Investigation of OM/OC Using Ambient Measurements

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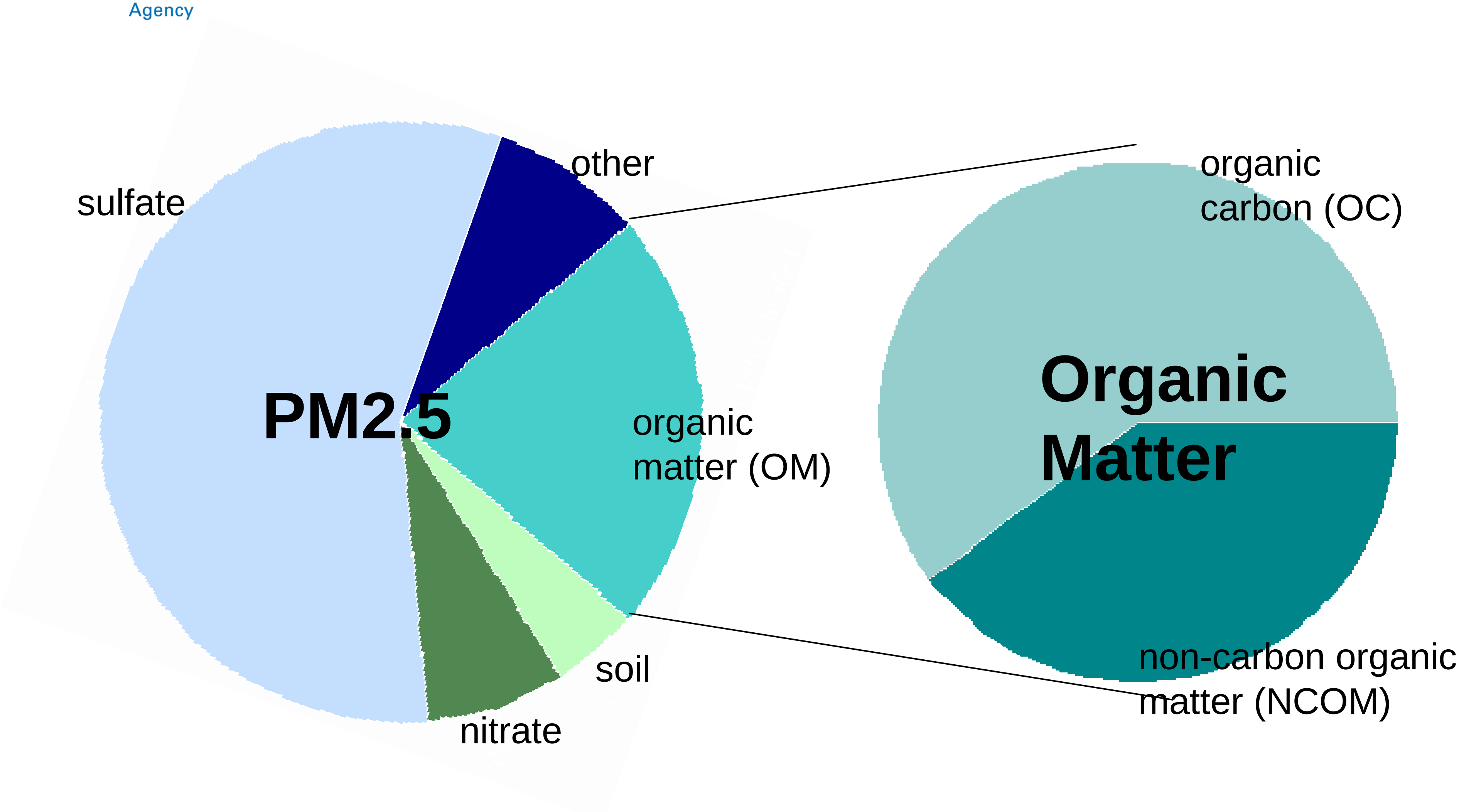
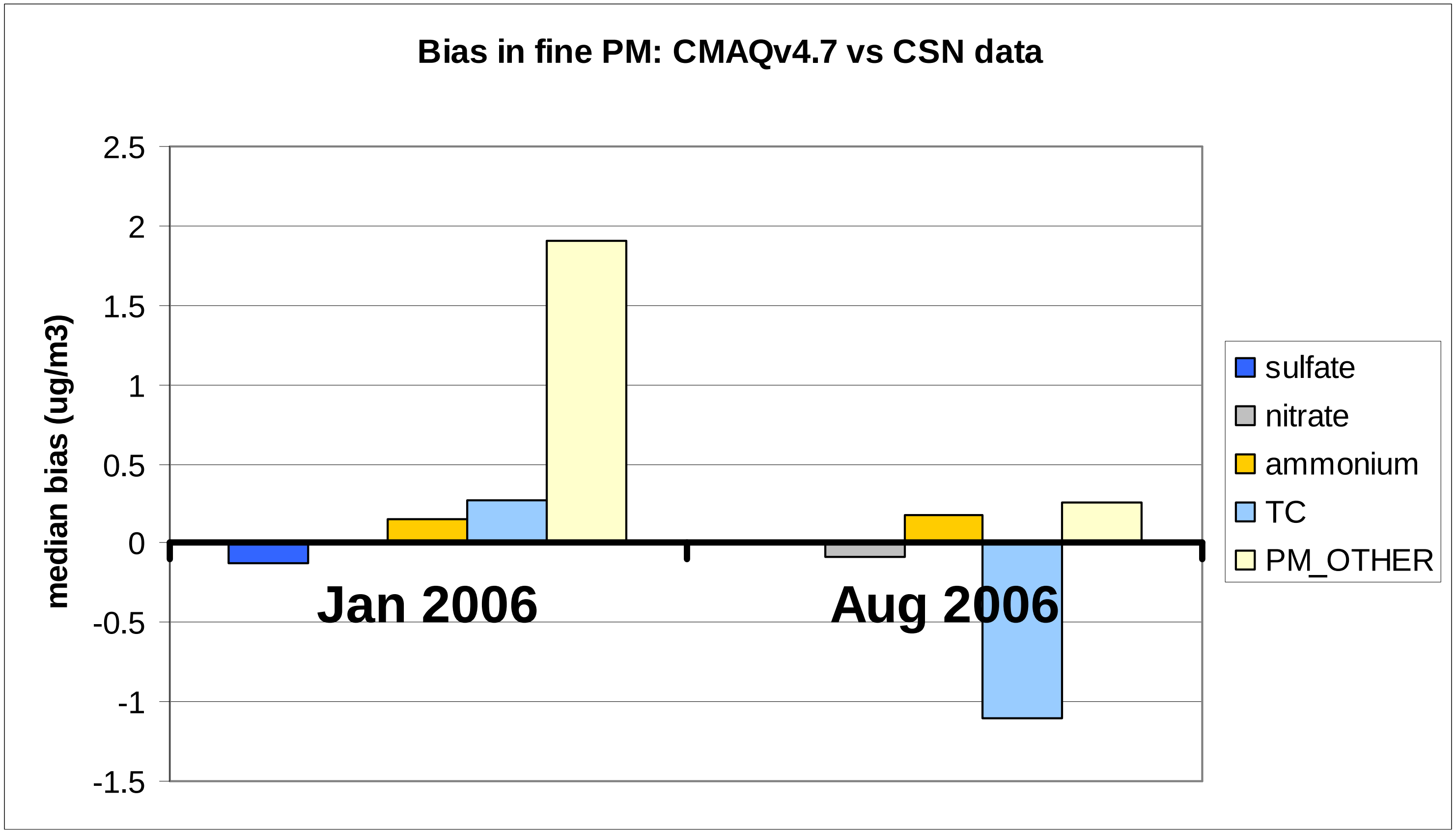
Organic Aerosol Components



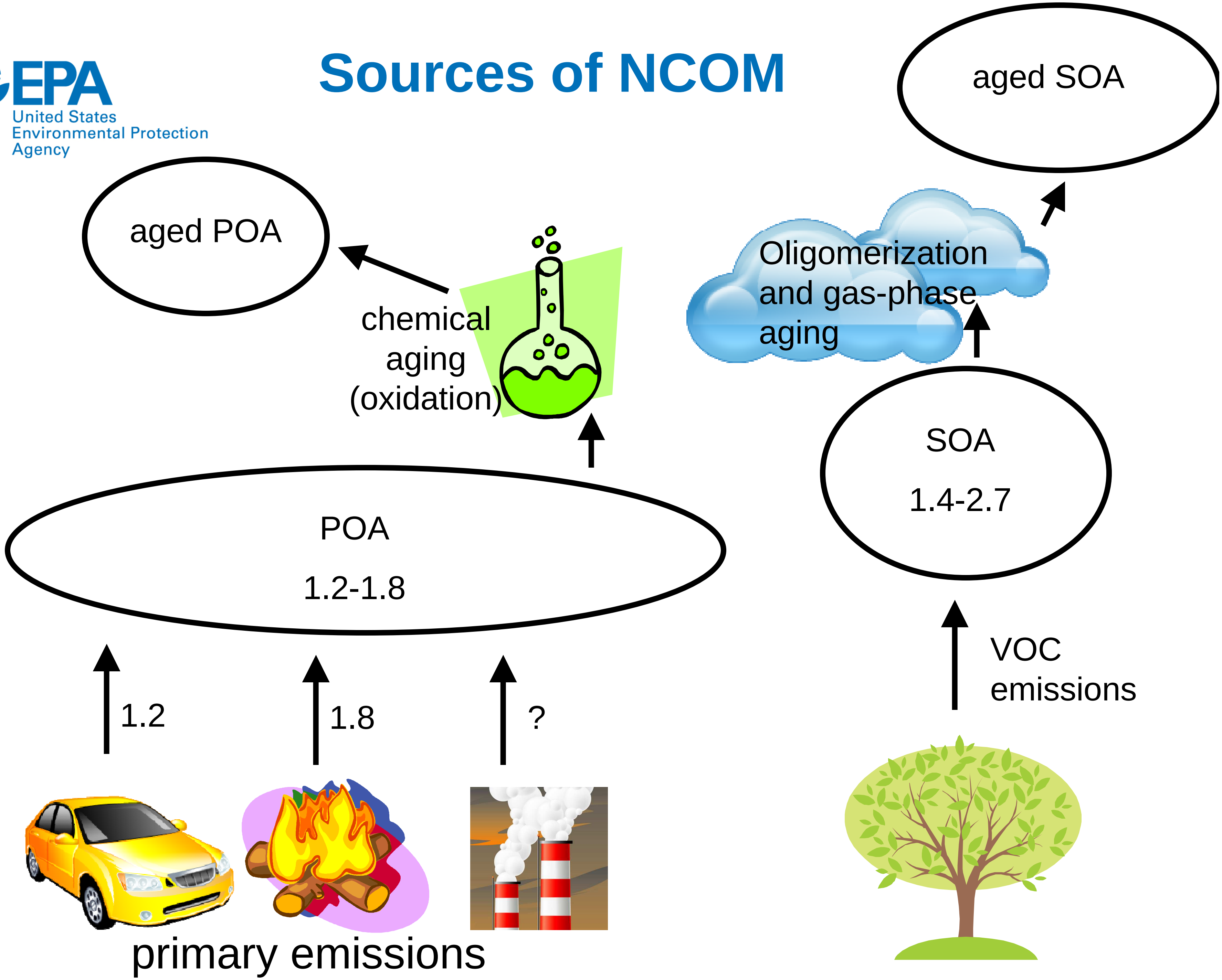
- A constant OM/OC is often used to convert between OC and OM.

Importance of OM/OC and NCOM

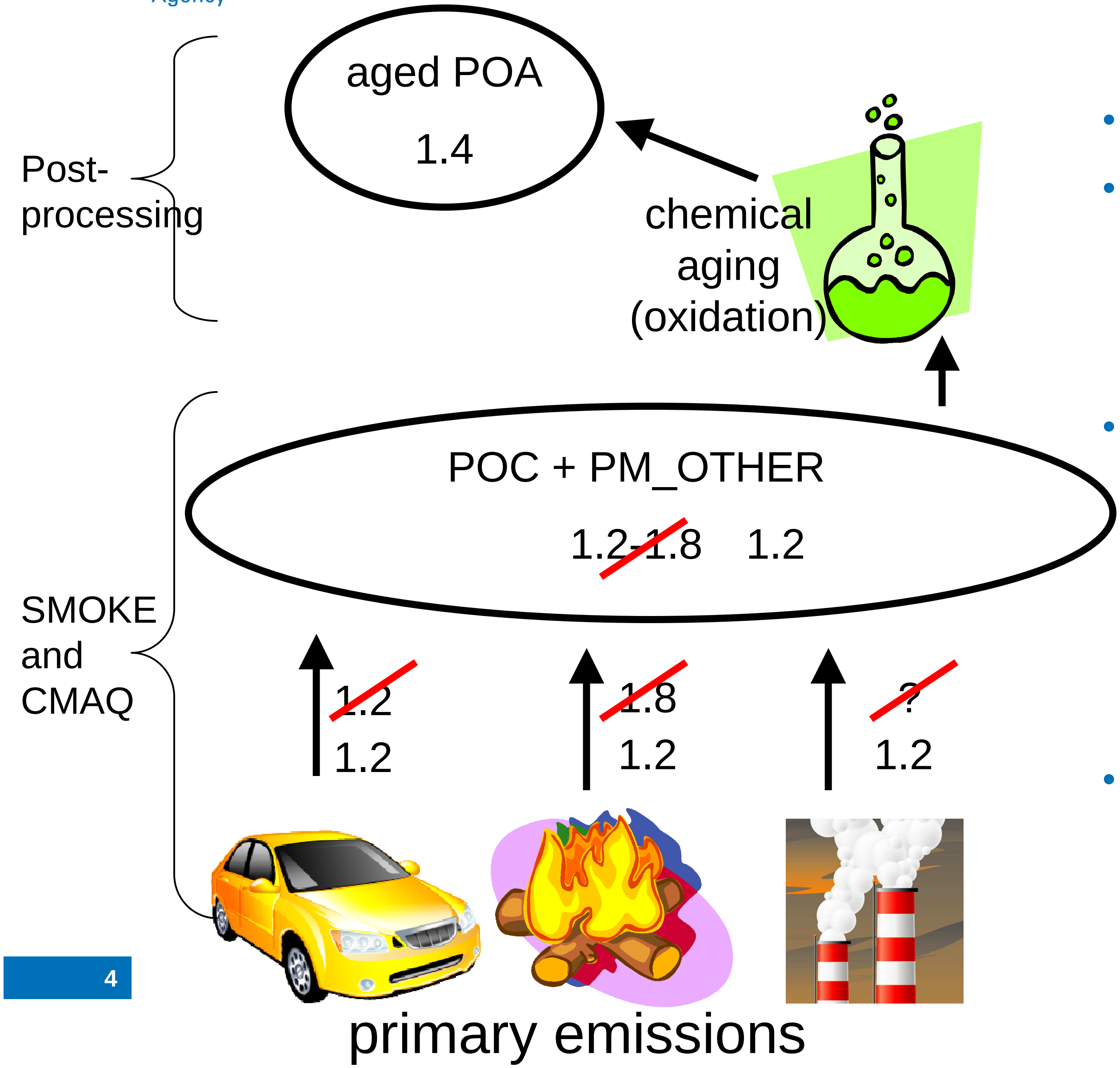


- Foley et al (2009) found:
  - Largest wintertime fine PM bias: PM_OTHER (includes NCOM)
  - Largest summertime fine PM bias: carbonaceous aerosol
- NCOM is at the intersection of these two aerosol components

Sources of NCOM



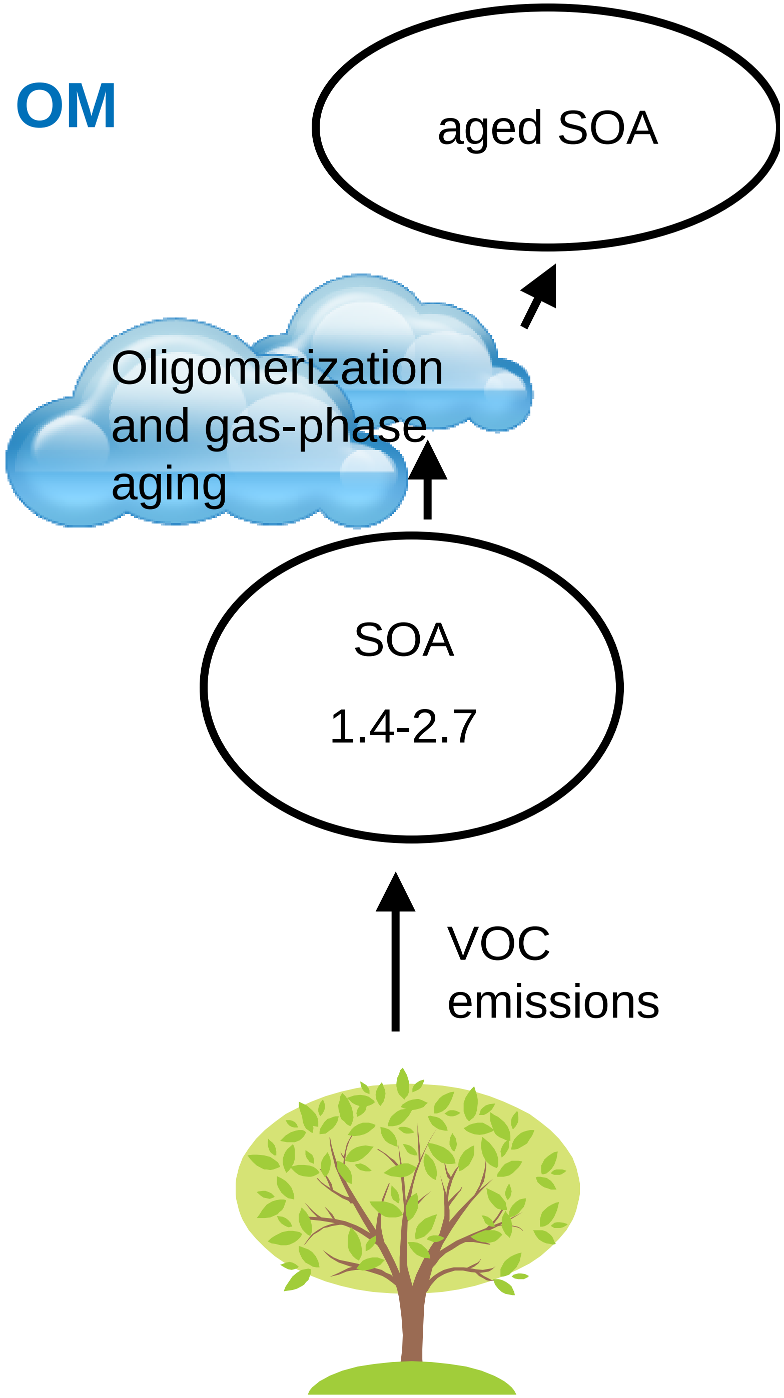
CMAQ's Treatment of OM and OC – Primary Organic Aerosols



- POA is modeled as OC
- NCOM is lumped with PM_OTHER (becomes indistinguishable from soil, trace metals, etc.)
- Although measurements suggest different OM/OC values from different sources, we currently use the same OM/OC for all sources
- Chemical aging is accounted for in post-processing by adding 0.2*POC to PM_OTHER

CMAQ's Treatment of OM and OC – Secondary Organic Aerosols

- Secondary organic aerosols are modeled as OM
- To compare model predictions of SOA (OM) to OC measurements, post-processing is needed
- Traditionally OM/OC ratios used in post-processing differ depending on the source VOC from which the SOA is formed.
  - Aromatic SOA: 2.0
  - Isoprene SOA: 1.6-2.7
  - Terpene SOA: 1.4
  - Sesquiterpene SOA: 2.1
  - Alkene SOA: 1.6
  - Cloud SOA: 2.0
  - Oligomerized SOA: 2.1



Driving Questions

- How accurately does CMAQ simulate OM/OC and NCOM?
- How much do inaccurate NCOM predictions contribute to bias in PM_OTHER?

First step: Estimate OM and NCOM from ambient data

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Current Measurement Techniques for OM/OC

- GC/MS speciation of ambient OM (Turpin and Lim)
- FTIR used to measure functional groups (several papers by Russell et al; Kiss et al.)
- Sequential extraction (El-Zanan et al.)
- Coupled thermal gravimetric and chemical analyses (Chen et al.)
- Mass closure using STN data (Frank)
- IMPROVE network data analysis
  - Mass closure

$$[OM] = PM_{2.5} - ([(NH_4)_2SO_4] + [NH_4NO_3] + [SOIL] + [EC] + [TraceElements])$$

    - Assumptions include fully neutralized sulfate, no particle-bound water, no nitrate volatilization
  - Regression – Hand and Malm

$$[PM_{2.5}] = \beta_1[OC] + \beta_2[(NH_4)_2SO_4] + \beta_3[NH_4NO_3] + \beta_4[SOIL] + \beta_5[EC] + \beta_6[SeaSalt]$$

    - Does not rely on assumptions about 1) the presence of unmeasured components (ammonium and water), 2) the amount of nitrate volatilization, or 3) the accuracy of the IMPROVE soil equation.
- We expand upon Hand and Malm's regression technique

Methods

- Use 2003-2008 data from IMPROVE network
- Samples were split up by site and quarter
- Sites that averaged less than 15 samples/quarter were not analyzed : 154 sites * 4 quarters = 616 regression analyses

$$[PM_{2.5}] = \beta_1[OC] + \beta_2[(NH_4)_2SO_4] + \beta_3[NH_4NO_3] + \beta_4[SOIL] + [EC] + 1.2[K_{non}] + 1.8[Cl^-]$$

$$[SOIL] = 3.48[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]$$

$$[K_{non}] = K - 0.6[Fe]$$

- β_1,β_2, and β_3 were allowed to vary by quarter. β_4 was held constant on an annual basis
- No filtering of sampling data within a site/quarter grouping

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- 409/616 regressions had reasonable values for all 4 regression coefficients and reasonably low correlation between independent variables

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Pitfalls of Multi-linear Regression Analysis

- Model selection – Does the regression equation capture all elements of the system?
- Dataset selection – datasets should be selected such that β_1, β_2, β_3, and β_4 are expected to be relatively constant
- Colinearity of independent variables
- Measurement uncertainty in independent variables
  - An in depth analysis suggests that independent variable uncertainty may bias results as follows:
    - β_1 is biased low by ~5% (10% in the winter)
    - β_2 is biased high by ~2%
    - β_3 is biased high by < 1%

Goal of the Ambient Data Analysis

- Identify key temporal and spatial trends in measured OM/OC

- Compare with CMAQv4.7

Spatial variation in OM/OC: Jan, Feb, Mar

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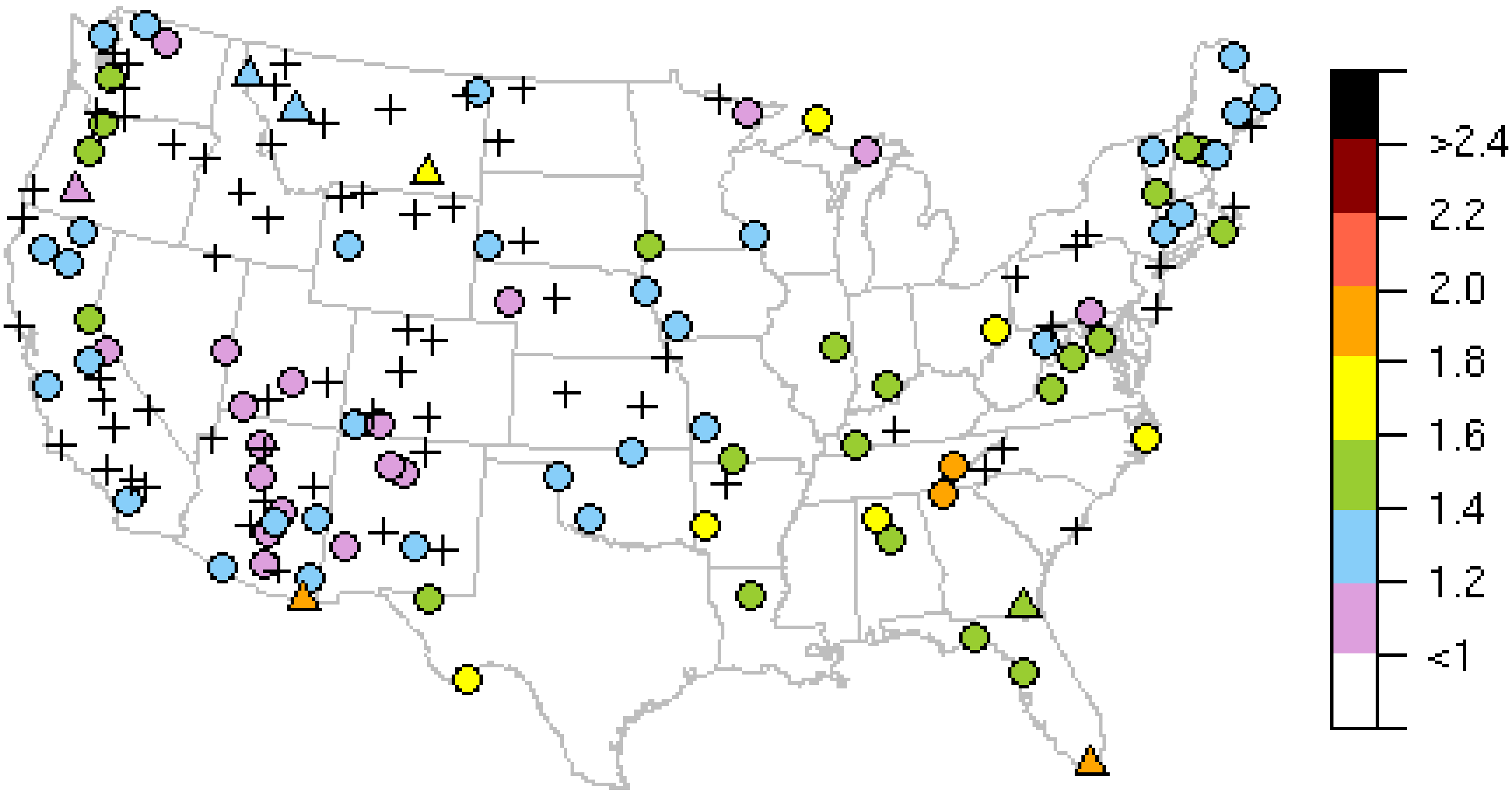
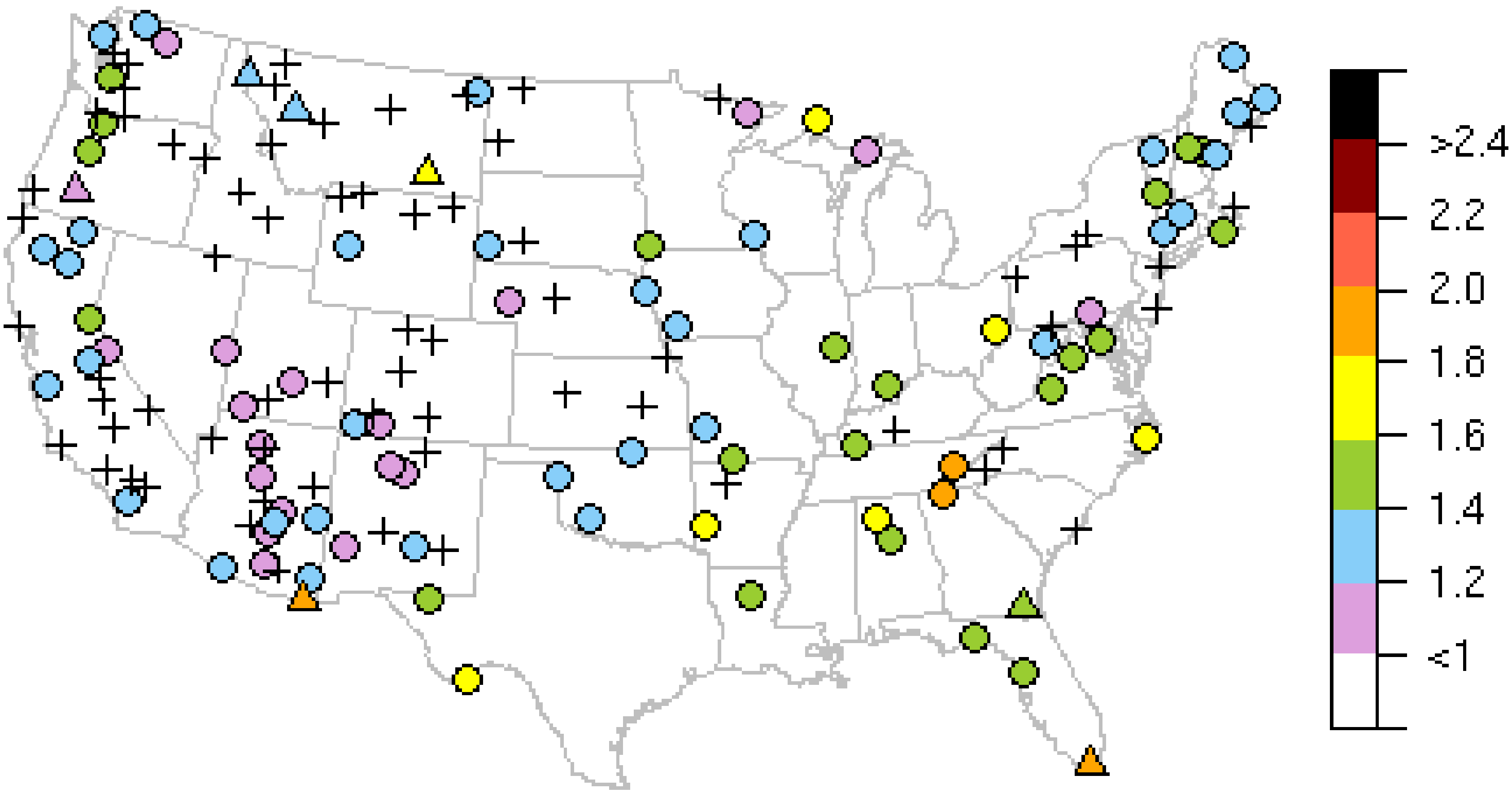


- Value are highest in the southeast (1.4-2.0 in SE, 1.0-1.6 in the rest of the US)
  - Due to biogenic SOA?

Spatial variation in OM/OC: Jan, Feb, Mar

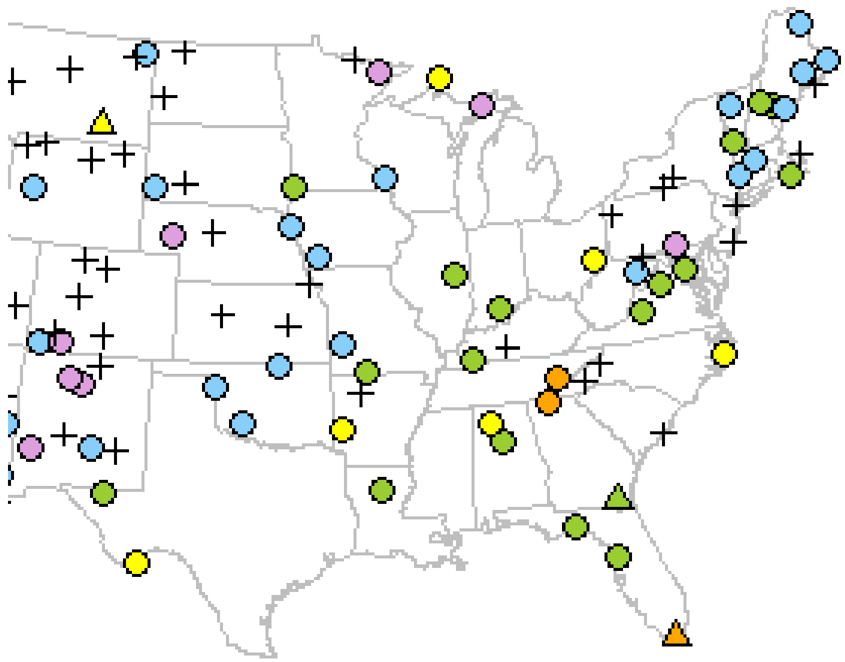


- Large number of sites with values less than 1 (+) in the west
  - Independent variable uncertainty correction might fix this
  - May be due to more OC volatilization from teflon than quartz

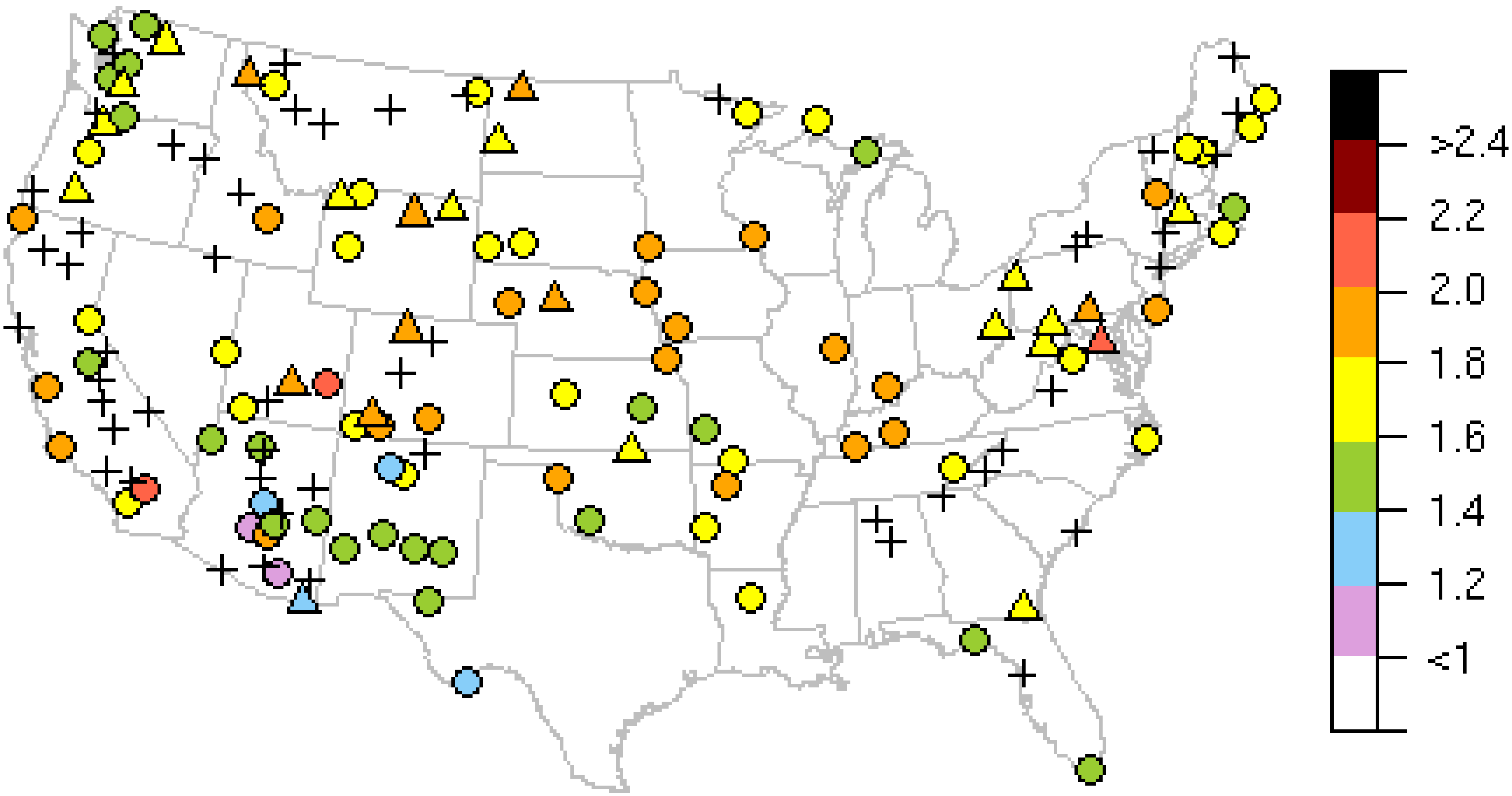
How Do Wintertime Measurements Compare to Wintertime CMAQ Predictions?

CMAQv4.7 : 2002-2005

IMPROVE regression analysis : 2002-2008



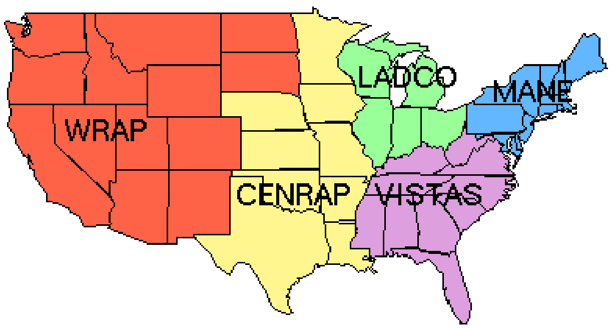
Spatial variation in OM/OC: Jul, Aug, Sep

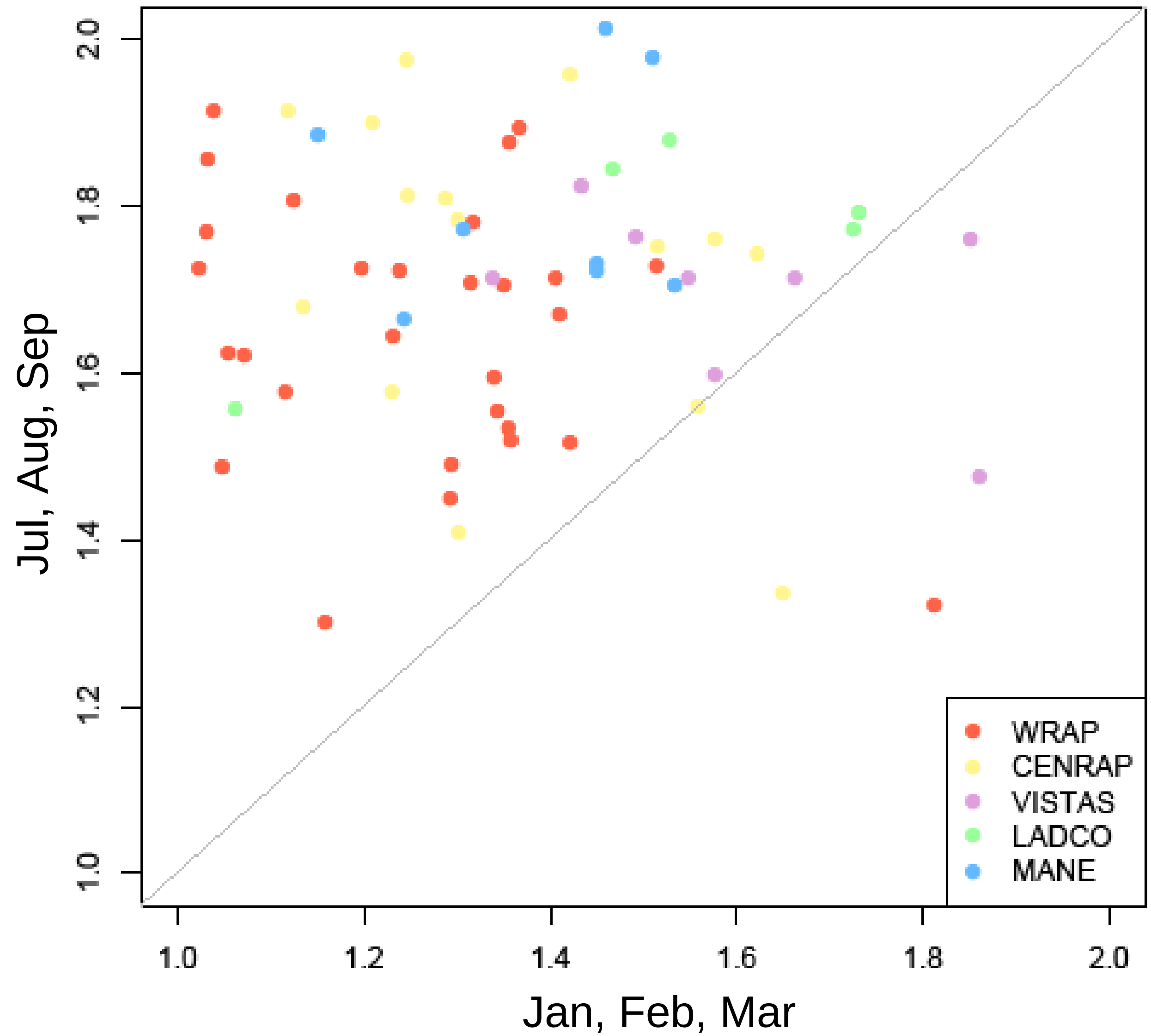


- Value are consistently higher than in the winter
  - More oxidation occurs in the summer
- Lowest values are in the Southwest
  - Lower levels of biogenic SOA in this area

Seasonal variation in β_1 (OM/OC)

More oxidation in the summer → higher OM/OC ratios





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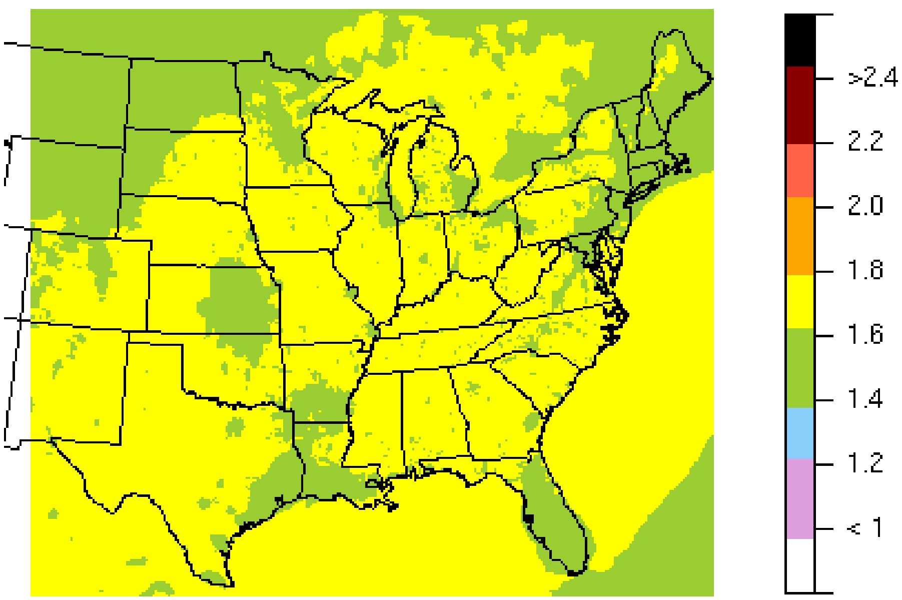
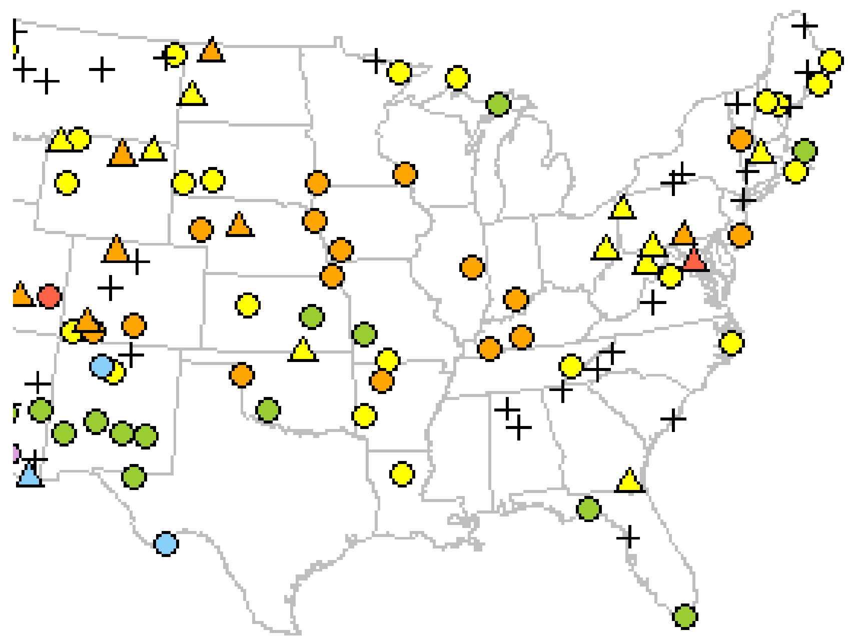
How Do Summertime Measurements Compare to Summertime CMAQ Predictions?

CMAQv4.7 : 2002-2005

IMPROVE regression analysis : 2002-2008





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Conclusions

- Developing a technique to calculate OM/OC from IMPROVE data is important for creating a comprehensive dataset of values covering a large spatial and temporal extent
- Regression analysis generally yielded realistic values
- Key spatial and temporal trends have been identified
- CMAQ tends to under-predict variability of OM/OC that is seen in ambient data

Next Steps

- Finish refining and analyzing regression technique for determining ambient OM/OC values
- Modify CMAQ to explicitly model NCOM
  - Add NCOM species to SMOKE and CMAQ
  - Process emissions to reflect different OM/OC values from different primary emission sources
  - Model an aging reaction for POA which leads to increased OM/OC and NCOM values
- Compare modified CMAQ to ambient data to determine if OM/OC and NCOM predictions are improved

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Physically Reasonable Coefficients

β1 (OC)

-This represents OM/OC and by definition cannot be less than 1

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Physically Reasonable Coefficients

β2 (ammonium sulfate)

-Values less than 1 represent non-fully neutralized sulfate: NH_4HSO4 would be equivalent to a value of 0.87

-Values greater than 1 represent hydrated aerosol. At high RH, the value could be as high as 1.53.

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Physically Reasonable Coefficients

β3 (ammonium nitrate)

-Values less than 1 represent partial or total nitrate volatilization. Minimum value would be 0.

-Values greater than 1 represent hydrated aerosol or $NaNO_3$. At high RH, the value could be as high as 1.35.

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Physically Reasonable Coefficients

β4 (soil)

-Values other than one indicate that soil composition is different from that used to create the IMPROVE soil equation

-β4 values were calculated for a large variety of reported soil compositions and ranged from 0.41 – 1.63

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Physically Reasonable Coefficients

- β_1 (OC)
  - This represents OM/OC and by definition cannot be less than 1
- β_2 (ammonium sulfate)
  - Values less than 1 represent non-fully neutralized sulfate: NH_4HSO_4 would be equivalent to a value of 0.87
  - Values greater than 1 represent hydrated aerosol. At high RH, the value could be as high as 1.53.
- β_3 (ammonium nitrate)
  - Values less than 1 represent partial or total nitrate volatilization. Minimum value would be 0.
  - Values greater than 1 represent hydrated aerosol or $NaNO_3$. At high RH, the value could be as high as 1.35.
- β_4 (soil)
  - Values other than one indicate that soil composition is different from that used to create the IMPROVE soil equation
  - β_4 values were calculated for a large variety of reported soil compositions and ranged from 0.41 – 1.63