

# Carbonaceous Matter in Air Quality Model Applications



Gopal Sistla, Prakash Doraiswamy\*, Kevin Civerolo,  
Christian Hogrefe and Winston Hao

Bureau of Air Quality Analysis and Research  
Division of Air Resources

New York State Department of Environmental Conservation  
Albany, NY 12233

\*On assignment from Atmospheric Sciences Research Center, University at Albany, Albany NY 12222

# PM<sub>2.5</sub> NAAQS

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- National Ambient Air Quality Standards for PM<sub>2.5</sub> promulgated in 1997
  - 24-hr: 65 µg/m<sup>3</sup>
  - Annual: 15 µg/m<sup>3</sup>
  - SIP due April 2008 for 10 county region of NY as part of NYCMSA
- September 2006 Revisions
  - 24-hr: 35 µg/m<sup>3</sup>
  - Annual: 15 µg/m<sup>3</sup>
  - State recommendations by December 2007 and EPA designation before December 2008
- Under the revised NAAQS, there is a potential for some of the urban counties in New York to exceed the new 24-hr standard

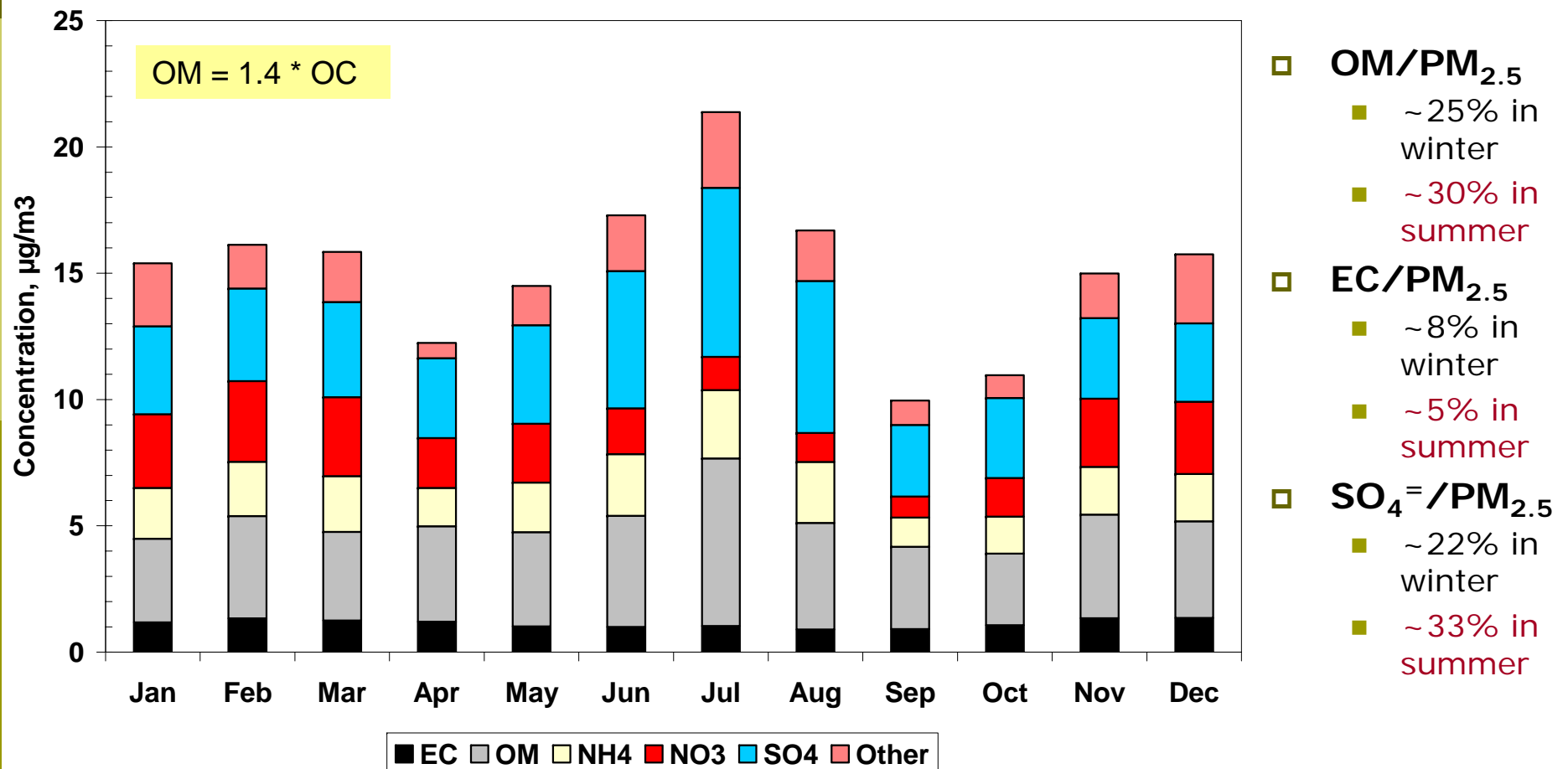
# What does PM<sub>2.5</sub> Contain ?

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- Over New York state, measured PM<sub>2.5</sub> mass typically consists of 60% or more secondary components, implying that in addition to control of primary emissions, there is a need to focus on important precursors (SO<sub>2</sub> and NO<sub>x</sub>).
- Measurements from IS52 (Bronx, NY) and Pinnacle State Park (PSP) indicate that sulfate and carbon [elemental (EC) and organic (OC)] together constitute ~47% during winter and as much as 65% during summer.

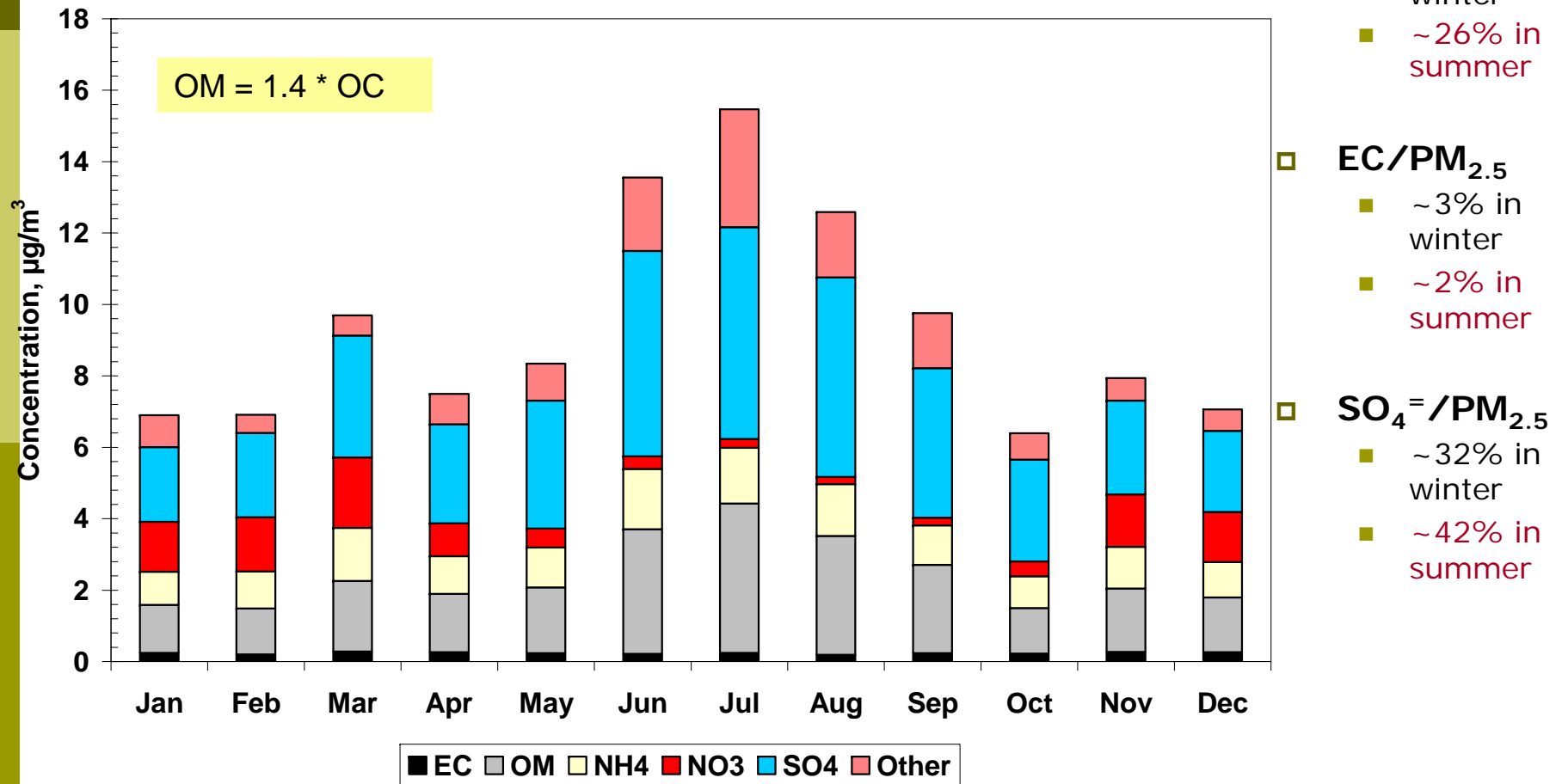
# at IS52 (Bronx, NY) monitor (2002-2006)

IS52, Bronx, NY  
Monthly Average 2002-2006



# Monthly Average PM<sub>2.5</sub> Composition at PSP monitor (2002-2006)

Pinnacle State Park, NY  
Monthly Average 2002-2006



# Why Worry about Carbon ?

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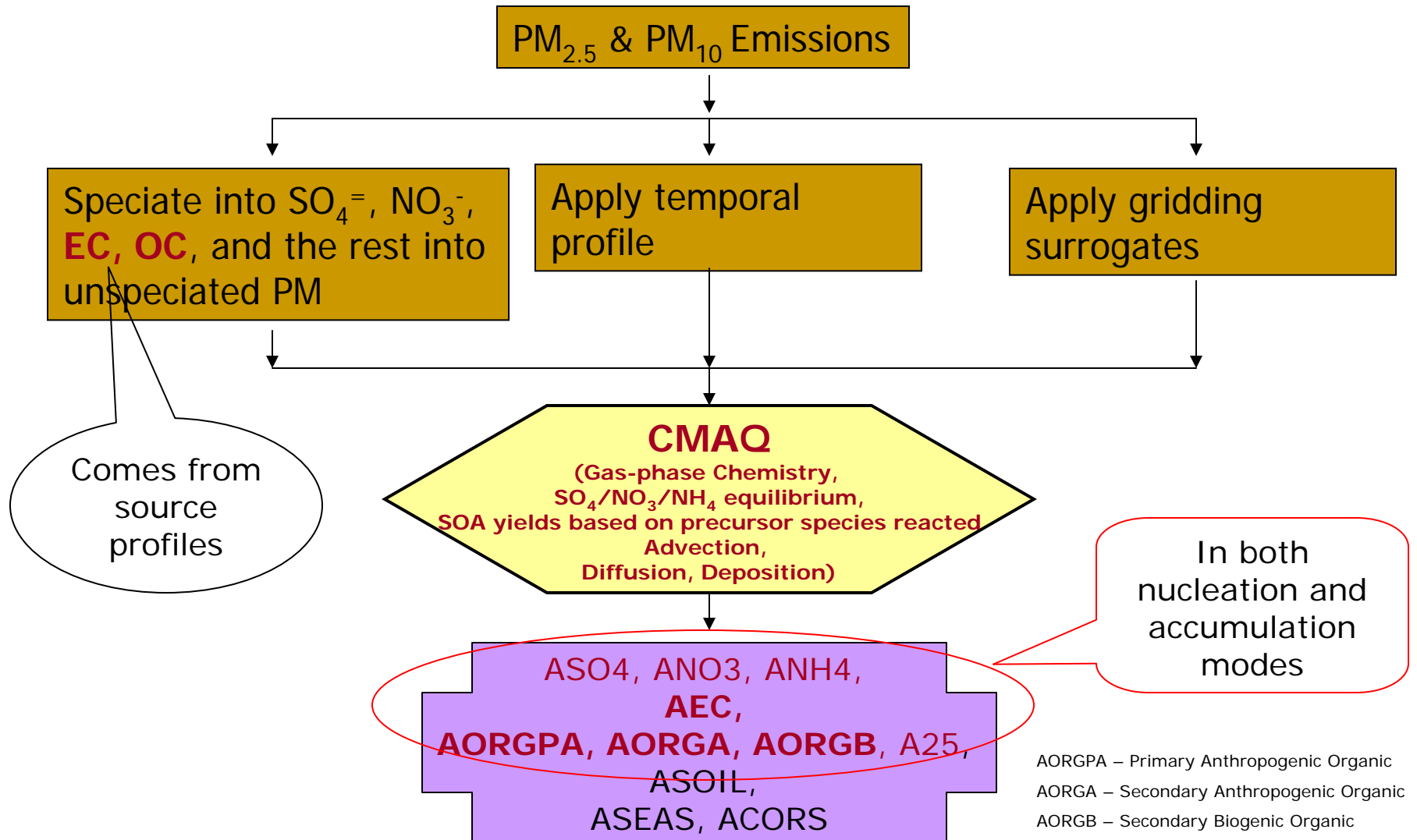
- Atmospheric chemistry of sulfate formation has been understood reasonably well arising from SO<sub>2</sub> emissions
  - Largely from combustion of coal and oil in electric utilities
  - And from combustion of diesel, gasoline, and fuel oil by on- and non-road mobile sources, and stationary sources
- Control programs such as Clean Air Interstate Rule (CAIR), Regional Haze Rule, and Low Sulfur Diesel Rule are expected to decrease the contribution of sulfate and nitrate to PM<sub>2.5</sub>, thereby increasing the need for a better understanding of the relative role of carbon and its contribution to PM<sub>2.5</sub> mass.
- Elemental (EC) and Organic Carbon (OC) are operationally defined
  - Differences between measurement and analytical methods
  - Wide range of conversion factors to convert OC to OM that vary by region and season
  - OC refers to a composite of species, a majority of which is not well characterized
  - Estimate of OC in blank filters

# Air Quality Models

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- Air quality models:
  - Provide temporal and spatial resolution of species concentrations that is not typically available in measured data at all locations.
  - Help to visualize and understand the atmospheric processes to the extent of the current scientific understanding and assumptions, and to evaluate control strategies.
  
- These models are driven by inputs derived from
  - Meteorology
  - Emissions
  - Chemical mechanisms
  
- We utilized the Carbon Bond IV (CB-IV) chemical mechanism, which is a set of representative chemical equations attempting to simulate the complex reality in a modeling framework

# Overview of PM Emissions Modeling & CMAQ Outputs

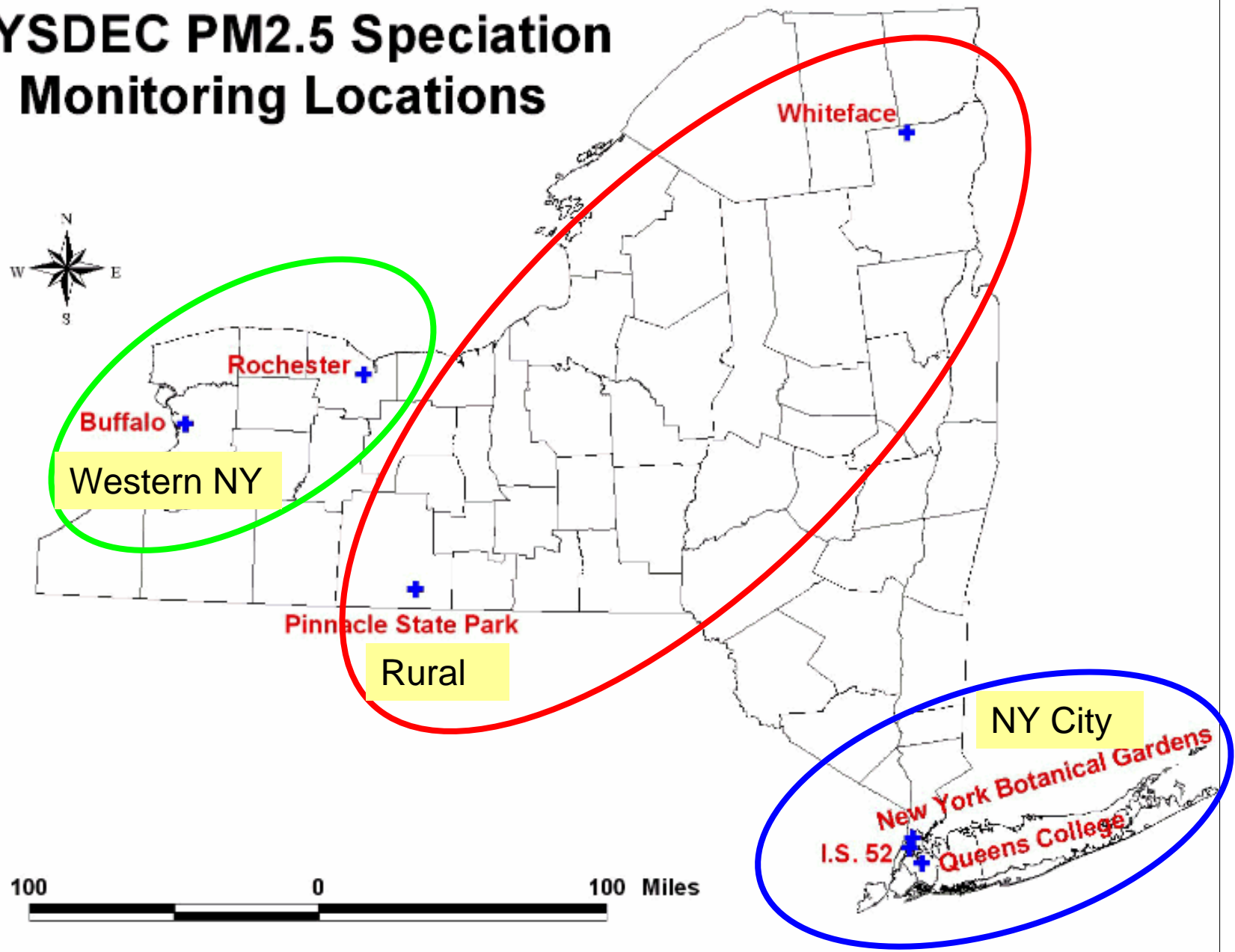


# How does the Model Compare with Observations

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- ❑ Model results are from CMAQ-based air quality forecasting simulations covering from June 2005 to Dec 2006
- ❑ Data from a single 12-km by 12-km grid cell that contained the monitor was used
- ❑ All measured mass and species concentrations used in the comparisons were obtained from the AQS database for all STN sites in NY
- ❑ Sites were grouped into three categories: NY City, Rural and Western NY (see map on next slide)
- ❑ Analysis was for summer (June, Jul, Aug) and winter (Dec, Jan, Feb) periods
- ❑ Also shown are the diurnal model predictions, which are compared with continuous monitoring data for IS52

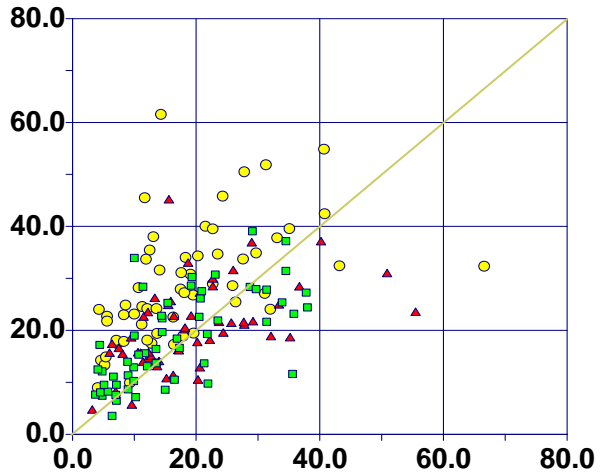
# NYSDEC PM2.5 Speciation Monitoring Locations



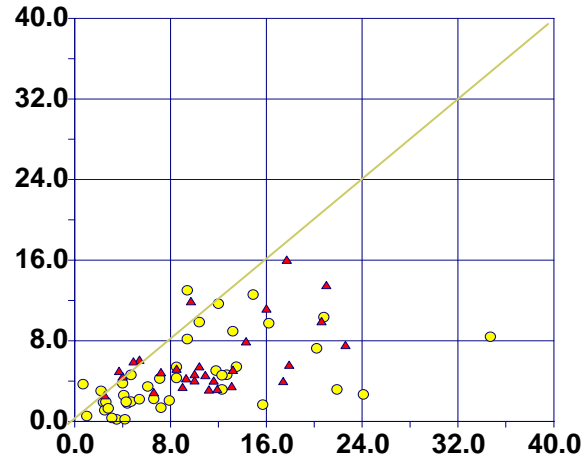
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> Mass (µg/m<sup>3</sup>)

Summer (June-Aug)

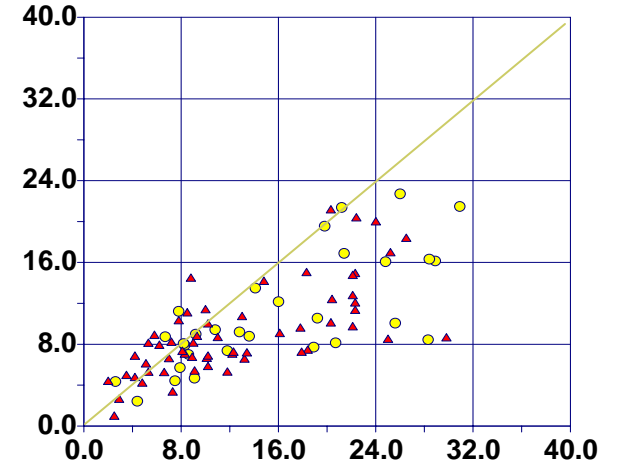
NY City



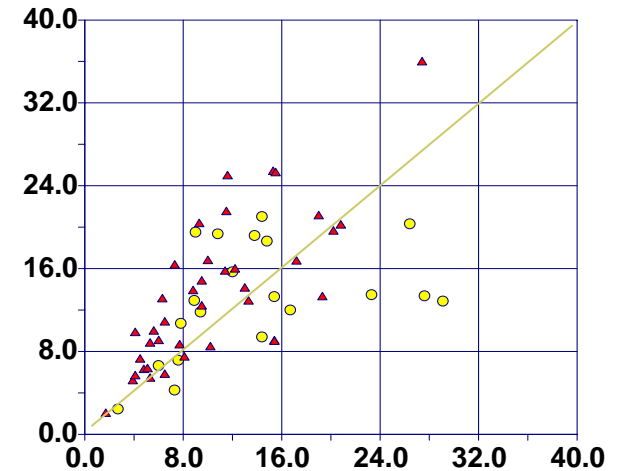
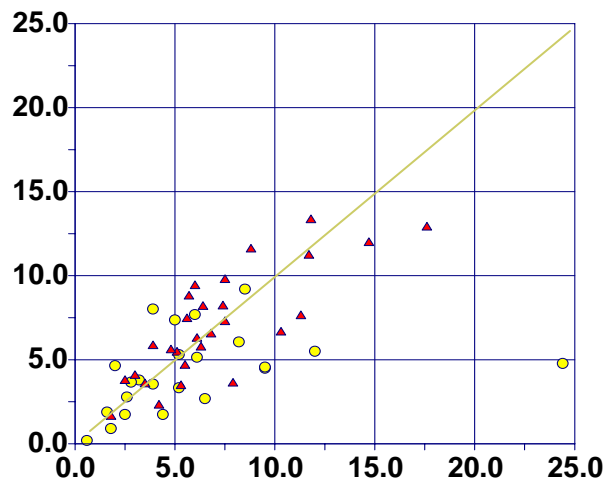
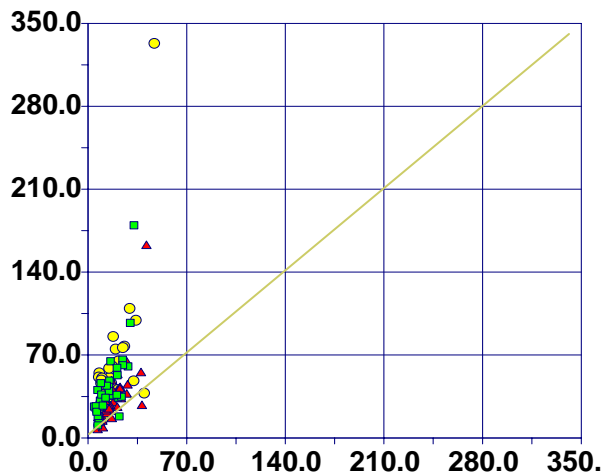
Rural



Western NY



Winter (Dec, Jan-Feb)



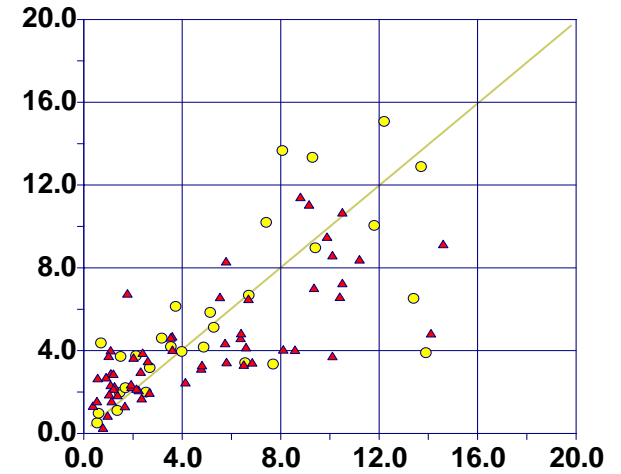
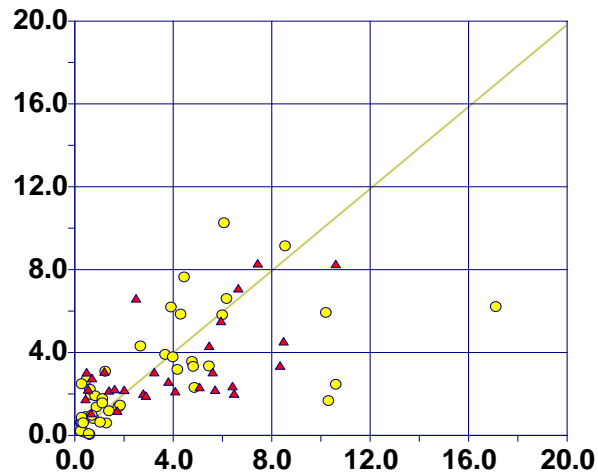
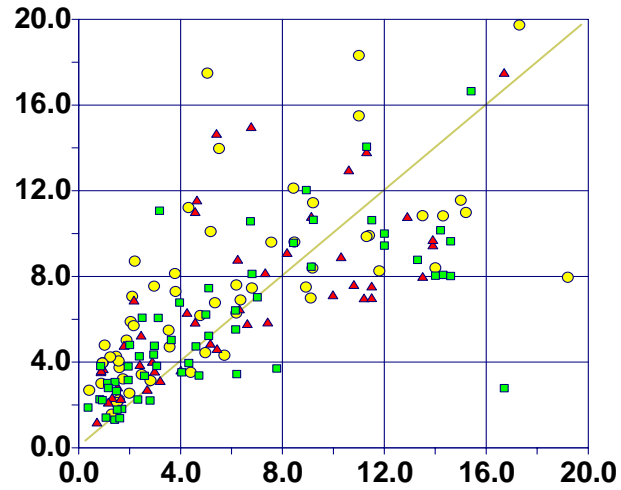
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> Sulfate ( $\mu\text{g}/\text{m}^3$ )

Summer (June-Aug)

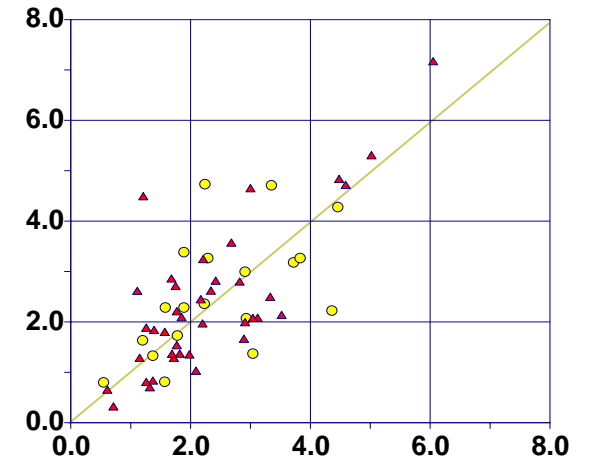
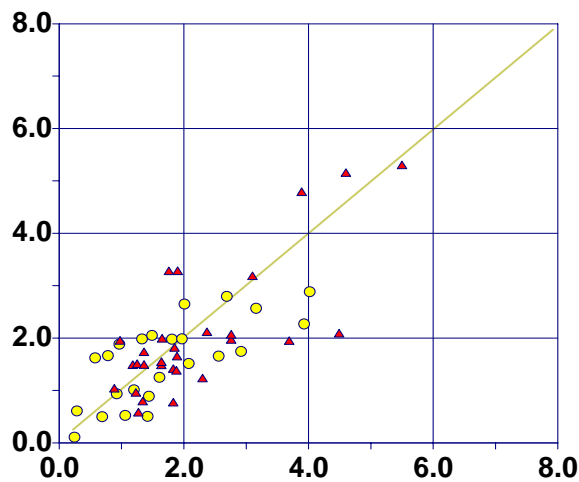
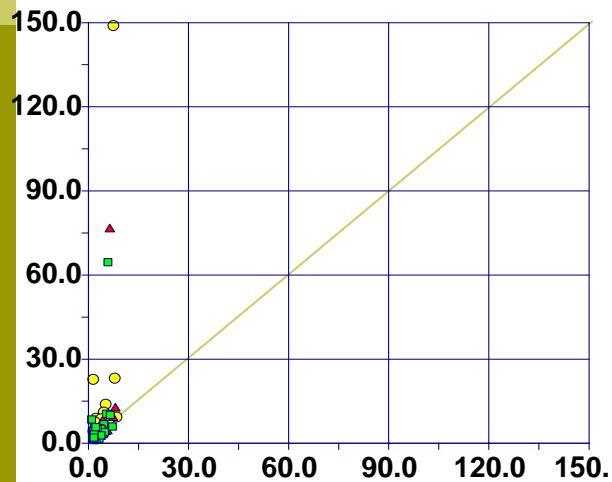
NY City

Rural

Western NY



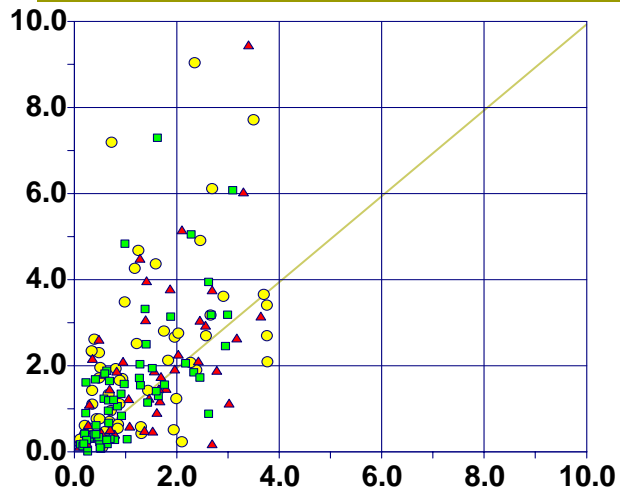
Winter (Dec, Jan-Feb)



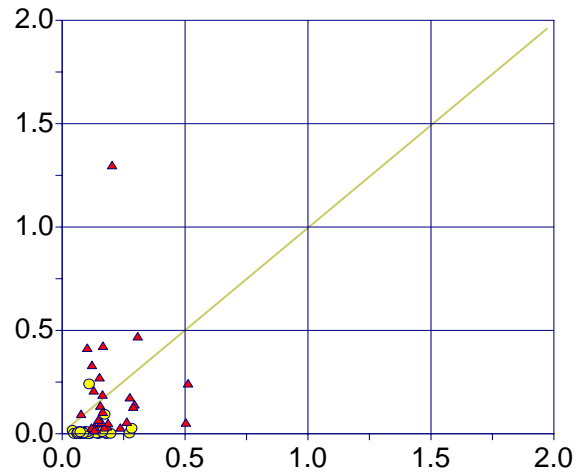
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> Nitrate (µg/m<sup>3</sup>)

Summer (June-Aug)

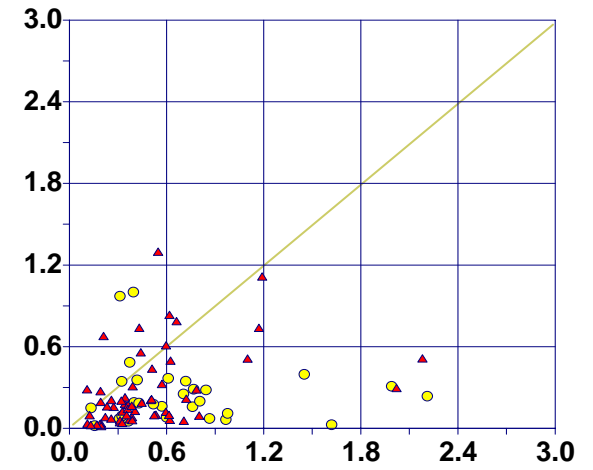
NY City



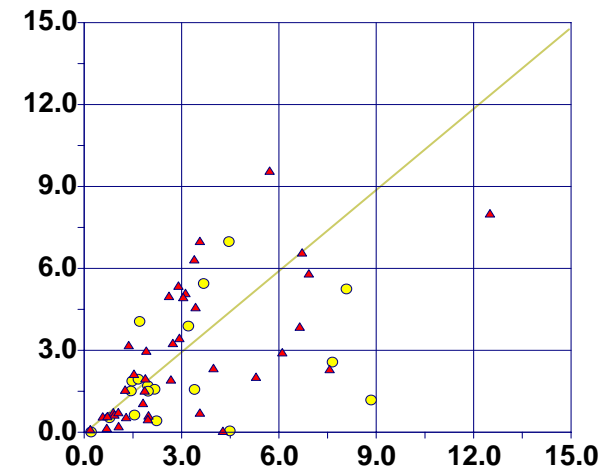
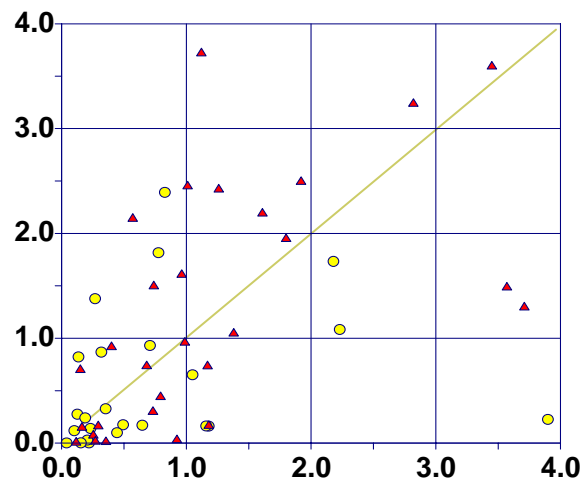
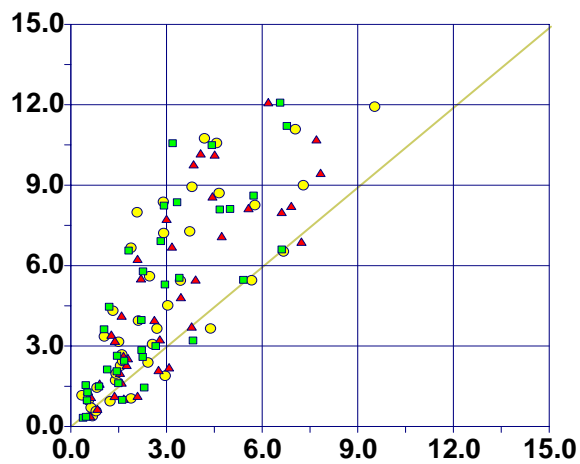
Rural



Western NY



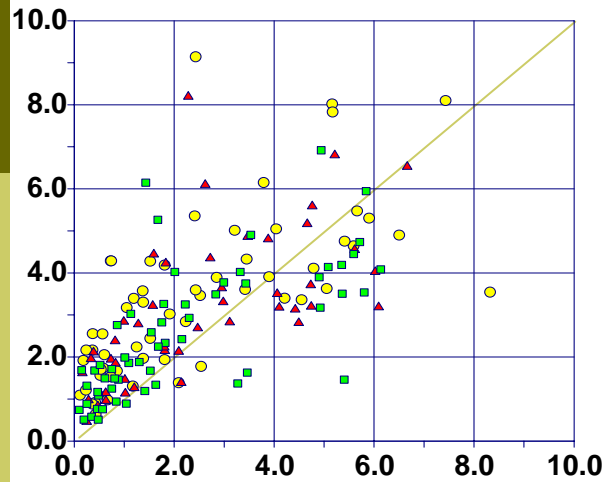
Winter (Dec, Jan-Feb)



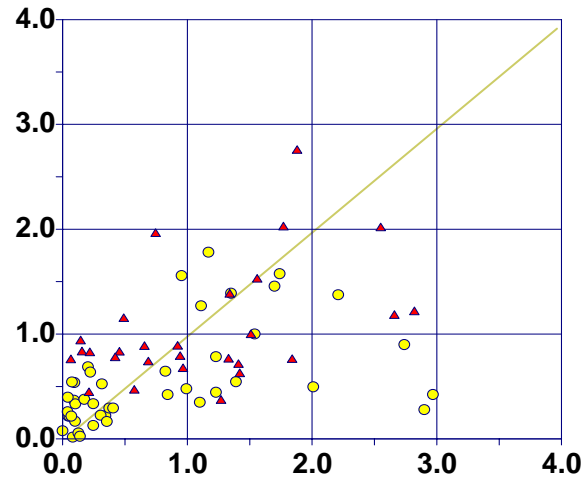
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> Ammonium ( $\mu\text{g}/\text{m}^3$ )

Summer (June-Aug)

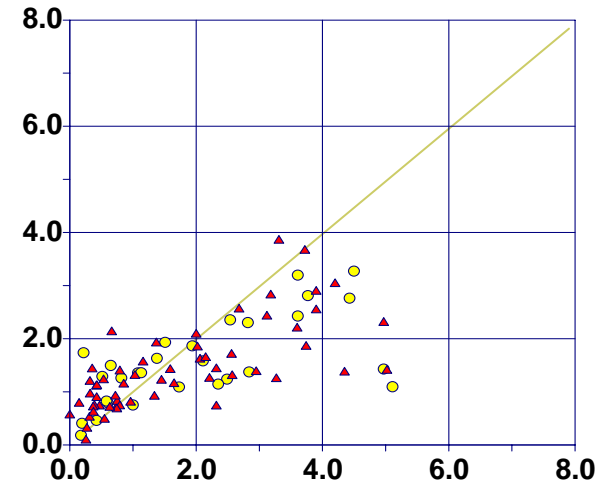
NY City



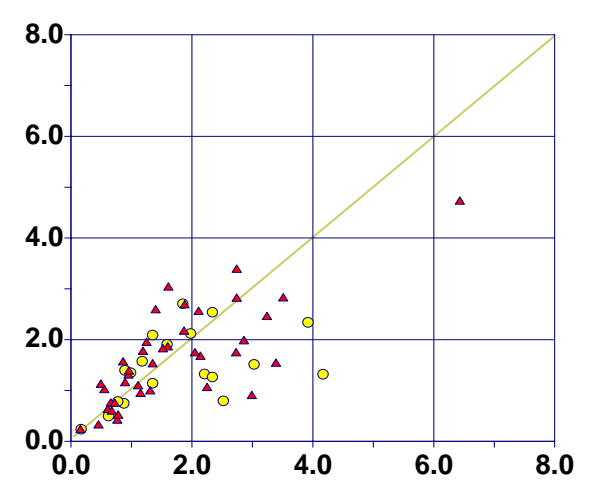
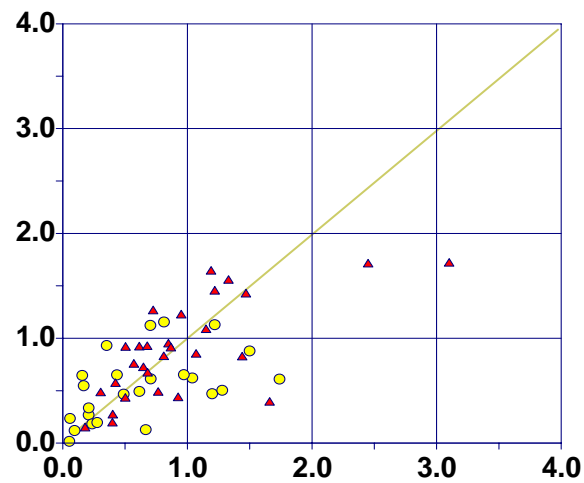
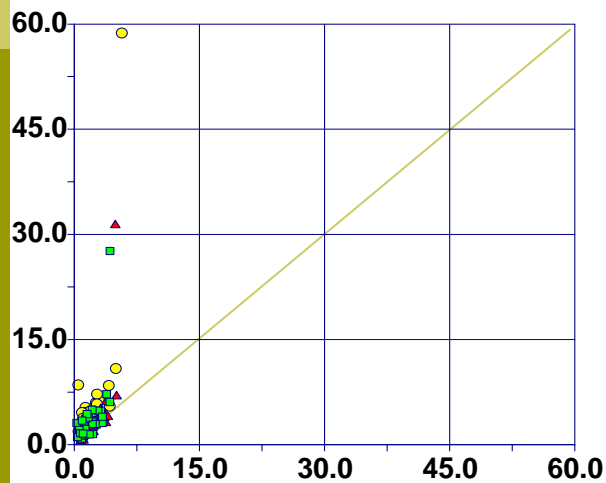
Rural



Western NY



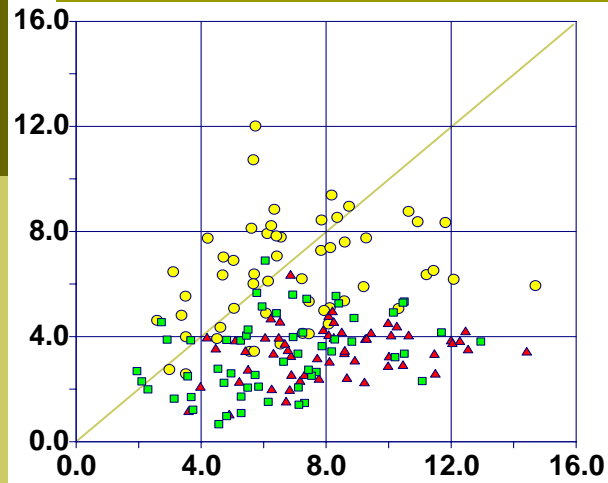
Winter (Dec, Jan-Feb)



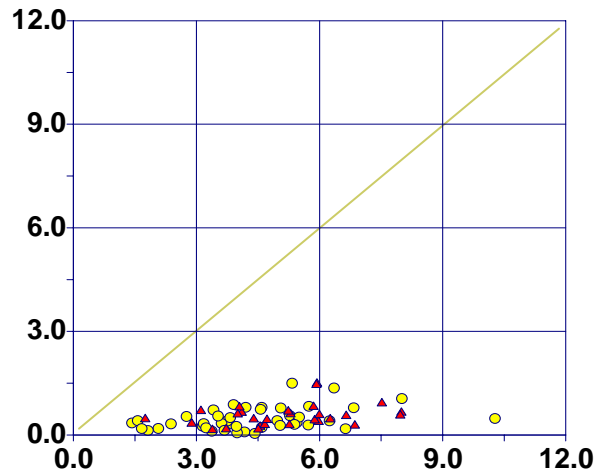
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> Org. Matter (µg/m<sup>3</sup>)

## Summer (June-Aug)

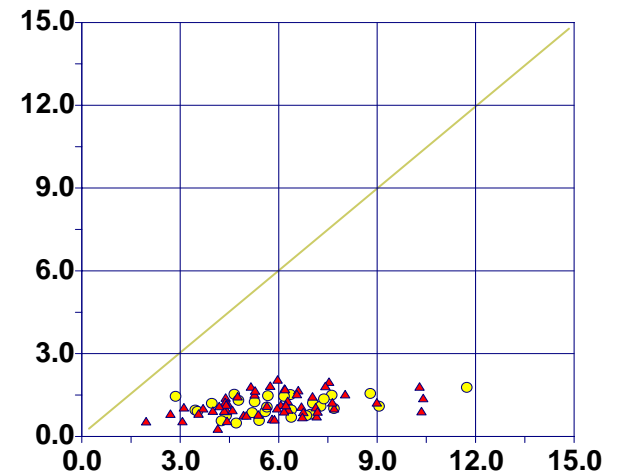
### NY City



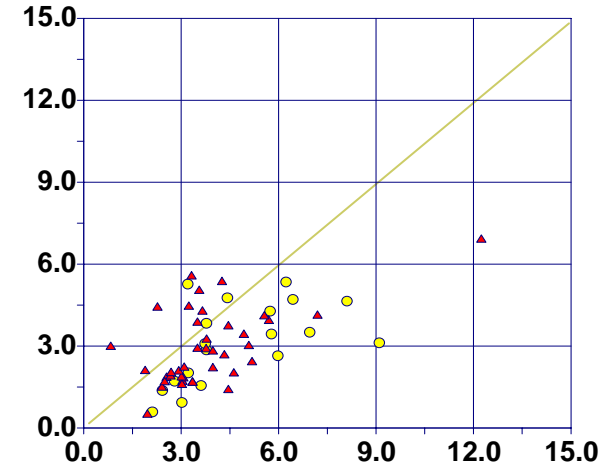
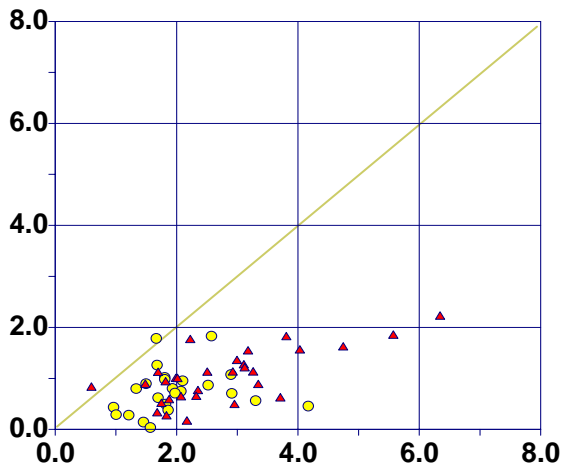
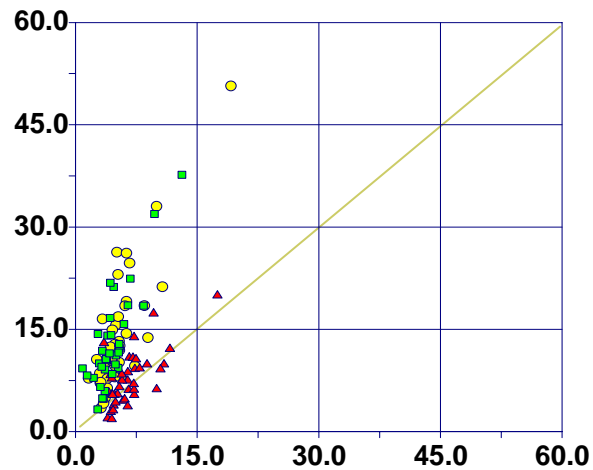
### Rural



### Western NY



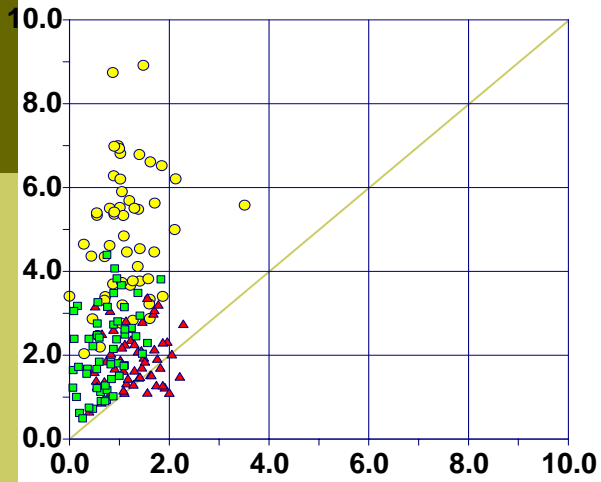
## Winter (Dec, Jan-Feb)



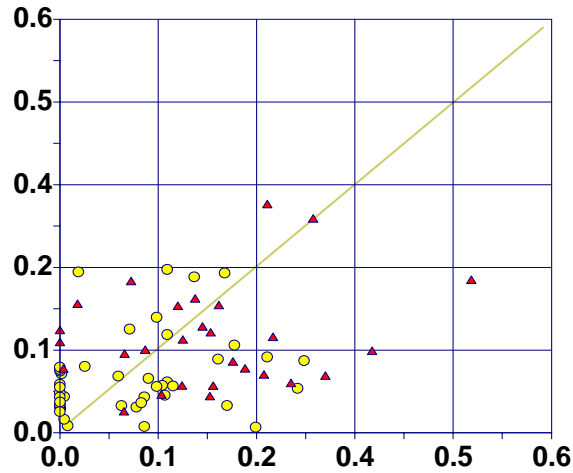
# CMAQ (y-axis) vs. STN (x-axis): PM<sub>2.5</sub> EC (μg/m<sup>3</sup>)

## Summer (June-Aug)

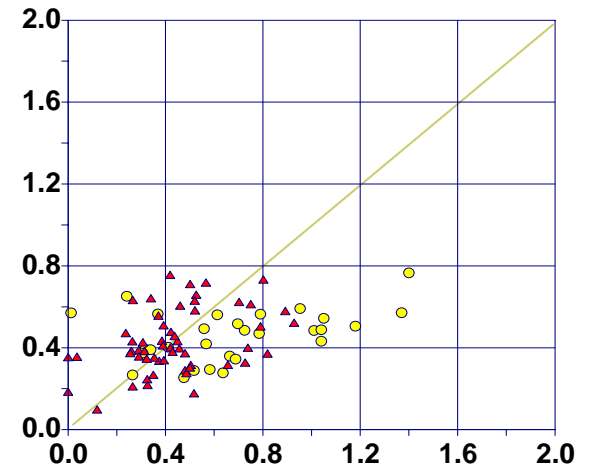
### NY City



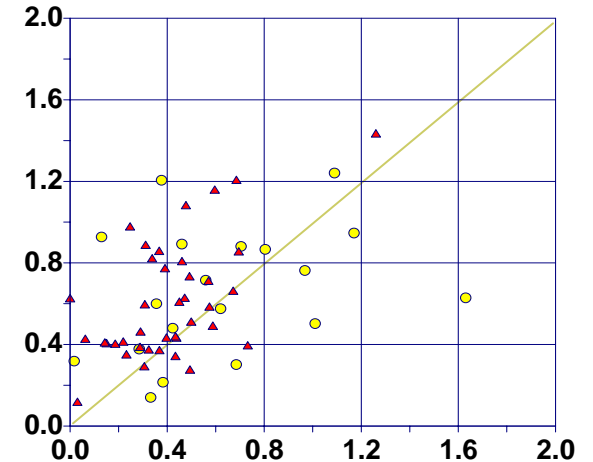
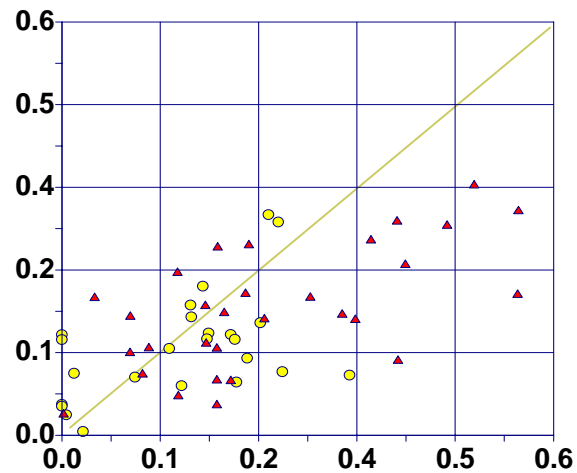
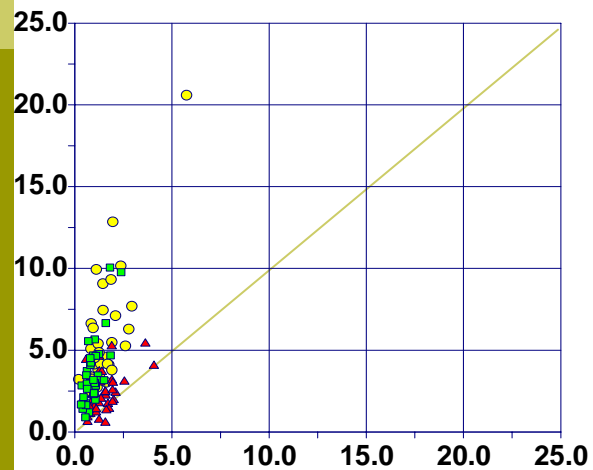
### Rural



### Western NY



## Winter (Dec, Jan-Feb)



# Comparison based on STN data

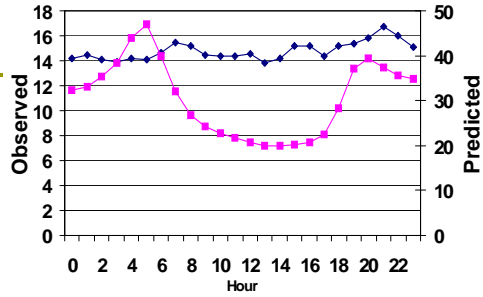
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- ❑ Primary PM emissions appear to be over-estimated for the 3 urban monitors in New York City, as illustrated by significant over-predictions of EC.
- ❑ OM in the summer period was found to be under-predicted much more so at rural and western NY monitors than those in New York City, which may be due to underestimation of secondary organic aerosols (SOA).
- ❑ Severe over-estimation of EC seen for the winter period for urban monitors in New York City is from a combination of shallow planetary boundary layer height and high primary emissions.

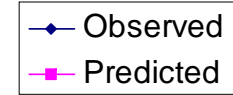
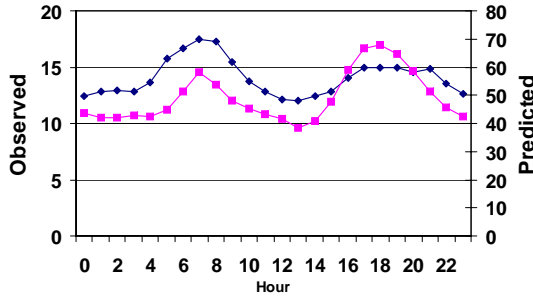
# Predicted and Observed Diurnal Profiles at IS52, Bronx, NY

Mass

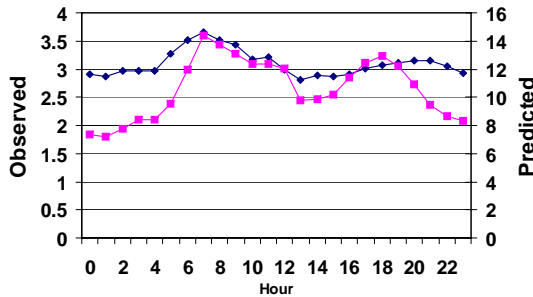
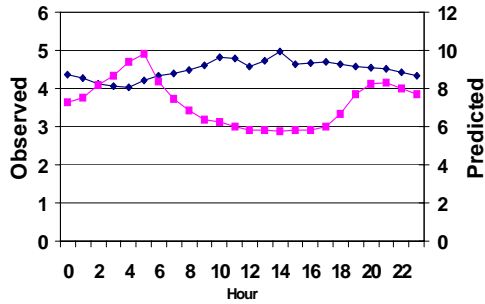
Summer



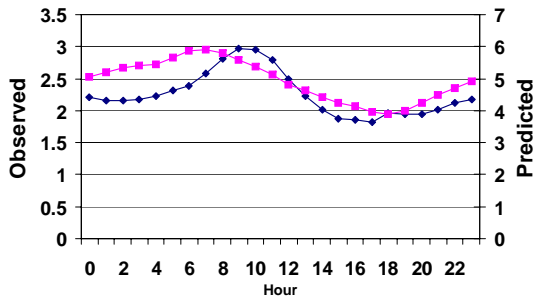
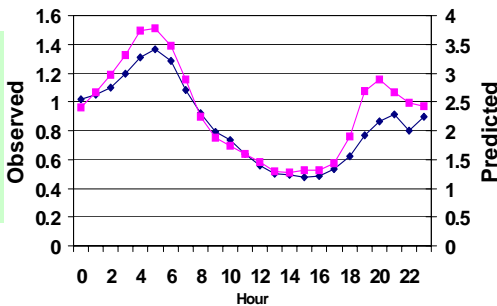
Winter



Sulfate



Nitrate

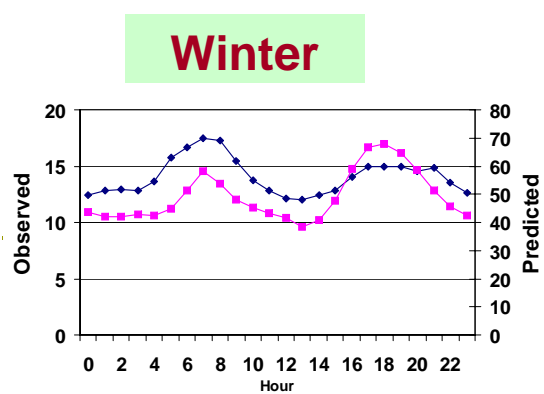
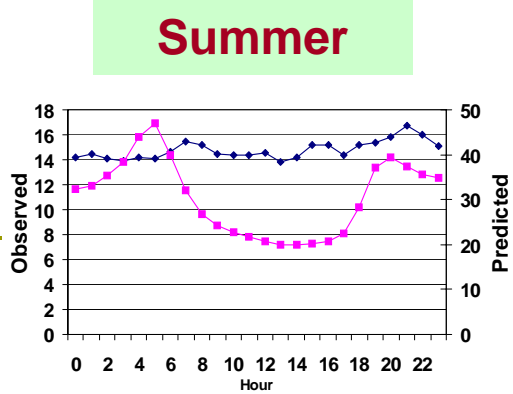


(All concentrations are in  $\mu\text{g}/\text{m}^3$ )

Note the use of different scales between Observed and Predicted Concentrations

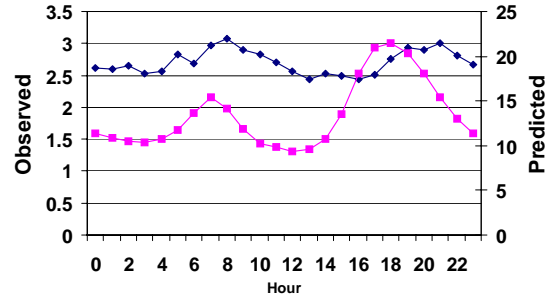
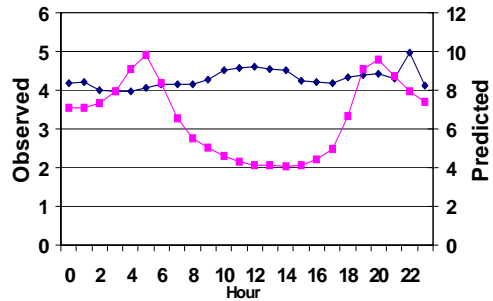
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Mass

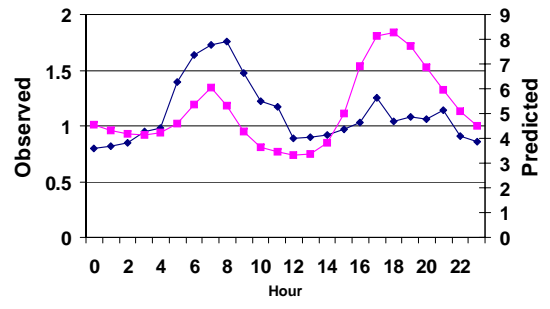
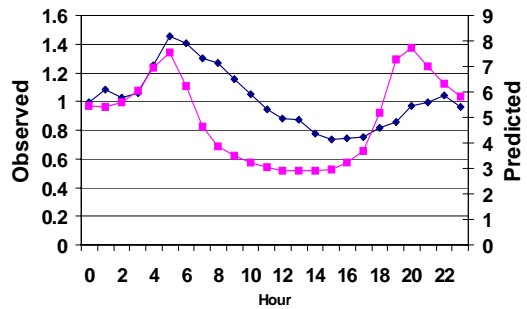


—●— Observed  
—■— Predicted

Org. Matter



EC



(All concentrations are in  $\mu\text{g}/\text{m}^3$ )

Note the use of different scales between Observed and Predicted Concentrations

# Comparison based on Continuous data

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- ❑ At IS52, even though the predicted hourly concentrations are higher than measurements, there seems to be a better agreement in the diurnal patterns for the winter period for PM<sub>2.5</sub> mass, sulfate and nitrate, but not for EC and OM
- ❑ Except for nitrate, all other species differ in their measured and predicted summer diurnal profiles, with predicted concentrations often higher by a factor of two or more for some species
- ❑ The non-capture of the overall diurnal pattern in summer for the species other than nitrate suggests the need for a closer examination of the speciation used in the emissions inventory and their temporal allocation

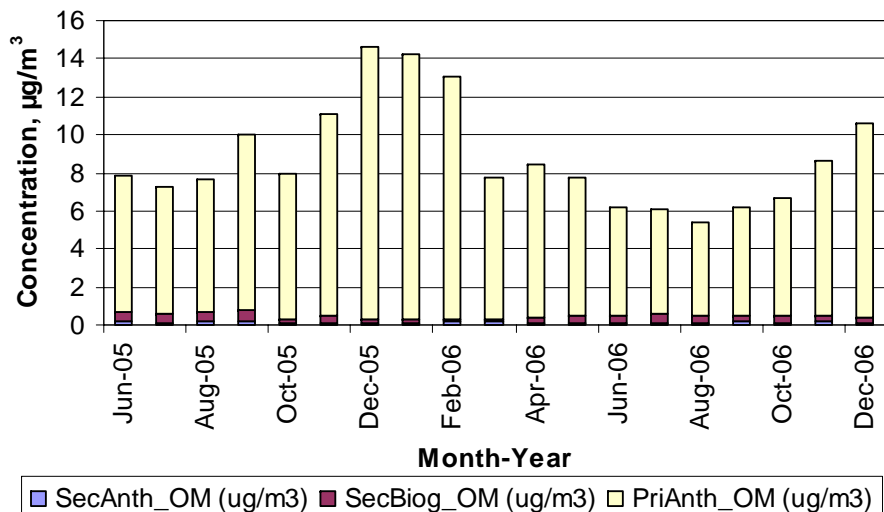
# What Does Model-Predicted Organic Matter (OM) Show?

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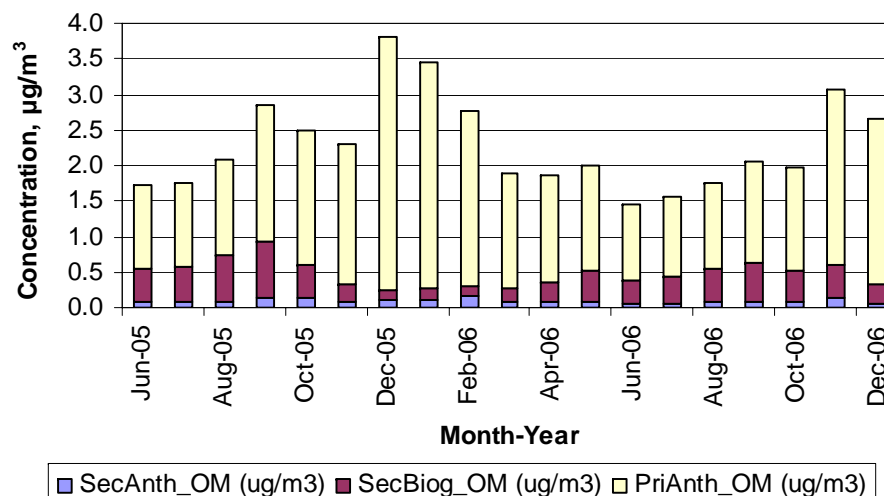
- Modeled OM is combination of contributions from
  - primary and secondary anthropogenics, and
  - secondary biogenics
  
- We calculated model-predicted hourly average concentrations of OM at
  - Urban (IS52)
  - Suburban (Albany)
  - Rural (Pinnacle State Park)
  - Remote (Whiteface Mountain)

# CMAQ-predicted Primary and Secondary Organic Concentrations

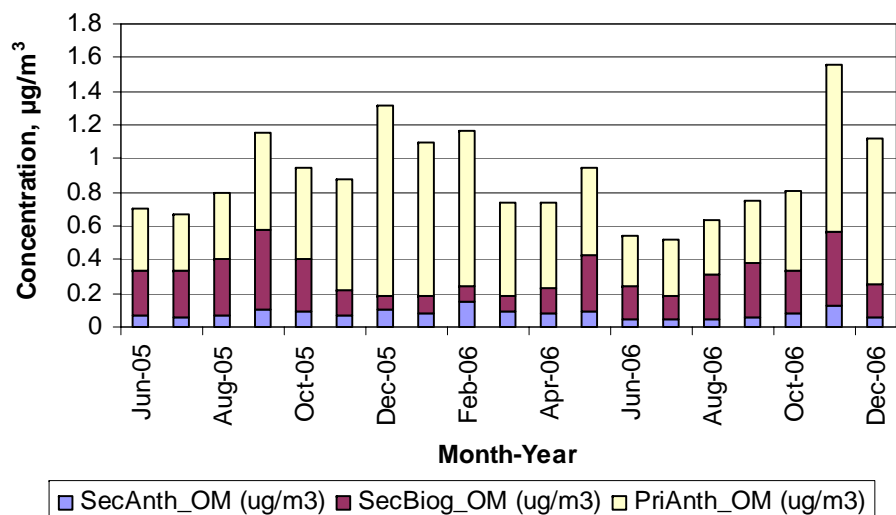
**Modeled Primary and Secondary OM Conc.  
IS52 Bronx**



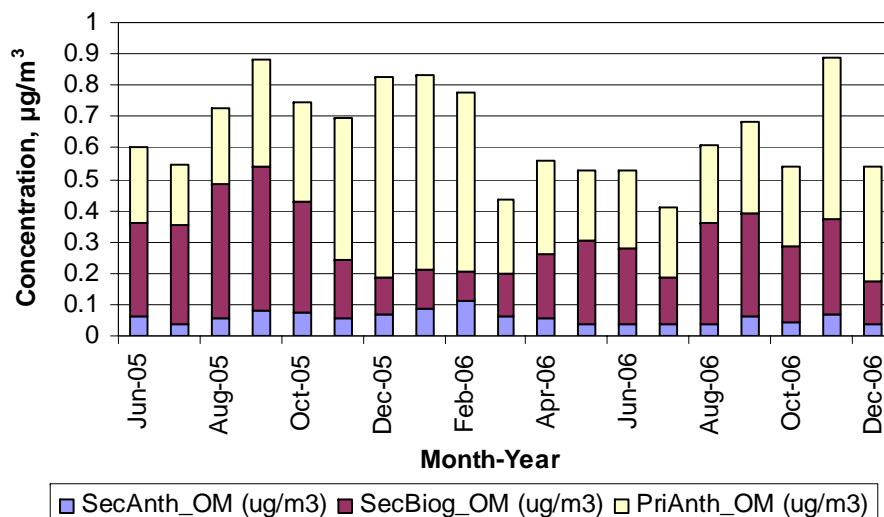
**Modeled Primary and Secondary OM Conc.  
Albany**



**Modeled Primary and Secondary OM Conc.  
Pinnacle State Park**



**Modeled Primary and Secondary OM Conc.  
Whiteface Mountain**



# Modeled Ratio of SOA to OM

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<b>Site</b>	<b>Summer/Fall</b>	<b>Winter</b>
IS 52 (urban)	< 10%	< 4%
Albany (suburban)	~ 35 to 40%	< 10%
Pinnacle SP (rural)	~ 40 to 45%	~ 20%
Whiteface Mountain (remote)	~ 50 to 60%	~ 20%

# What does this mean?

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- ❑ Model-based data suggests that the primary anthropogenic organic matter (PAOM) often dominates compared to the other organic components at all these locations
- ❑ PAOM is substantial even at rural locations, suggesting the need for examination of the emissions inventory and its processing
- ❑ Unlike the photochemical model, routine ambient measurement techniques do not provide for a distinction between primary and secondary organic aerosols
- ❑ Techniques based on continuous EC and OC to estimate SOA are under investigation

# Conclusions

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- The over-prediction of EC and primary organics points to the need for detailed assessment of the emissions inventory and its processing
- The PM speciation in the model for carbon is limited only to OC and EC components by the current available source characterization data and needs further refinement/improvement
- Need linkages between ambient measurements of organics and its speciated compounds to model-based estimates

# Acknowledgements

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- We would like to express our thanks to the Bureau of Air Quality Surveillance staff for providing the measured PM<sub>2.5</sub> mass and species concentrations.