb | Nitrate_mass | Crustal | EC | Passive





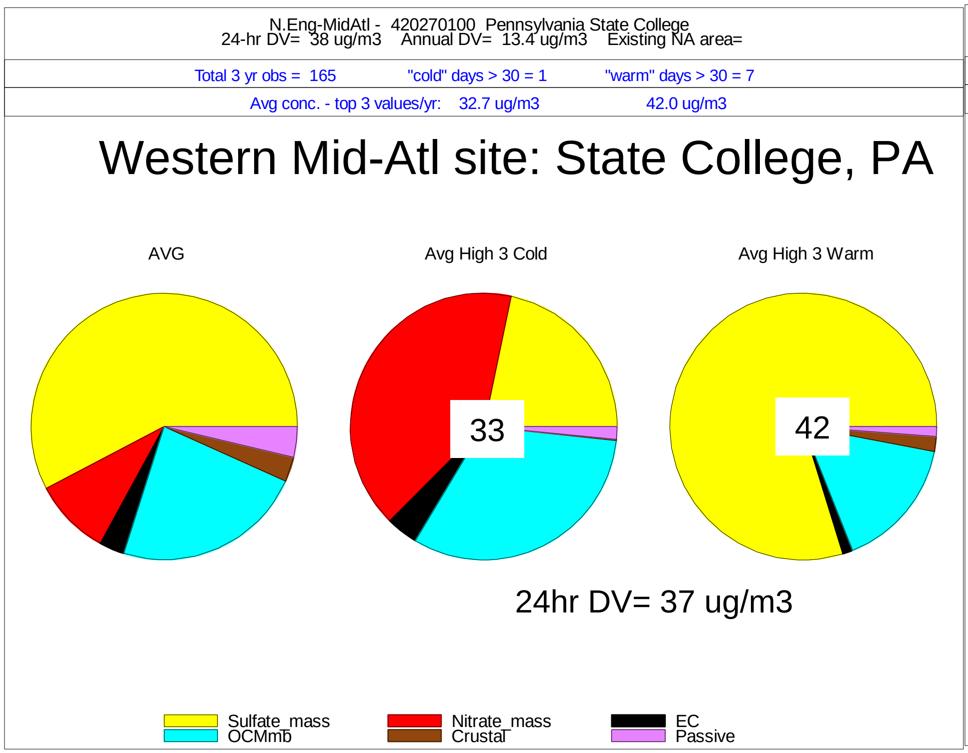


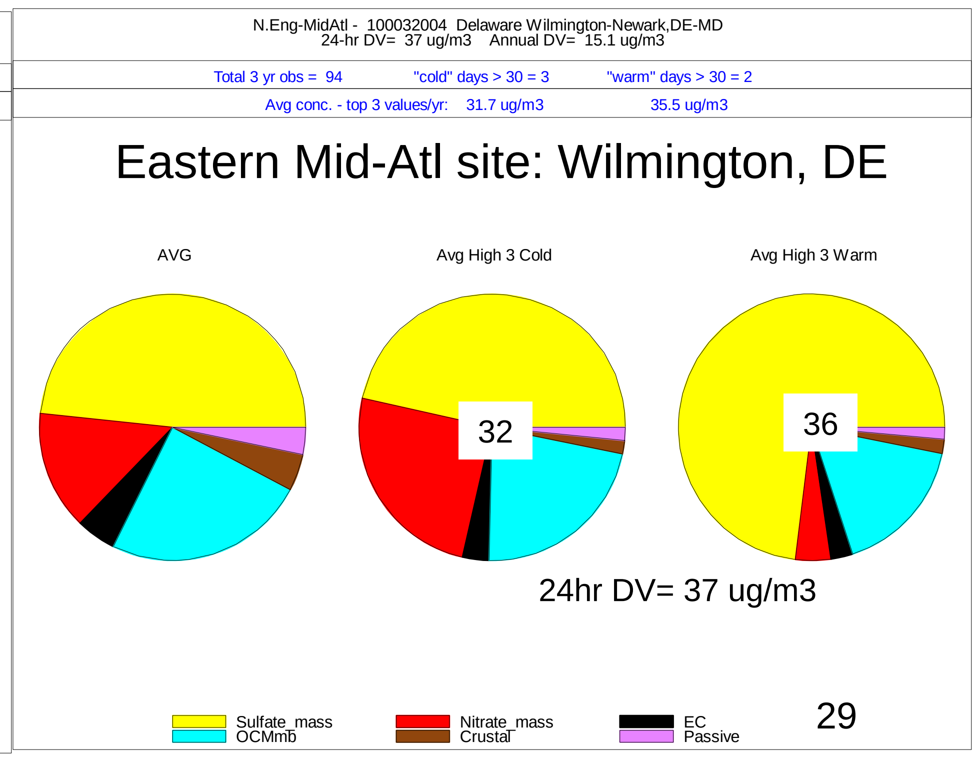


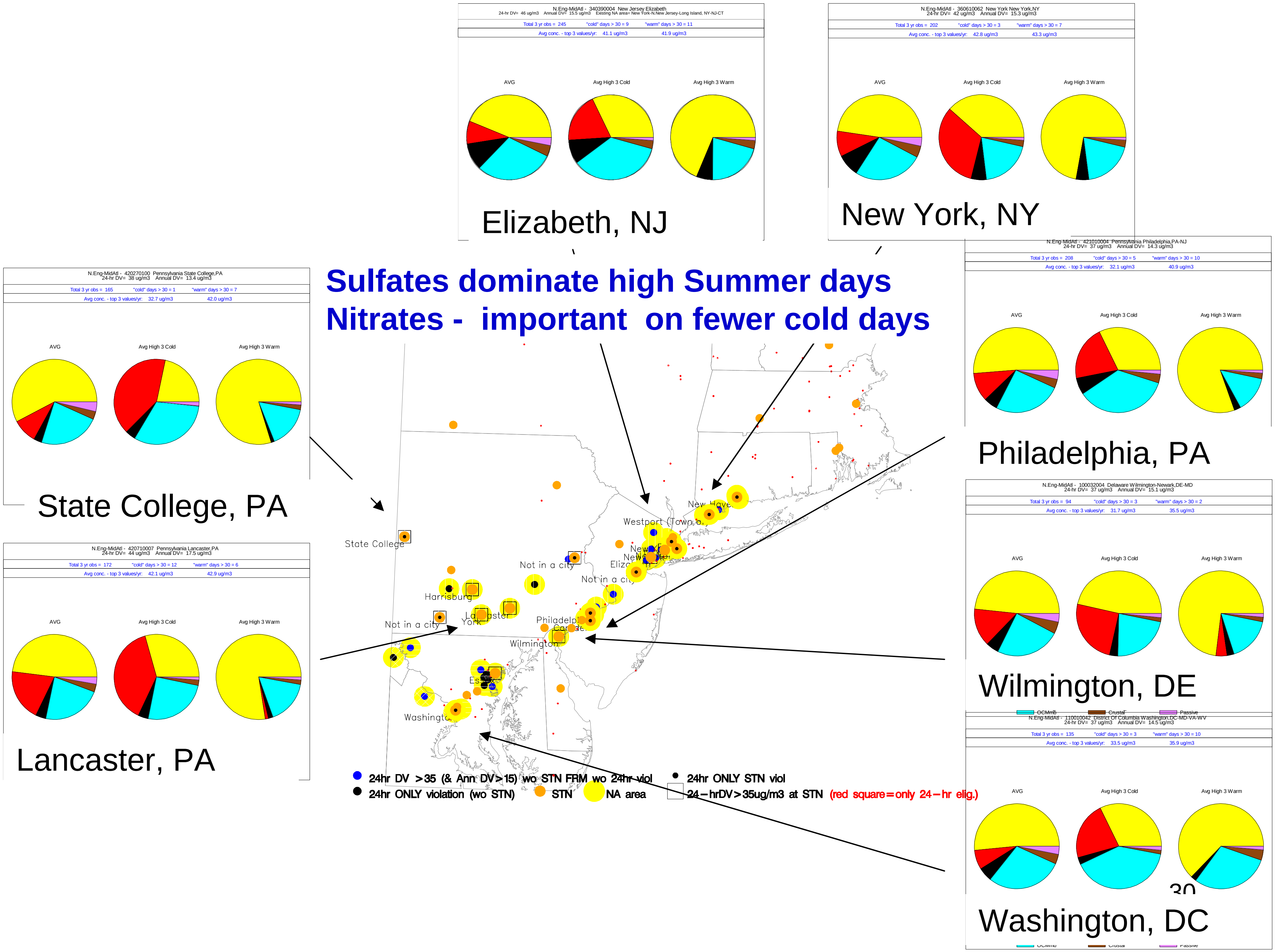
Mid_Atlantic Region

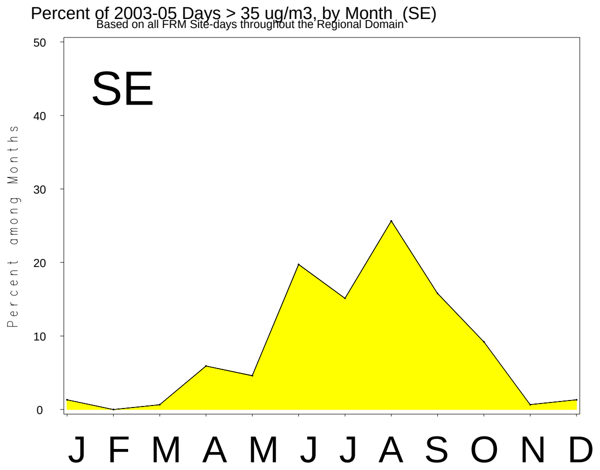
Generally Sulfate dominated episodes everywhere in summer

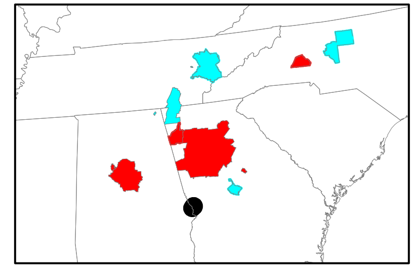
Fewer Nitrate contributed winter-time values (except in SE. PA)






Sulfates dominate high Summer days
Nitrates - important on fewer cold days
Elizabeth, NJ
New York, NY
Philadelphia, PA
State College, PA
Wilmington, DE
Lancaster, PA
Washington, DC
AVG
Avg High 3 Cold
Avg High 3 Warm
State College
Harrisburg
Not in a city
York
Lancaster
Philadelphia
Camden
Wilmington
Washington
Westport (Town of)
New Haven
Elizabeth
Newark
24hr DV >35 (& Ann DV>15) wo STN FRM wo 24hr viol
24hr ONLY STN viol
24hr ONLY violation (wo STN)
STN
NA area
24-hrDV>35ug/m3 at STN (red square=only 24-hr elig.)
OCMmb
Crustal
Passive



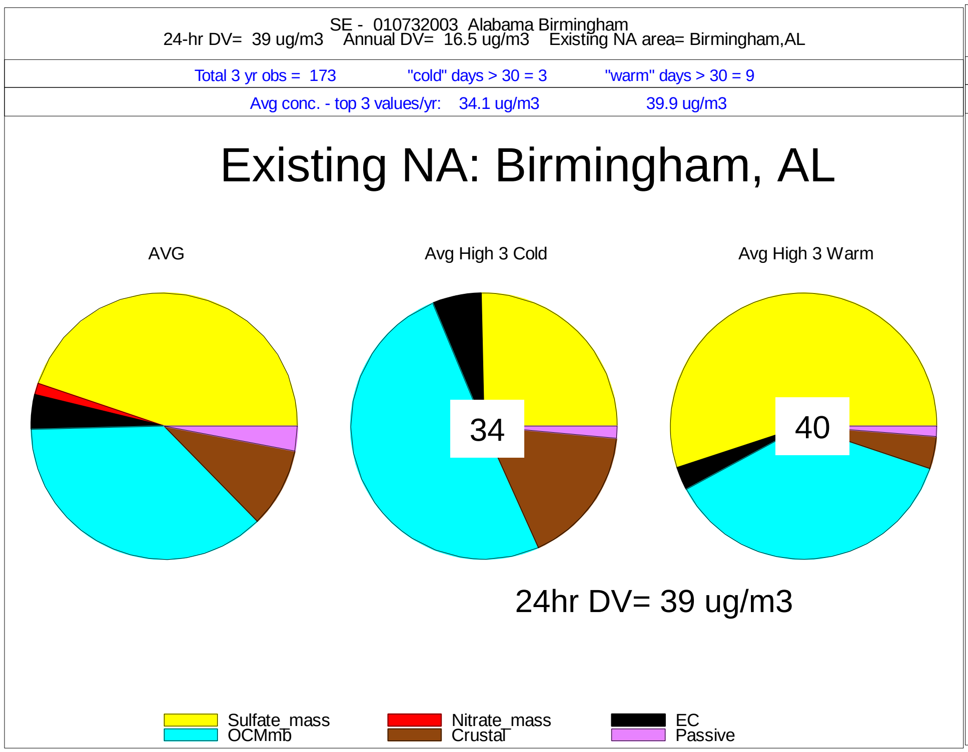


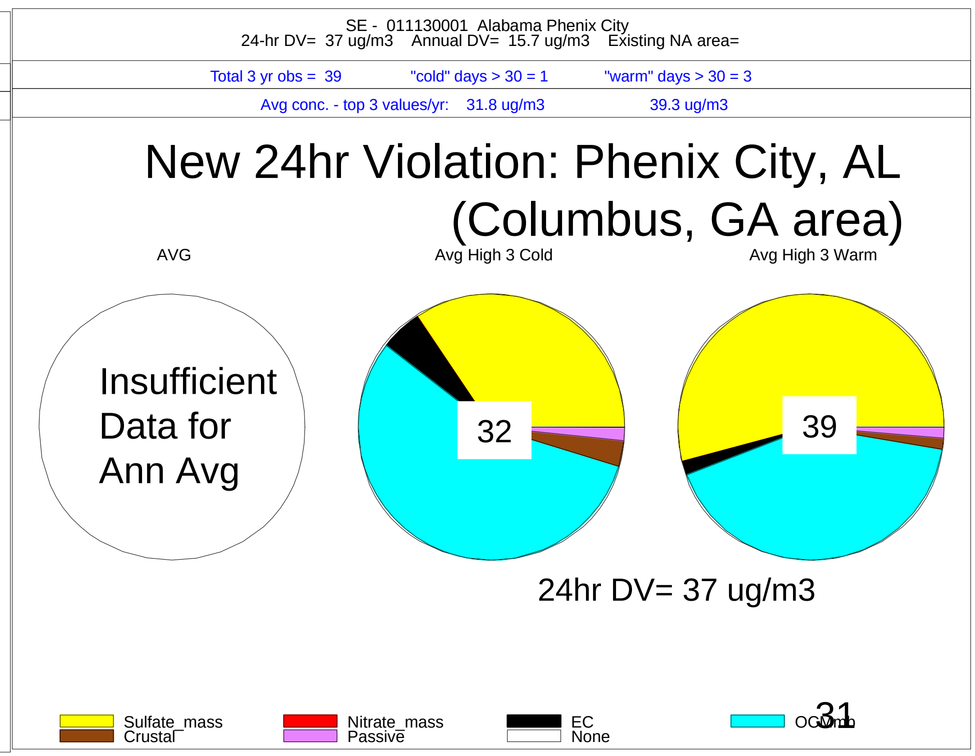
South East Region

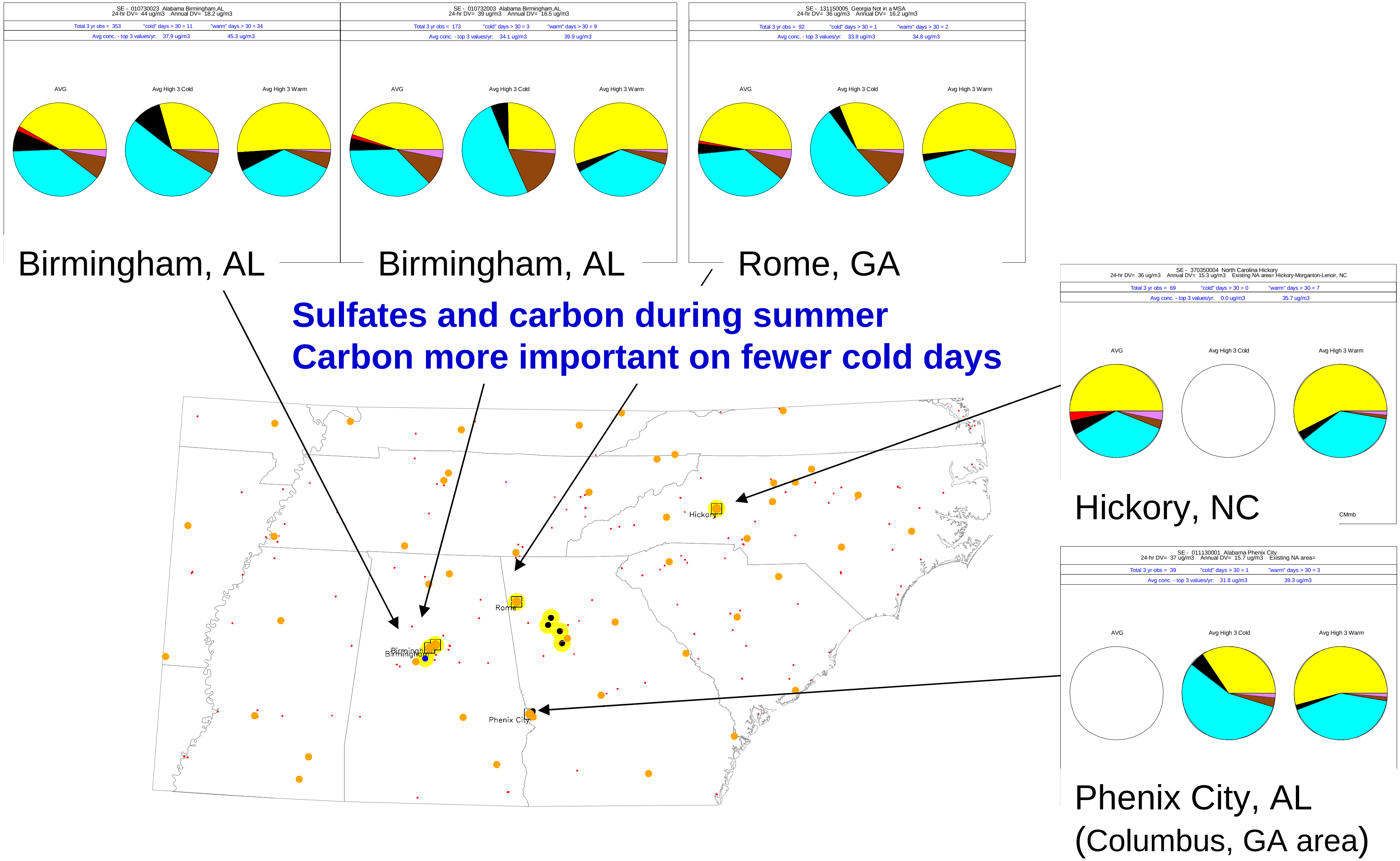
Mostly sulfate dominated + OC episodes, in summer

-- shows influence of biogenics and other SOA

Fewer cold-season exceedances (& are driven by carbon)

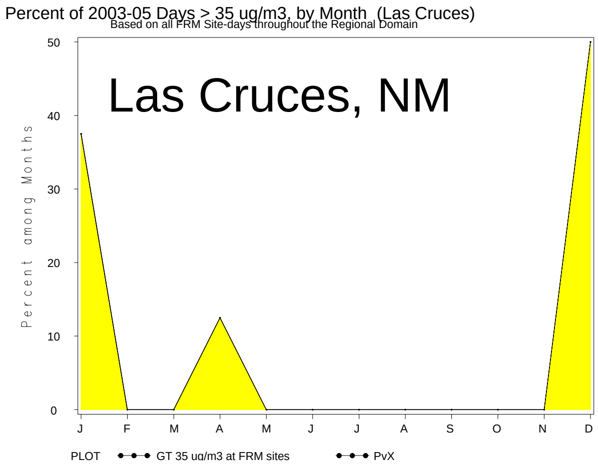


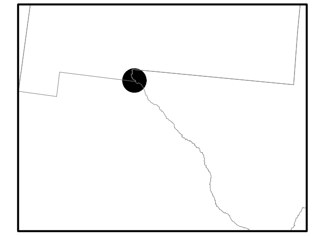




24hr DV >35 (& Ann DV>15) wo STN FRM wo 24hr viol
24hr ONLY violation (wo STN)
STN
NA area
24hr ONLY STN viol
24–hrDV>35ug/m3 at STN (red square=or

Note: Columbus area designated Attainment in 2005 on basis of spatial averaging.

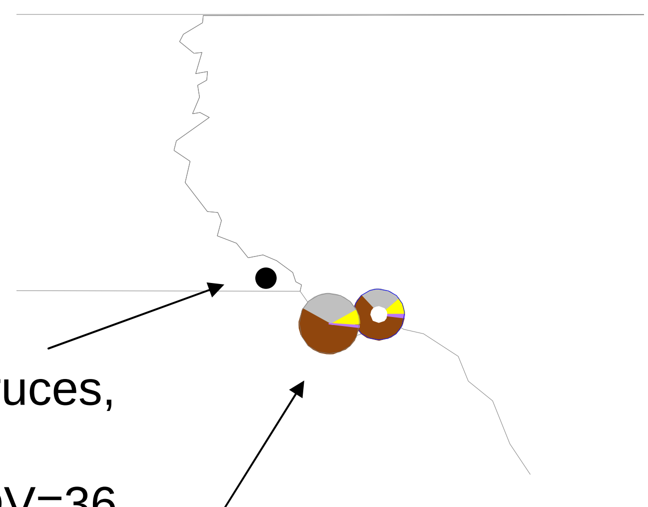




Southwestern US

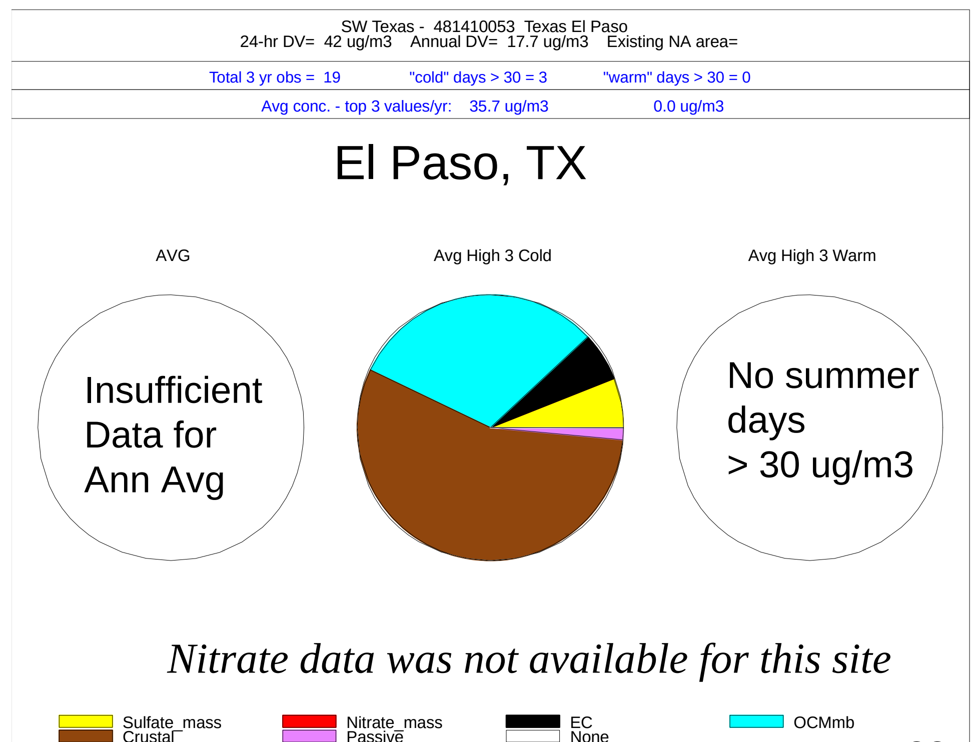
- Speciation data (from El Paso) suggest emission sources creating crustal and carbon
- Shows effect of aridity and wind

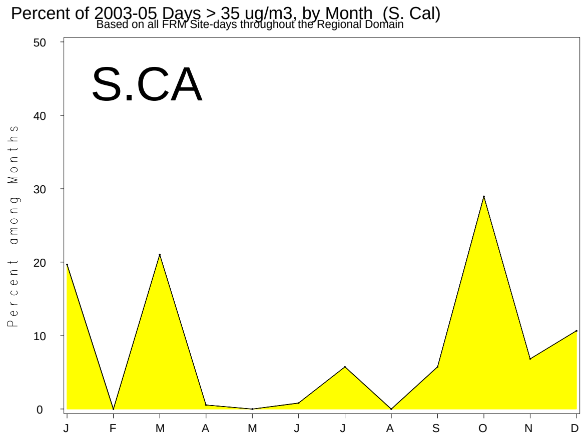
PM2.5 speciation - 02/02/2003

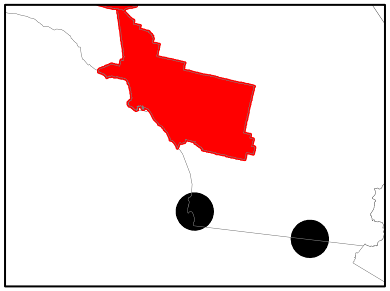


Las Cruces, NM
24hr DV=36
Ann DV=10.4

24hr DV=42 (not pop- oriented?)
Ann DV=17.3

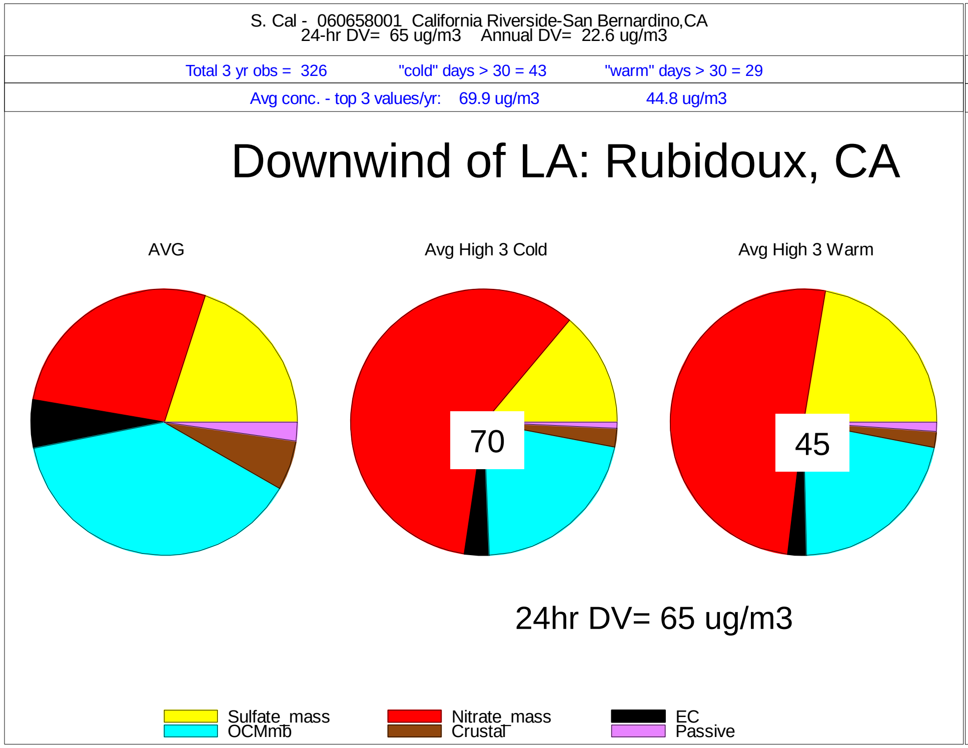


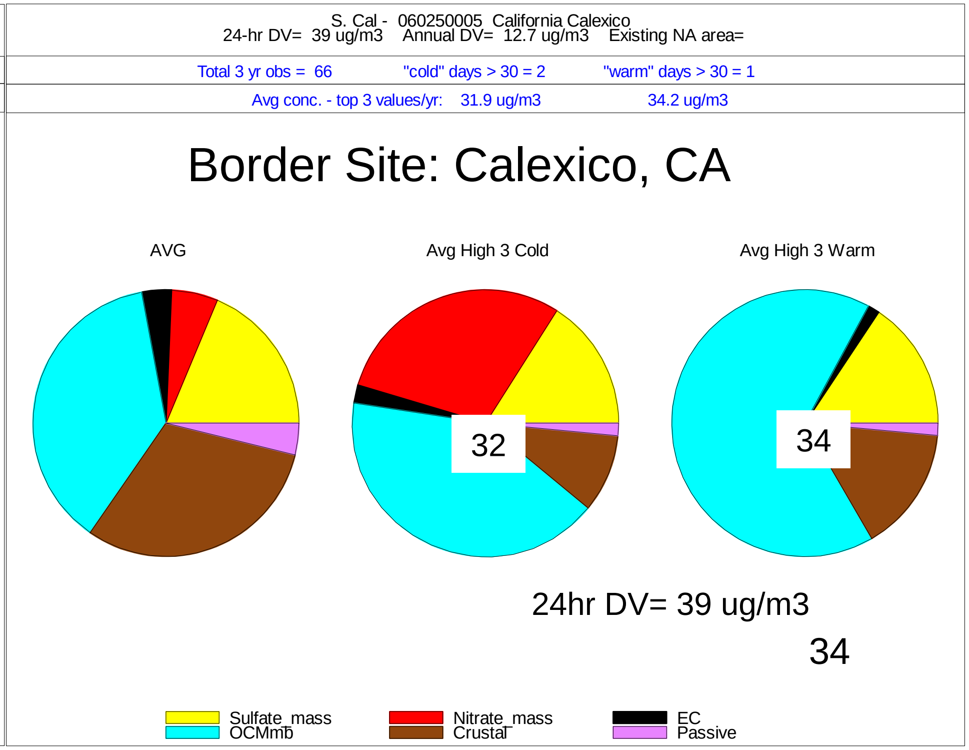


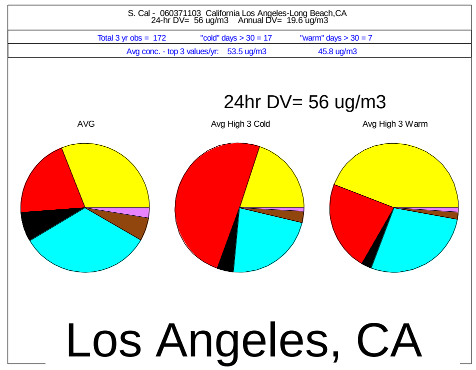


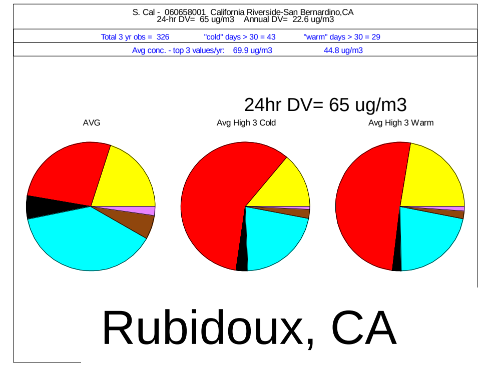
Southern California

- Nitrates dominate High PM2.5 in LA.
- Carbon (summer) and also nitrates (winter) in Calexico
  - Lower % crustal on high days

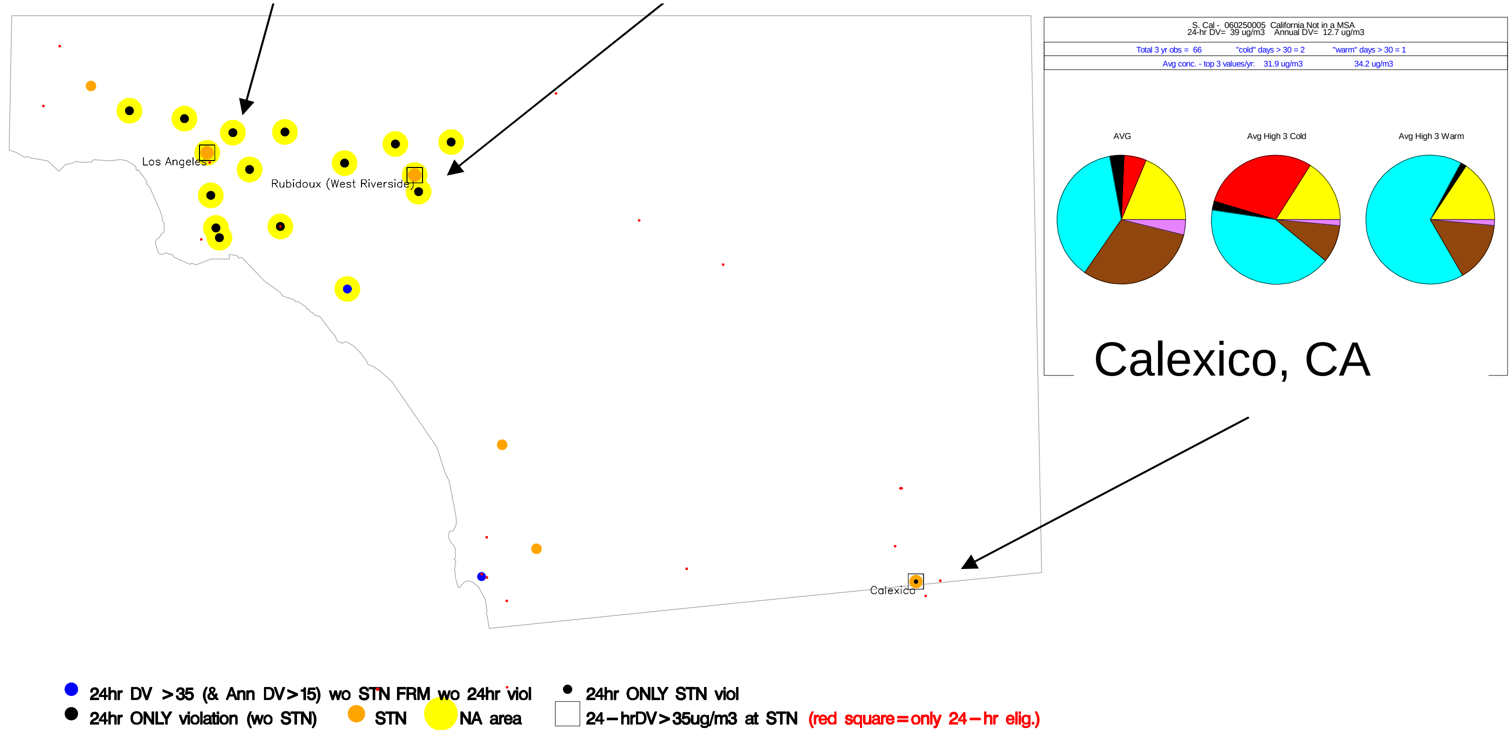


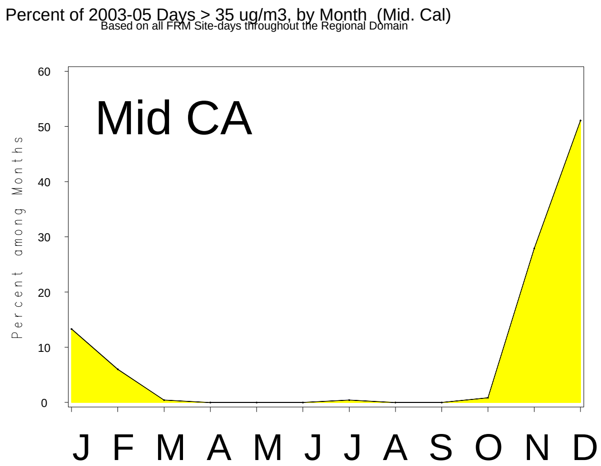


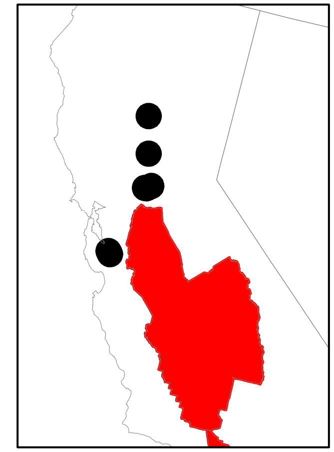




Composition Varies Across this Diverse CA Domain

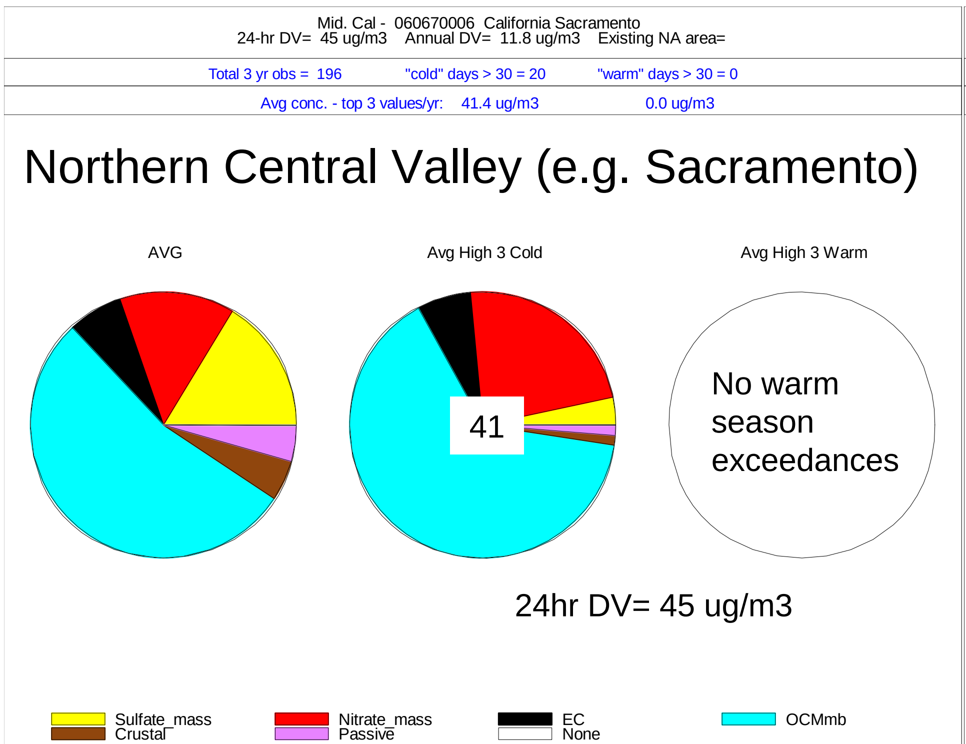


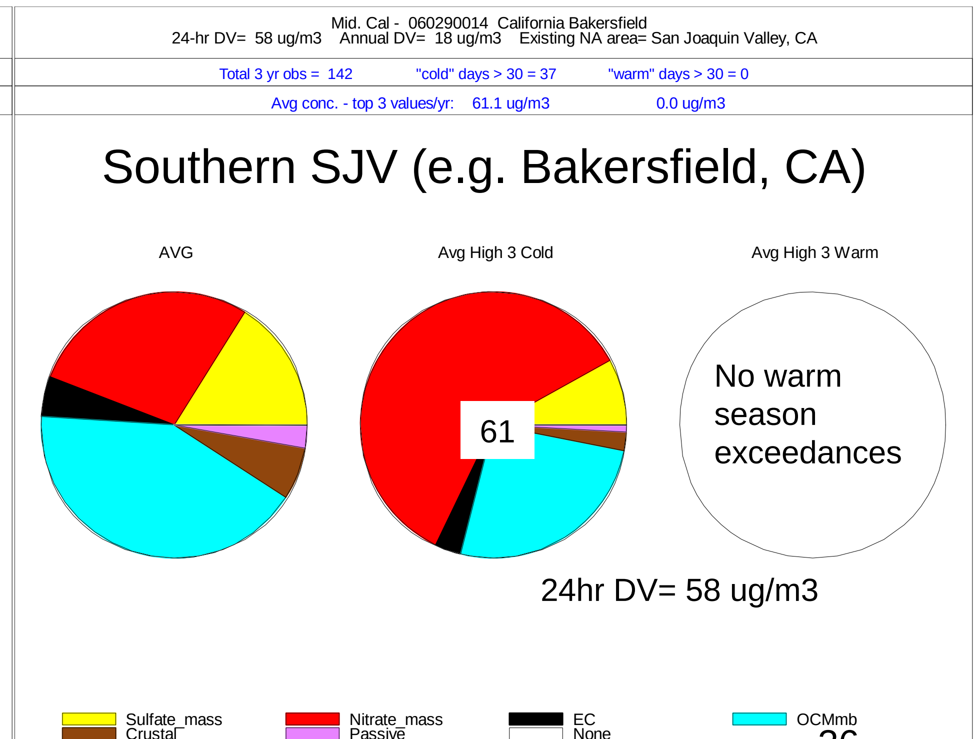




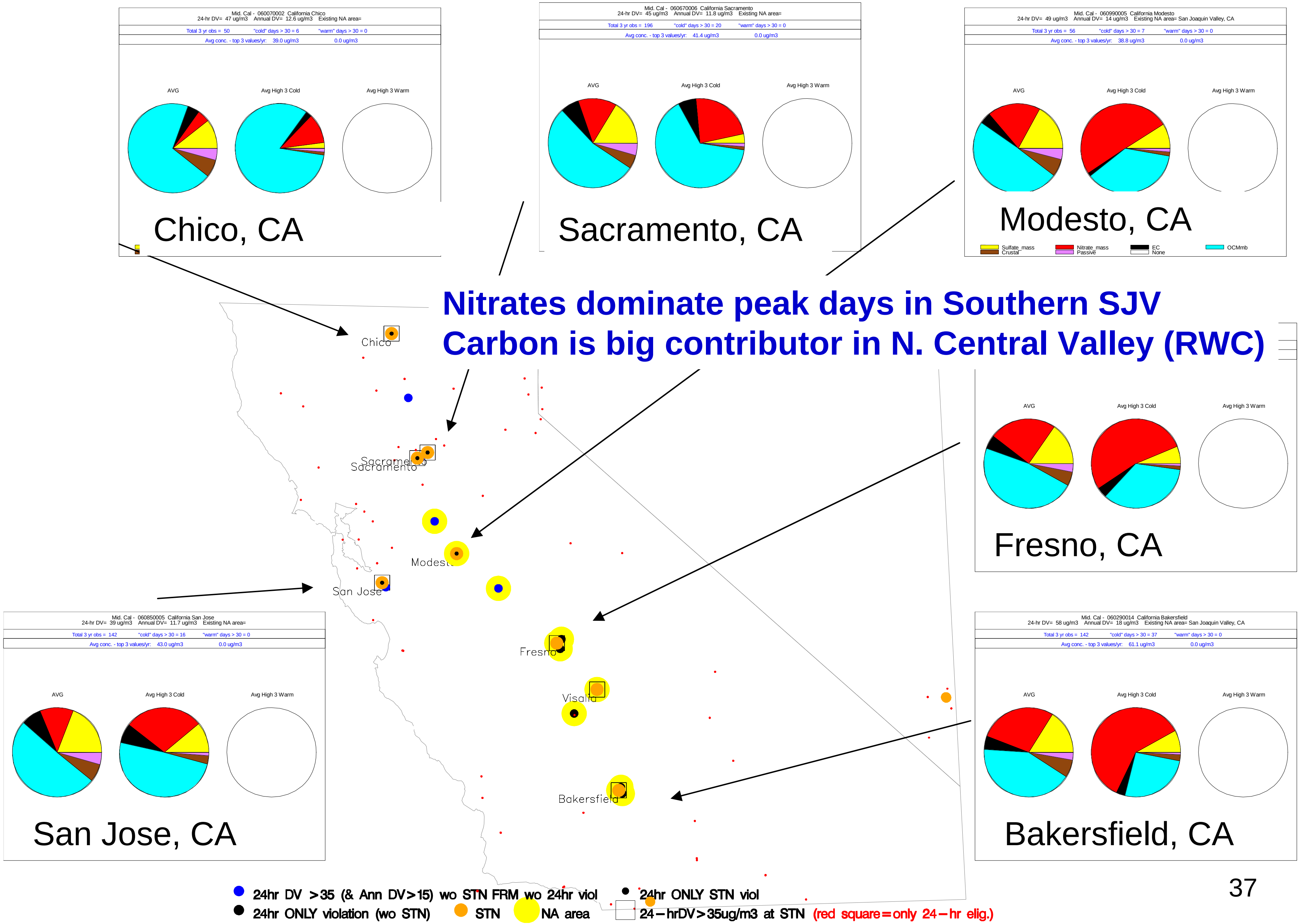
Middle California

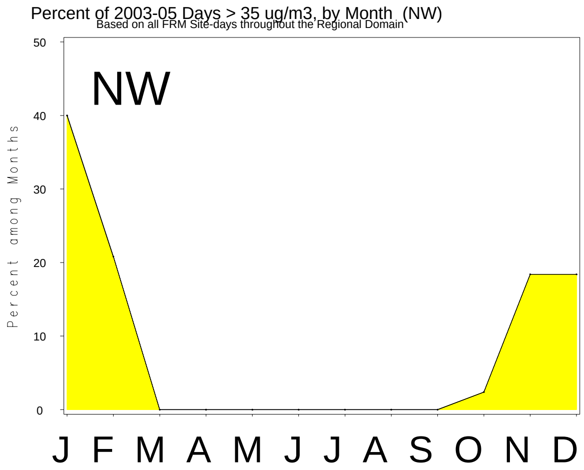
- Carbon in Northern Central Valley
  - from RWC?
- Nitrates dominate High PM2.5 in lower SJV





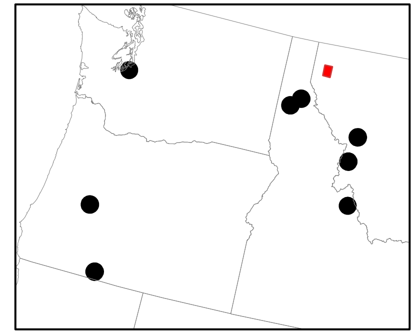
Nitrates dominate peak days in Southern SJV
Carbon is big contributor in N. Central Valley (RWC)

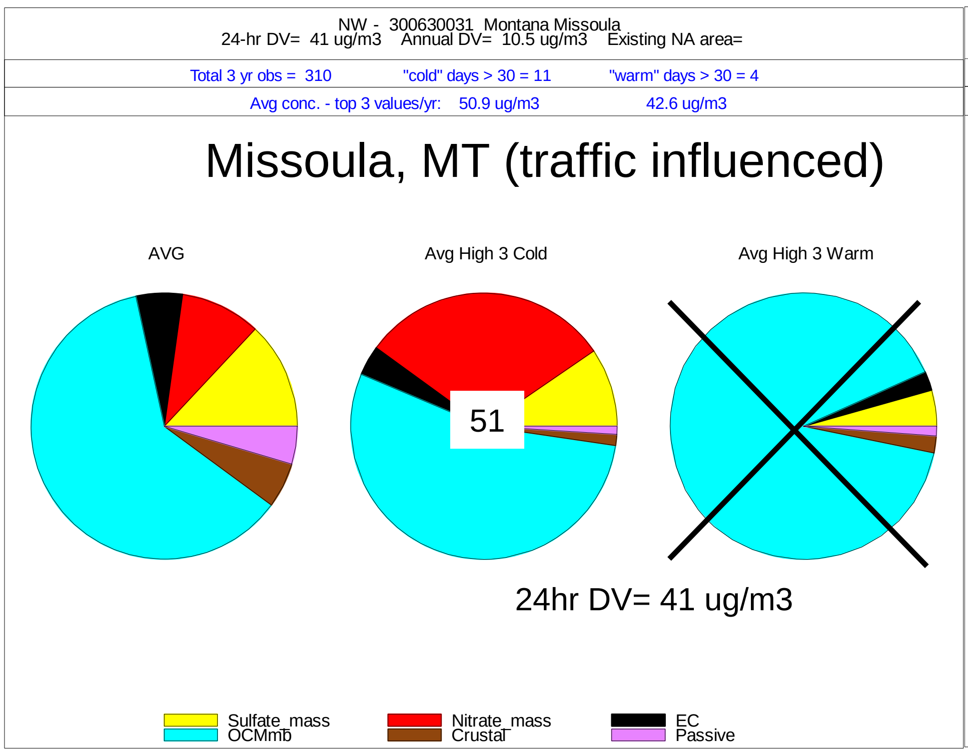


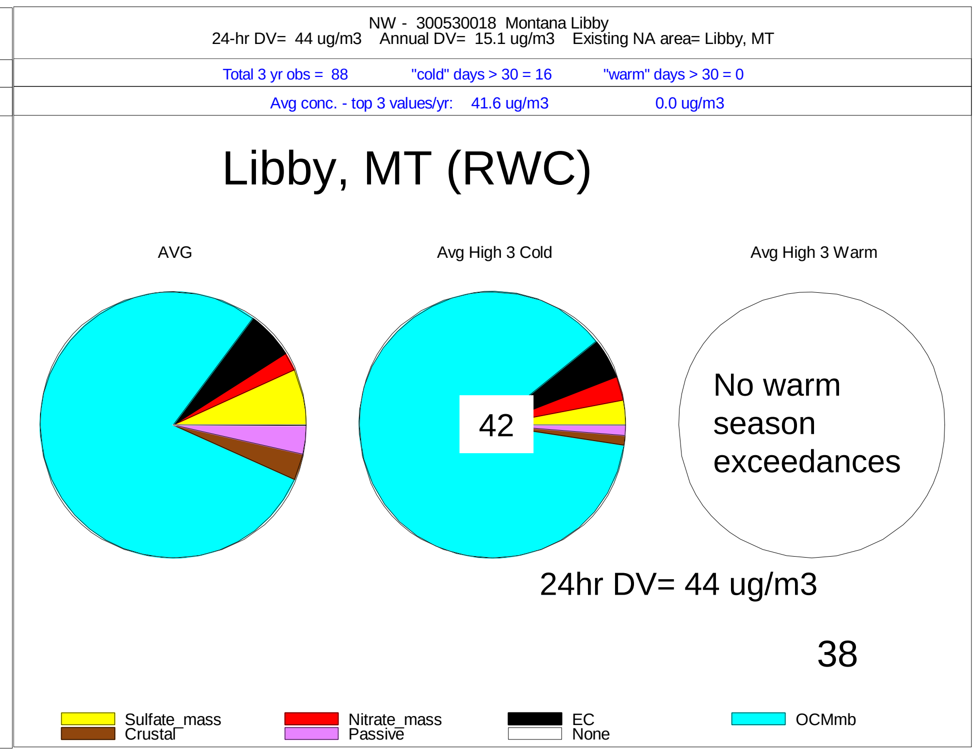


North West

- Carbon dominates Libby (from RWC?)
- Nitrates are also found on high winter days in Missoula (and elsewhere, e.g. Boise)
  - -- mobile and valley influence or ?
- Summer days are flagged fires
  - (not concurred?)

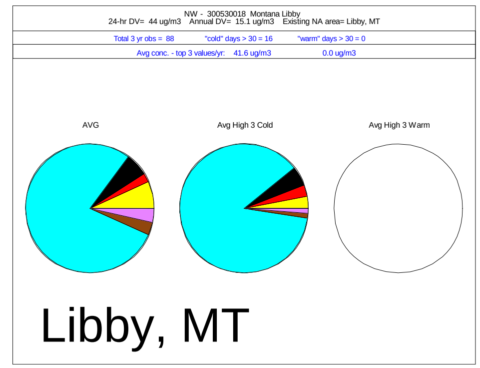






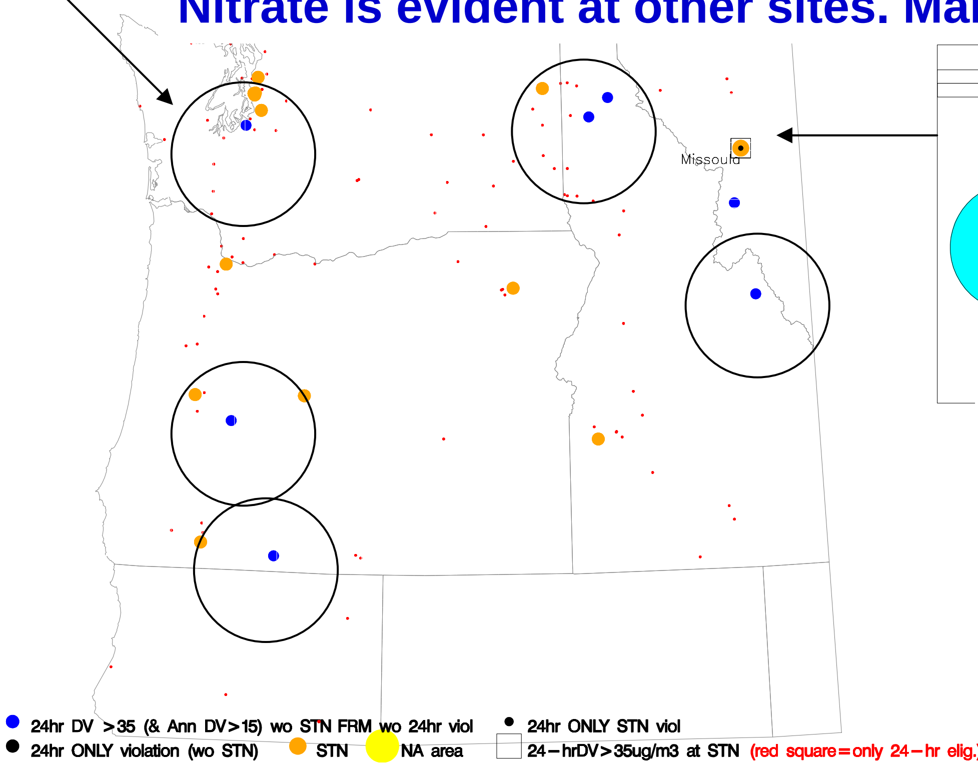
Difficult to predict composition from nearby locations

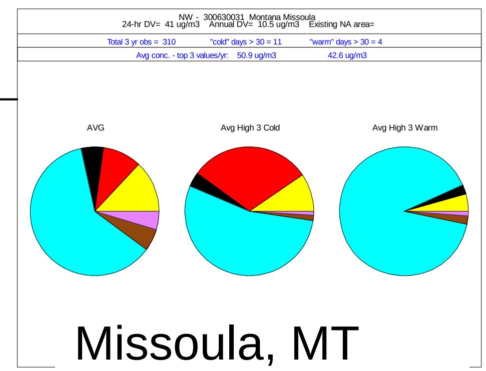
(e.g. Missoula composition is similar to Boise but different than Libby)

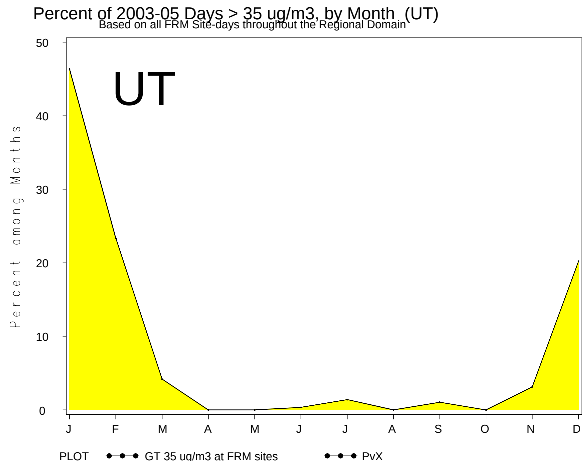


New violation locations without STN data

Composition Varies. Only Carbon at some locations. Nitrate is evident at other sites. Many Viol sites wo STN

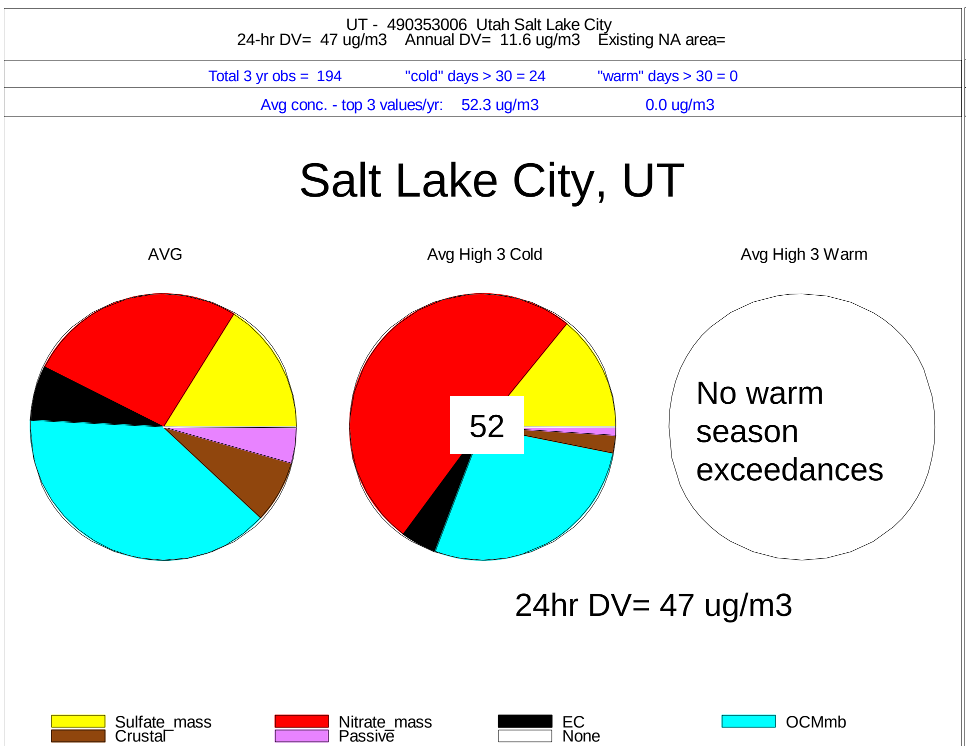


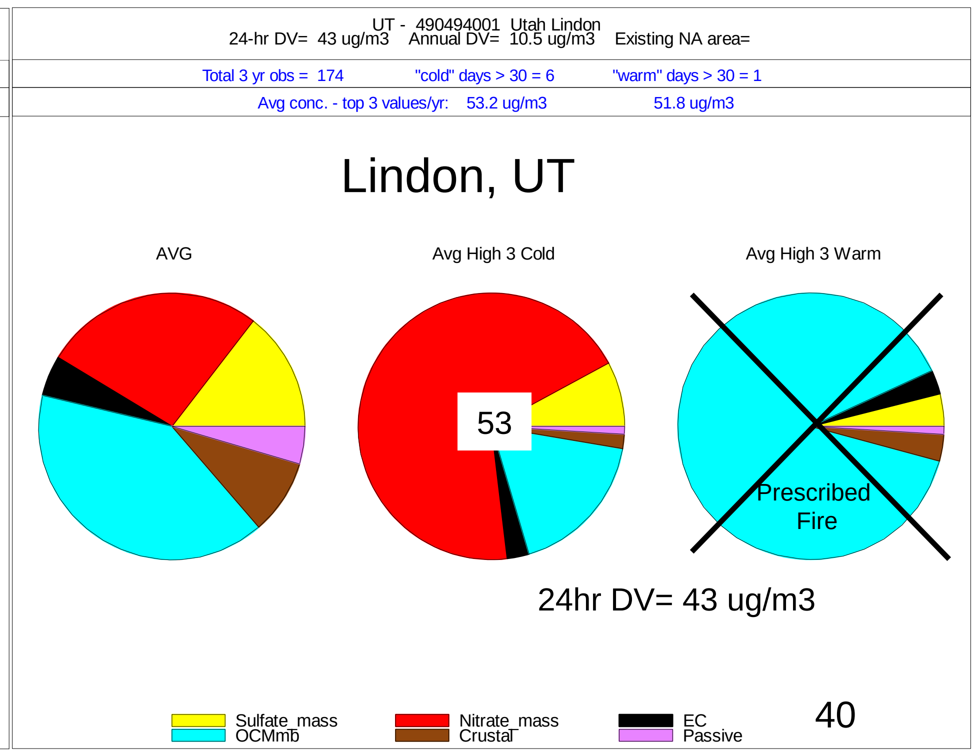




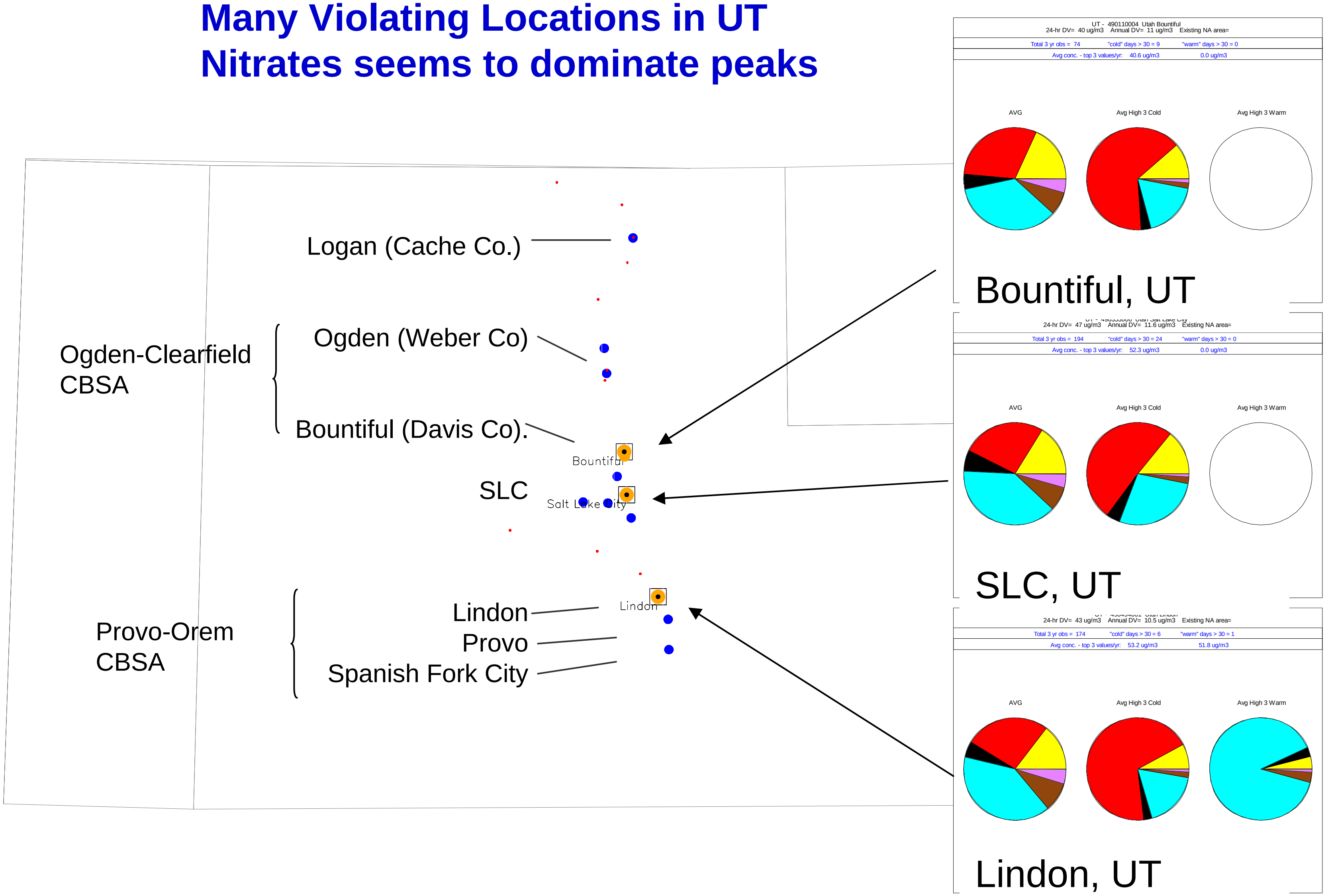
High PM2.5 in Utah

- Consistently more Nitrates on high days
- SLC has similar % Sulfates as ann avg
- Lindon – one summer exceedance
    - unflagged fire?

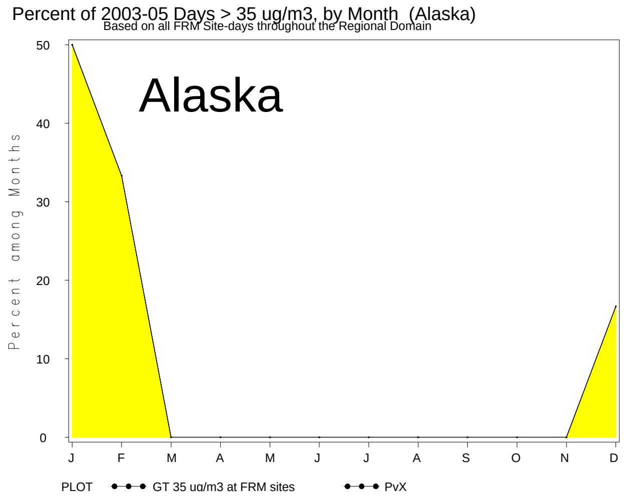


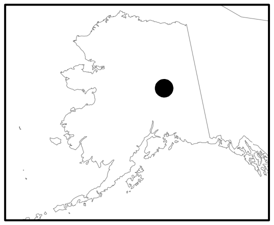


Many Violating Locations in UT
Nitrates seems to dominate peaks



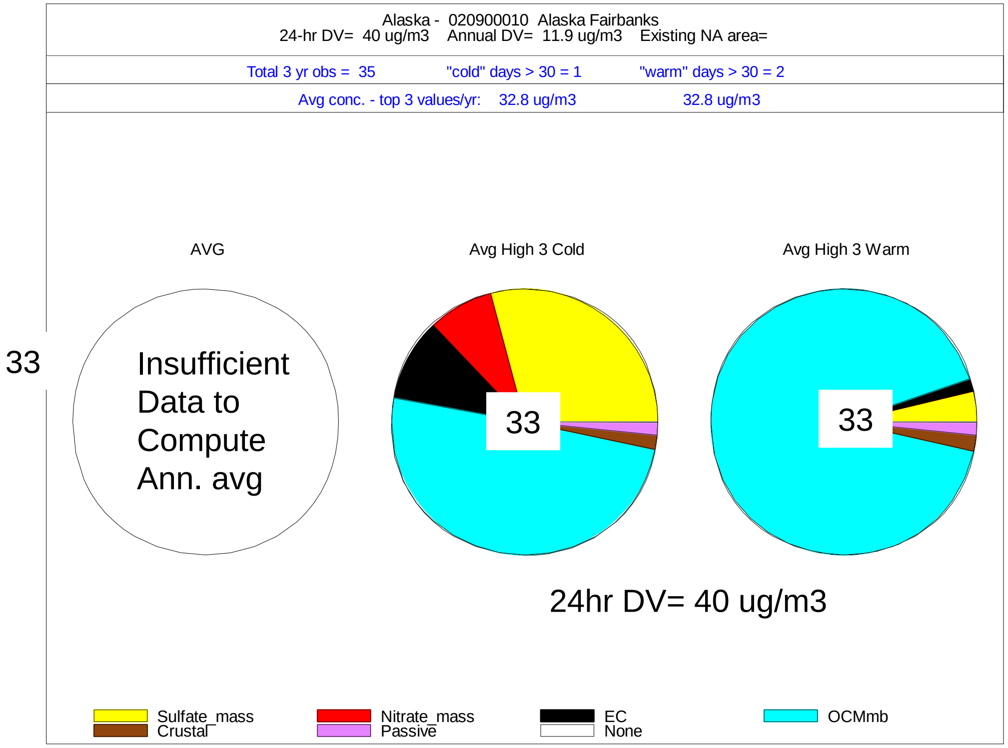
- 24hr DV >35 (& Ann DV>15) wo STN FRM wo 24hr viol
- 24hr ONLY STN viol
- 24hr ONLY violation (wo STN)
- STN
- NA area
- 24–hrDV>35ug/m3 at STN (red square=only 24–hr elig.)





High PM2.5 in Alaska (Fairbanks)

- 50% carbon on winter exceedance day
- Two summer exceedances are flagged fires (not concurred)



Potential Source Influences by Season and Scale

Season & Affected Domains	Major PM2.5 Components	Source category	Typical Scales of Influence		
			Regional	Urban	Micro
Cold • IMW • Mid-Atl • S. CA • UT • Mid CA • NM • AK	**Nitrate**	**EGU (NOx)**	✓	*	
		Ag (NH3)	✓	*	
		Mobile (NOx+NH3)	✓	✓	✓
	Sulfate	**EGU (SO2)**	✓	*	
	Carbon	**Mobile, Area/RWC, Industry**	✓	✓	✓
	Crustal	**Industry, Mobile**			✓
Warm • IMW • Mid-Atl • SE • S. CA	**Sulfate**	**EGU (SO2)**	✓	*	
	Carbon	**Mobile, Area, Industry, Biogenics and Smoke**	✓	✓	✓
	Crustal	**Mobile, Area, Industry**		*	✓

Underlined text indicates dominant season for the domain   Carbon includes OC and EC   *Sometimes occurs