Carbonaceous Matter in Air Quality Model Applications

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$PM_{2.5}$ NAAQS

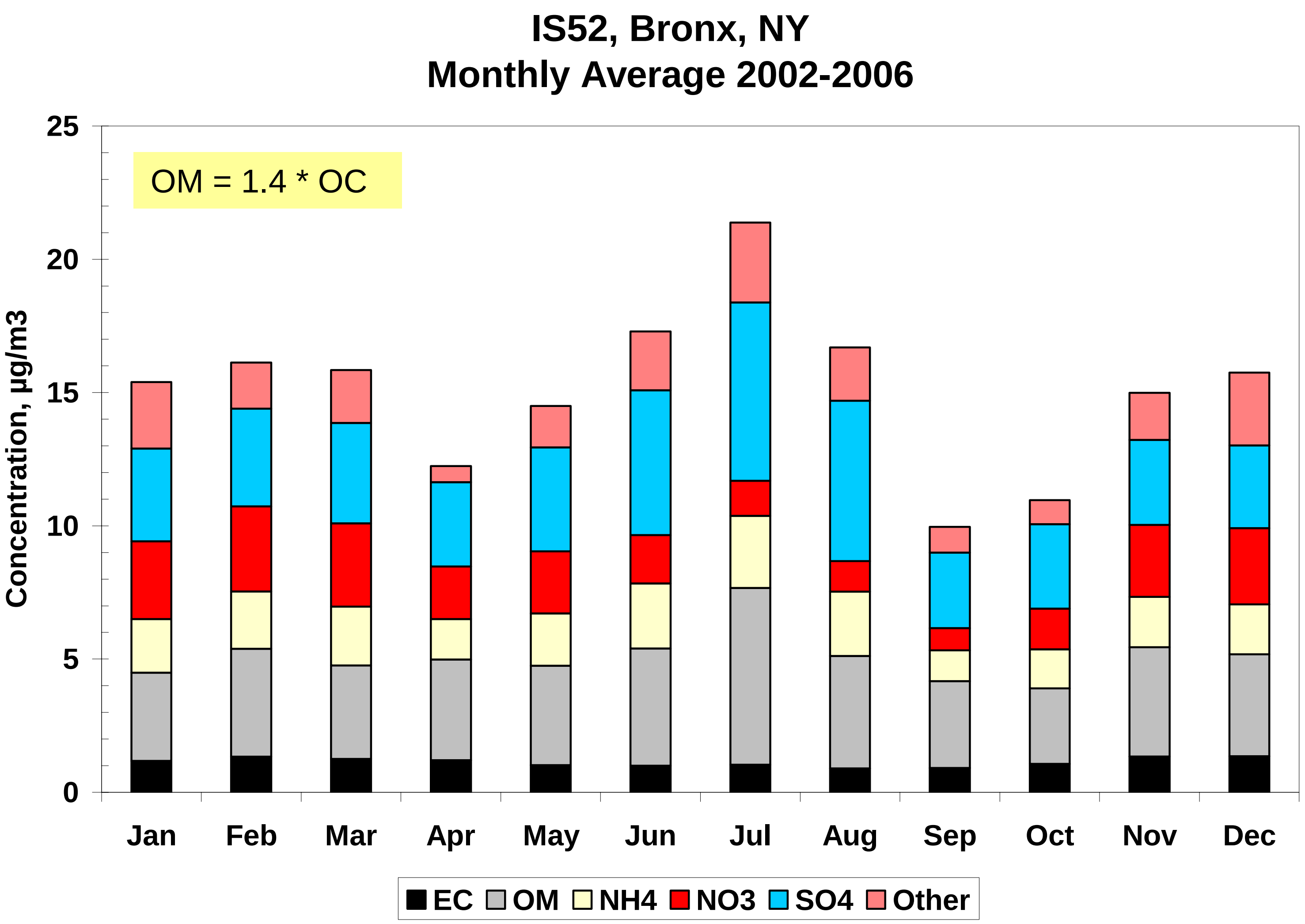
- National Ambient Air Quality Standards for $PM_{2.5}$ promulgated in 1997
  - 24-hr: 65 $\mu g/m^3$
  - Annual: 15 $\mu g/m^3$
  - SIP due April 2008 for 10 county region of NY as part of NYCMSA
- September 2006 Revisions
  - 24-hr: 35 $\mu g/m^3$
  - Annual: 15 $\mu g/m^3$
  - State recommendations 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 $PM_{2.5}$ Contain ?

- Over New York state, measured $PM_{2.5}$ 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_2 and NO_x).

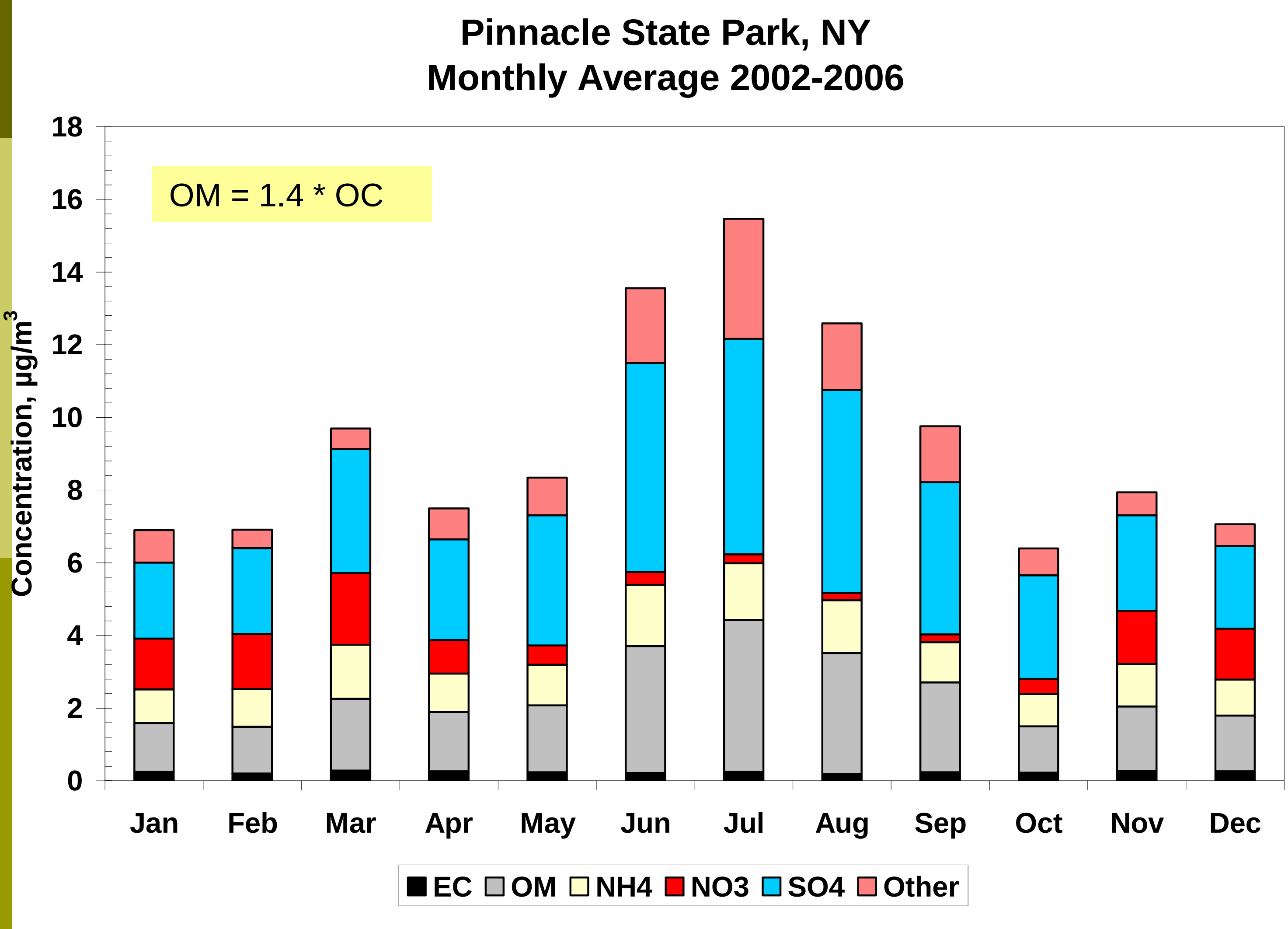
- Measurements from IS52 (Bronx, NY) and Pinnacle State Park (PSP) indicate that sulfate and carbon [elemental (EC) and organic (OC)] together constitute ~47% during winter and as much as 65% during summer.

Monthly Average $PM_{2.5}$ Composition at IS52 (Bronx, NY) monitor (2002-2006)



- **$OM / PM_{2.5}$**
  - ~25% in winter
  - ~30% in summer
- **$EC / PM_{2.5}$**
  - ~8% in winter
  - ~5% in summer
- **$SO_4^= / PM_{2.5}$**
  - ~22% in winter
  - ~33% in summer

Monthly Average $PM_{2.5}$ Composition at PSP monitor (2002-2006)



- **$OM / PM_{2.5}$**
  - ~20% in winter
  - ~26% in summer
- **$EC / PM_{2.5}$**
  - ~3% in winter
  - ~2% in summer
- **$SO_4^{=} / PM_{2.5}$**
  - ~32% in winter
  - ~42% in summer

Why Worry about Carbon ?

- Atmospheric chemistry of sulfate formation has been understood reasonably well arising from SO_2 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 $PM_{2.5}$, thereby increasing the need for a better understanding of the relative role of carbon and its contribution to $PM_{2.5}$ 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

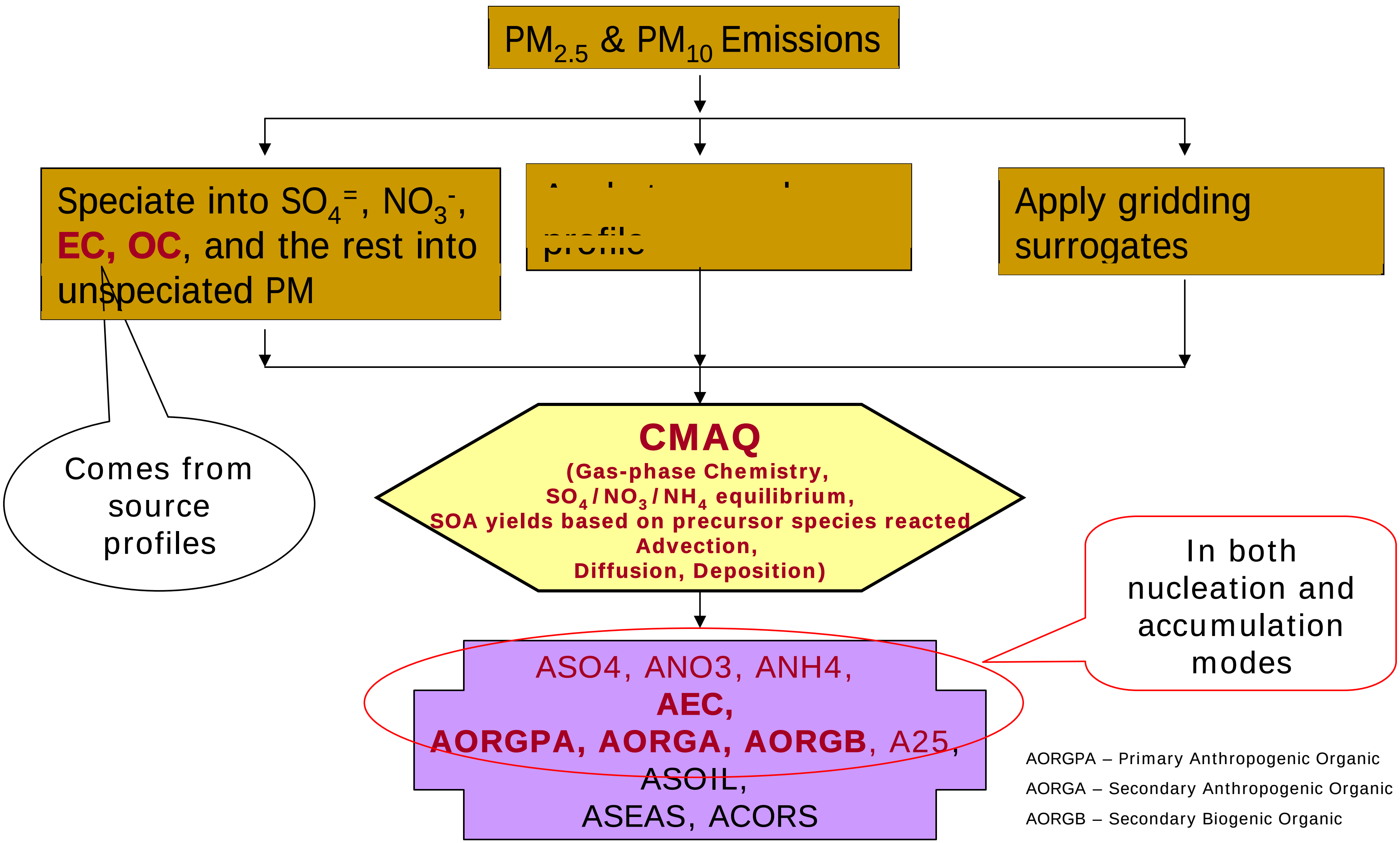
Air Quality Models

- 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

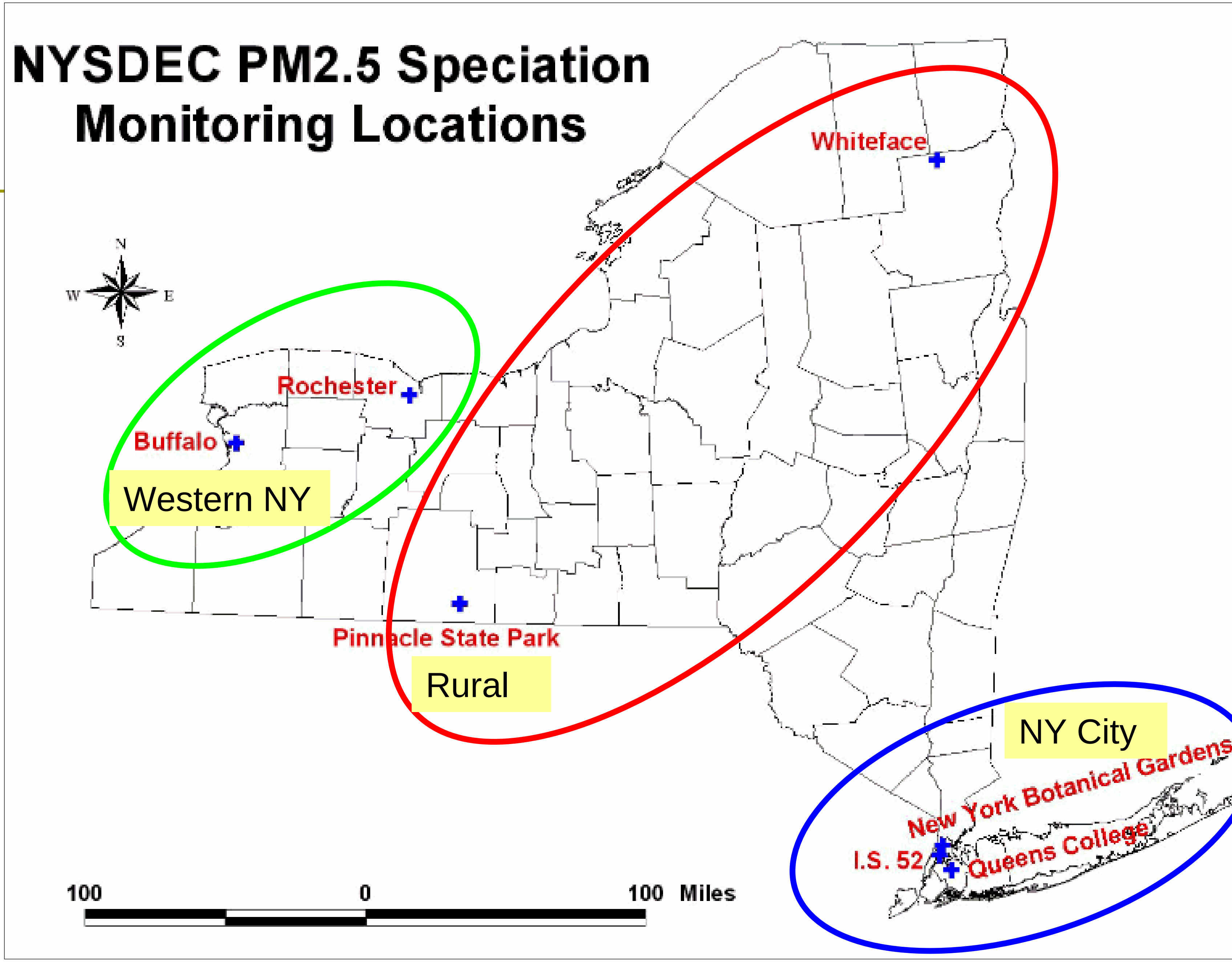
- We utilized the Carbon Bond IV (CB-IV) chemical mechanism, which is a set of representative chemical equations attempting to simulate the complex reality in a modeling framework

Overview of PM Emissions Modeling & CMAQ Outputs



How does the Model Compare with Observations

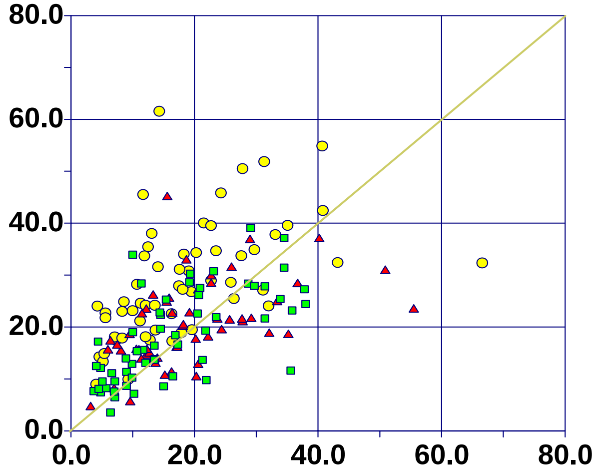
- Model results are from CMAQ-based air quality forecasting simulations covering from June 2005 to Dec 2006
- Data from a single 12-km by 12-km grid cell that contained the monitor was used
- All measured mass and species concentrations used in the comparisons were obtained from the AQS database for 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
N
W
E
S
Whiteface
Rochester
Buffalo
Western NY
Pinnacle State Park
Rural
NY City
New York Botanical Gardens
I.S. 52
Queens College
100
0
100 Miles

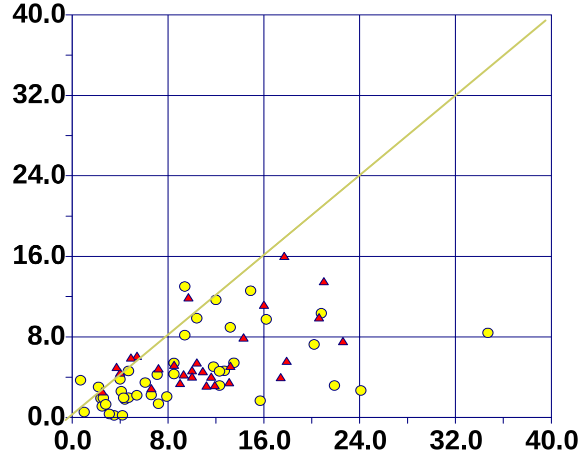
CMAQ (y-axis) vs. STN (x-axis): $PM_{2.5}$ Mass ($\mu g/m^3$)

Summer (June-Aug)

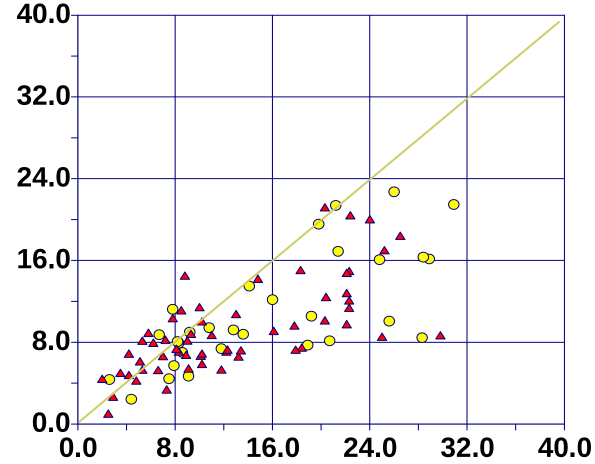
NY City



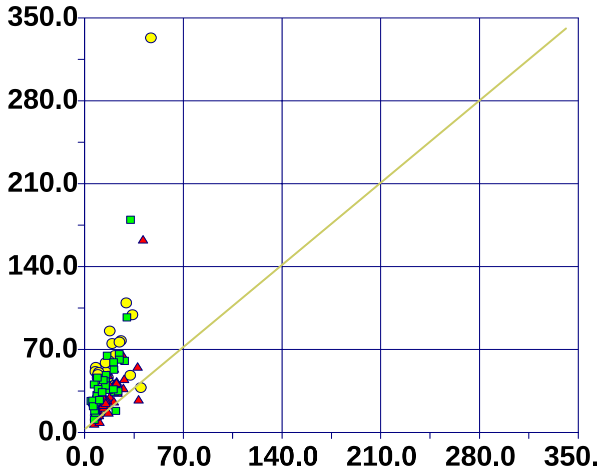
Rural

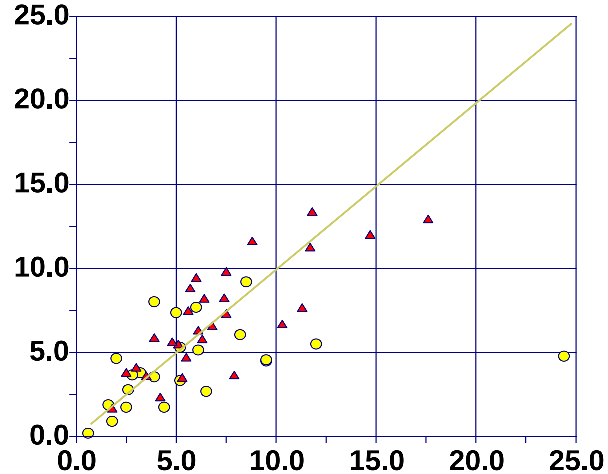


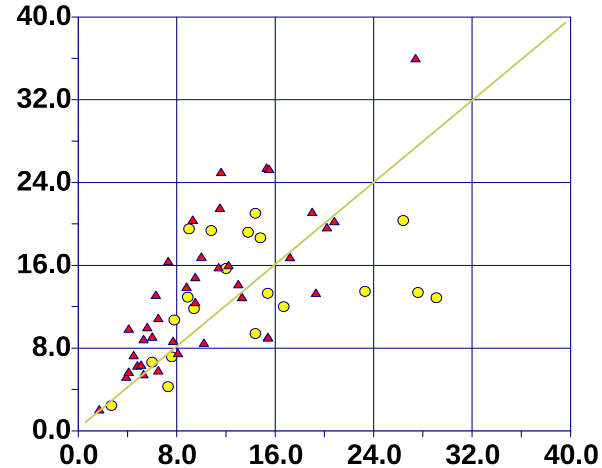
Western NY



Winter (Dec, Jan-Feb)



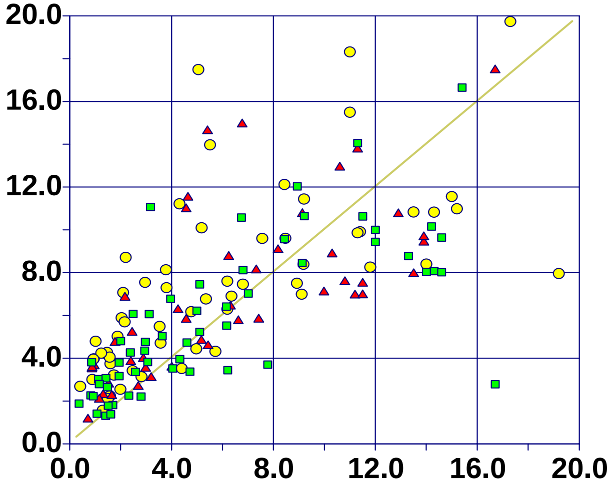




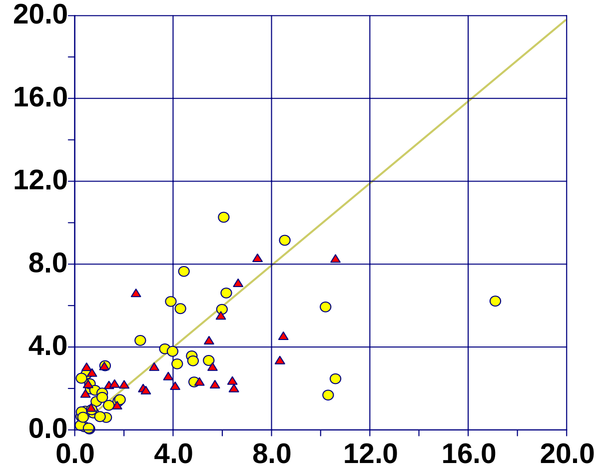
CMAQ (y-axis) vs. STN (x-axis): $PM_{2.5}$ Sulfate ($\mu g/m^3$)

Summer (June-Aug)

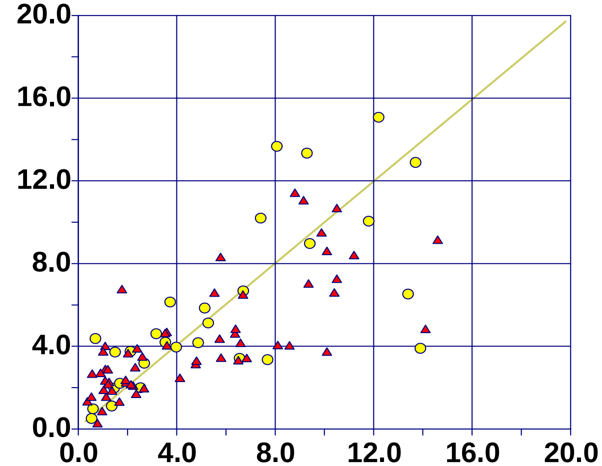
NY City



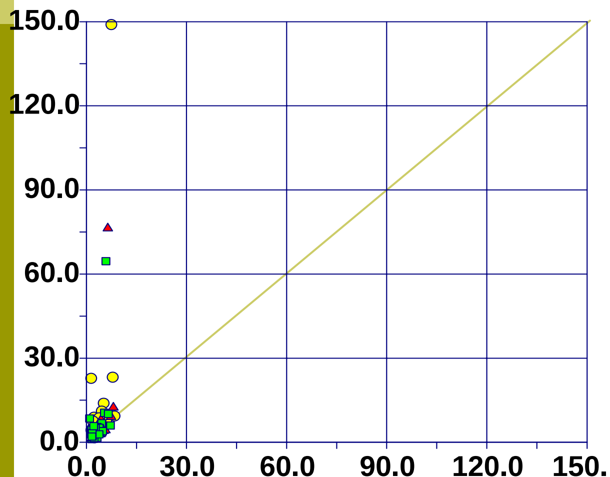
Rural

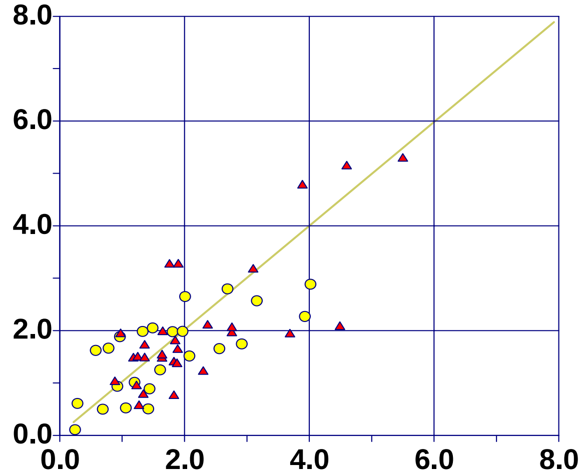


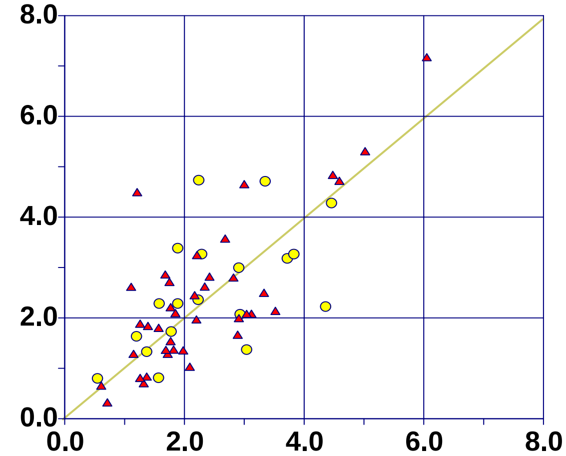
Western NY



Winter (Dec, Jan-Feb)



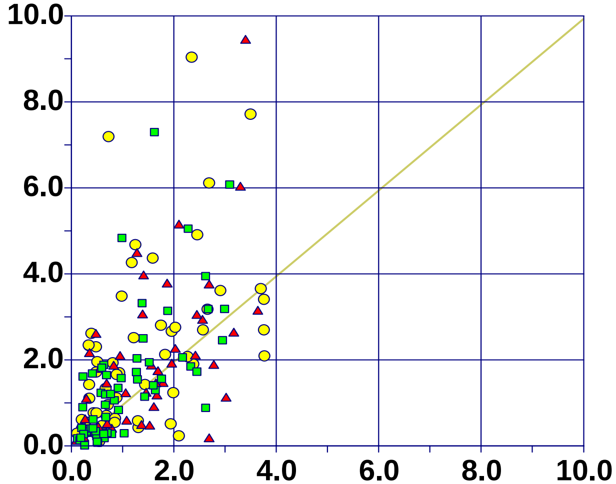




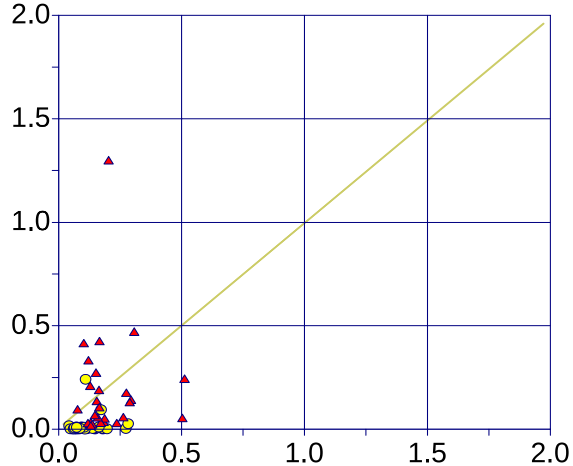
CMAQ (y-axis) vs. STN (x-axis): PM$_{2.5}$ Nitrate (µg/m^3)

Summer (June-Aug)

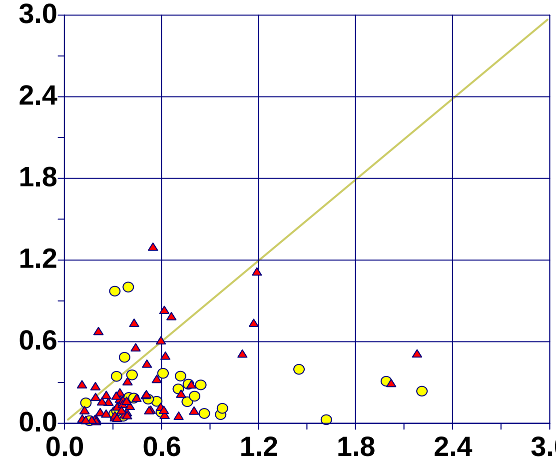
NY City



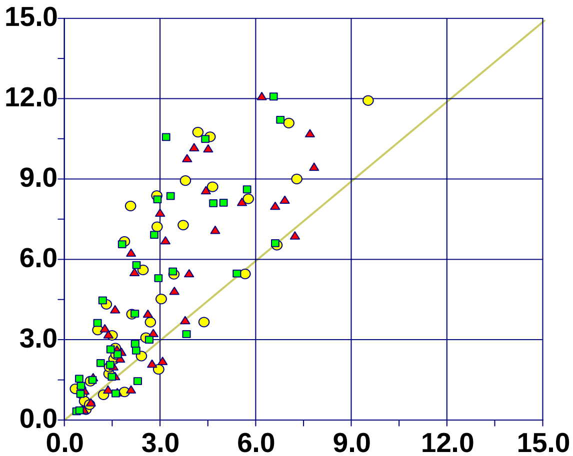
Rural

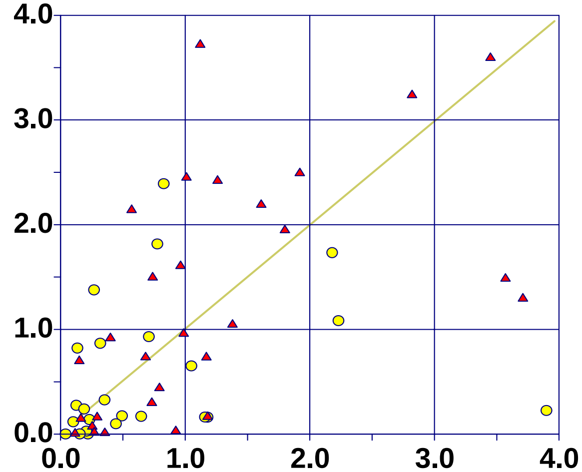


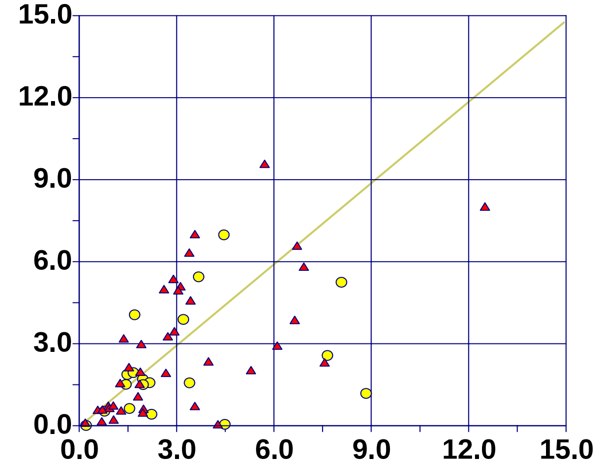
Western NY



Winter (Dec, Jan-Feb)



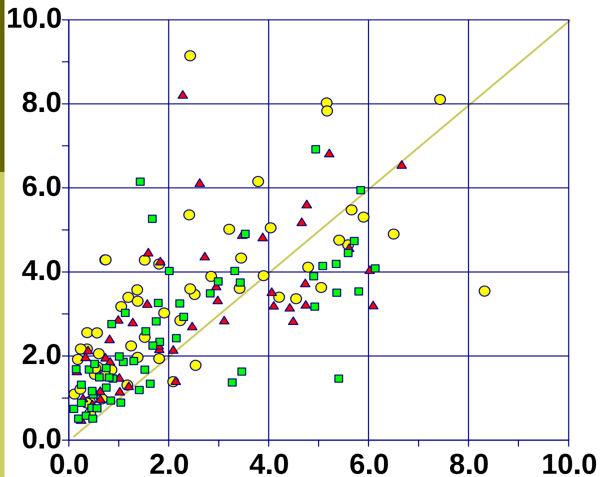




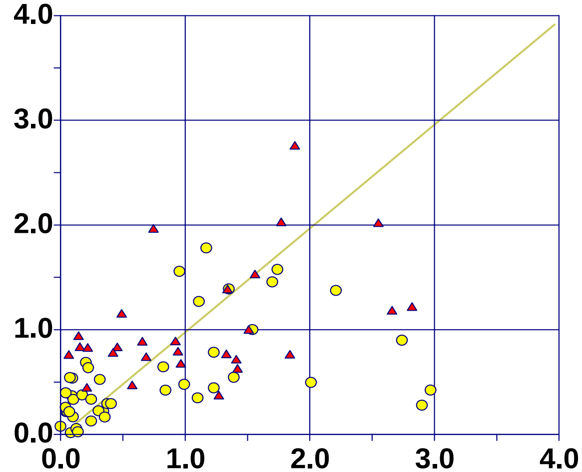
CMAQ (y-axis) vs. STN (x-axis): $PM_{2.5}$ Ammonium ($\mu g/m^3$)

Summer (June-Aug)

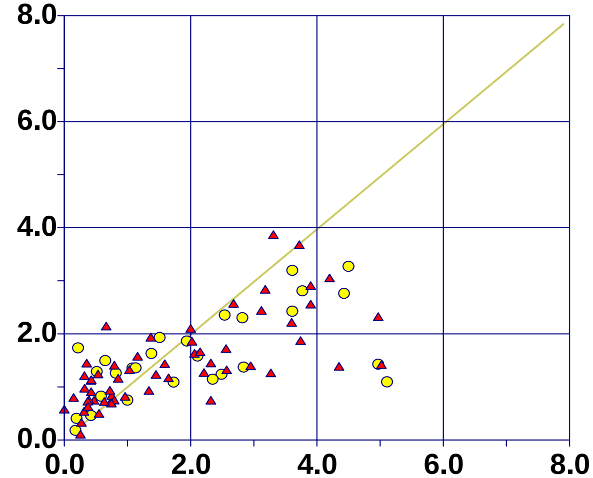
NY City



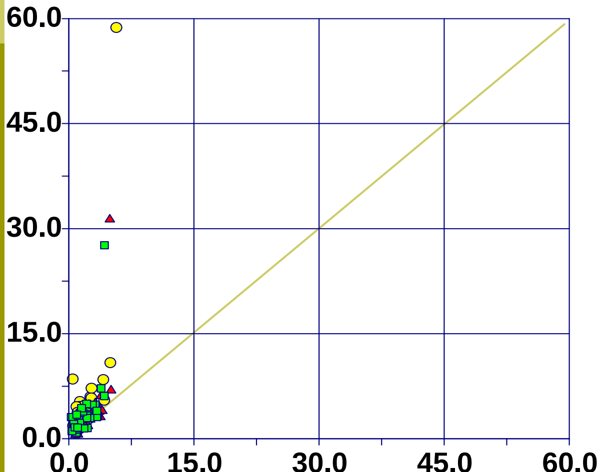
Rural

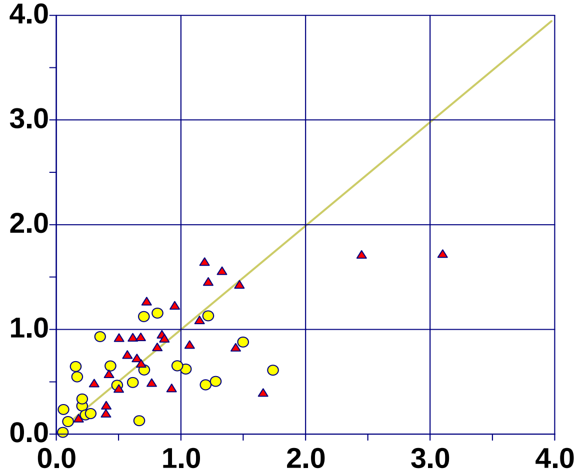


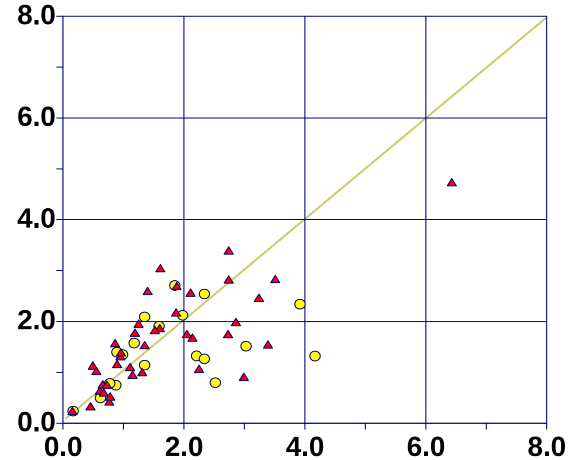
Western NY



Winter (Dec, Jan-Feb)



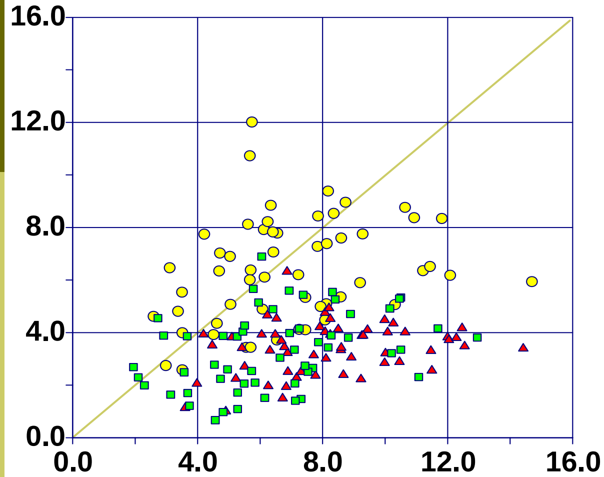




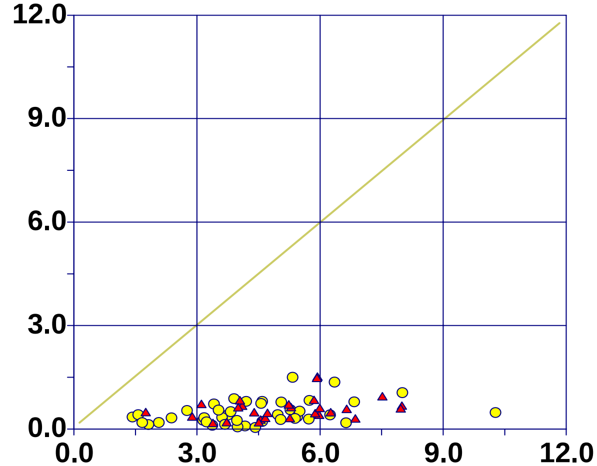
CMAQ (y-axis) vs. STN (x-axis): $PM_{2.5}$ Org. Matter ($\mu g/m^3$)

Summer (June-Aug)

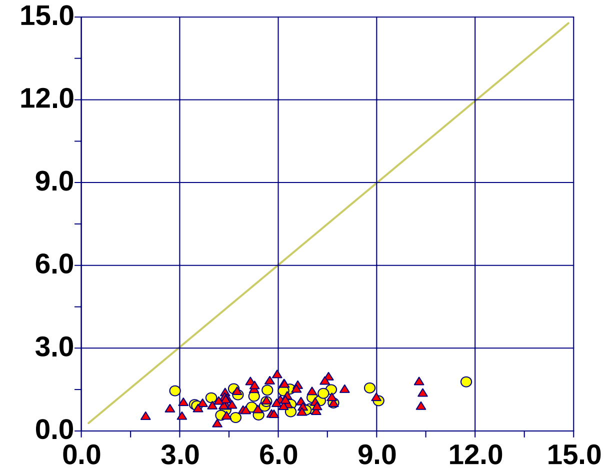
NY City



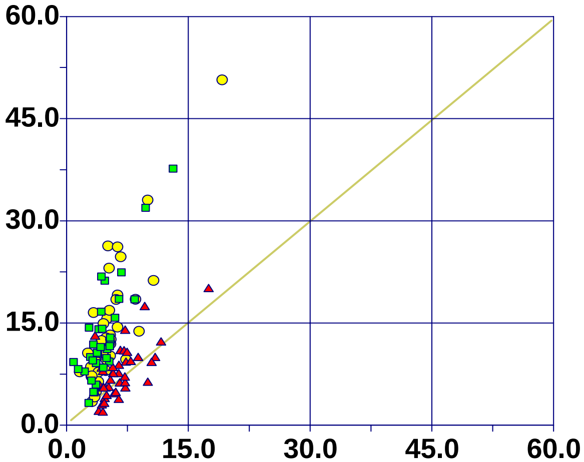
Rural

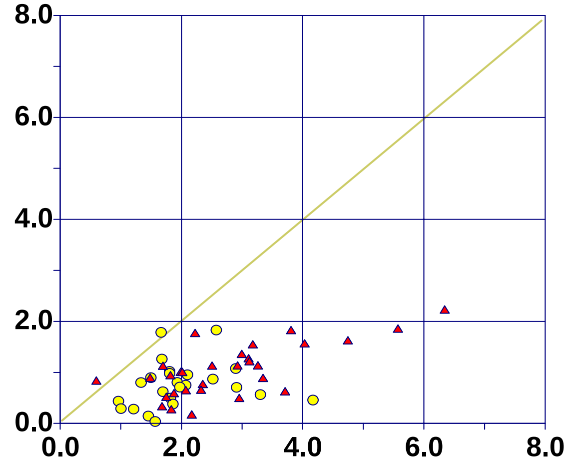


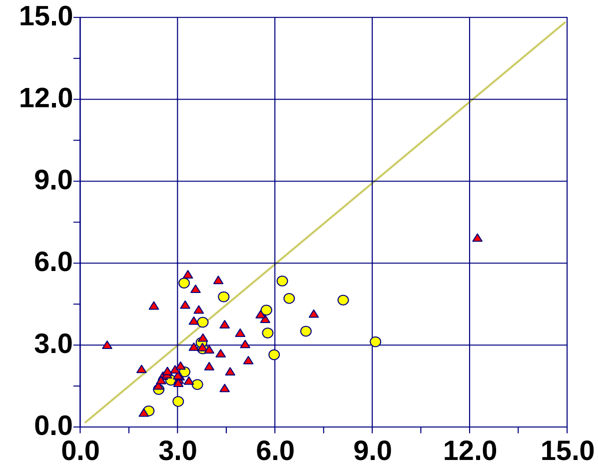
Western NY



Winter (Dec, Jan-Feb)



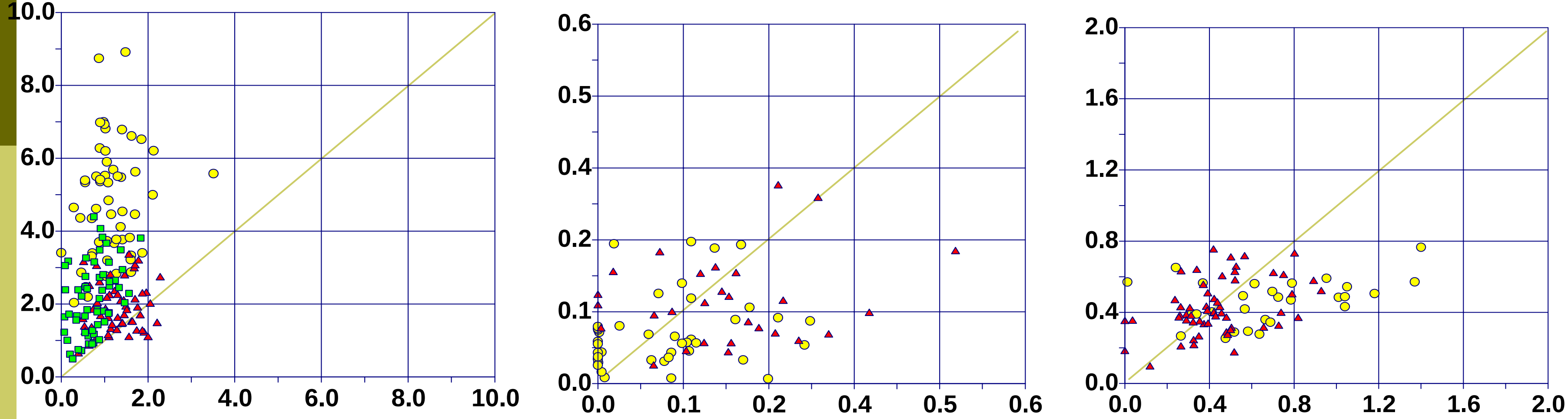




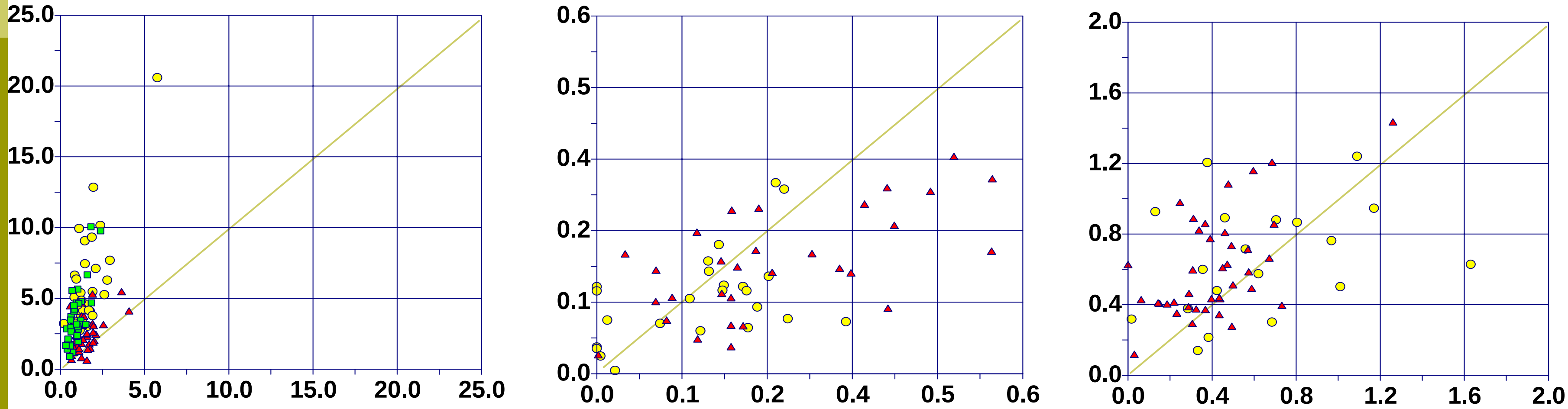
CMAQ (y-axis) vs. STN (x-axis): $PM_{2.5}$ EC ($\mu g/m^3$)

Summer (June-Aug)

NY City | **Rural** | **Western NY**



Winter (Dec, Jan-Feb)



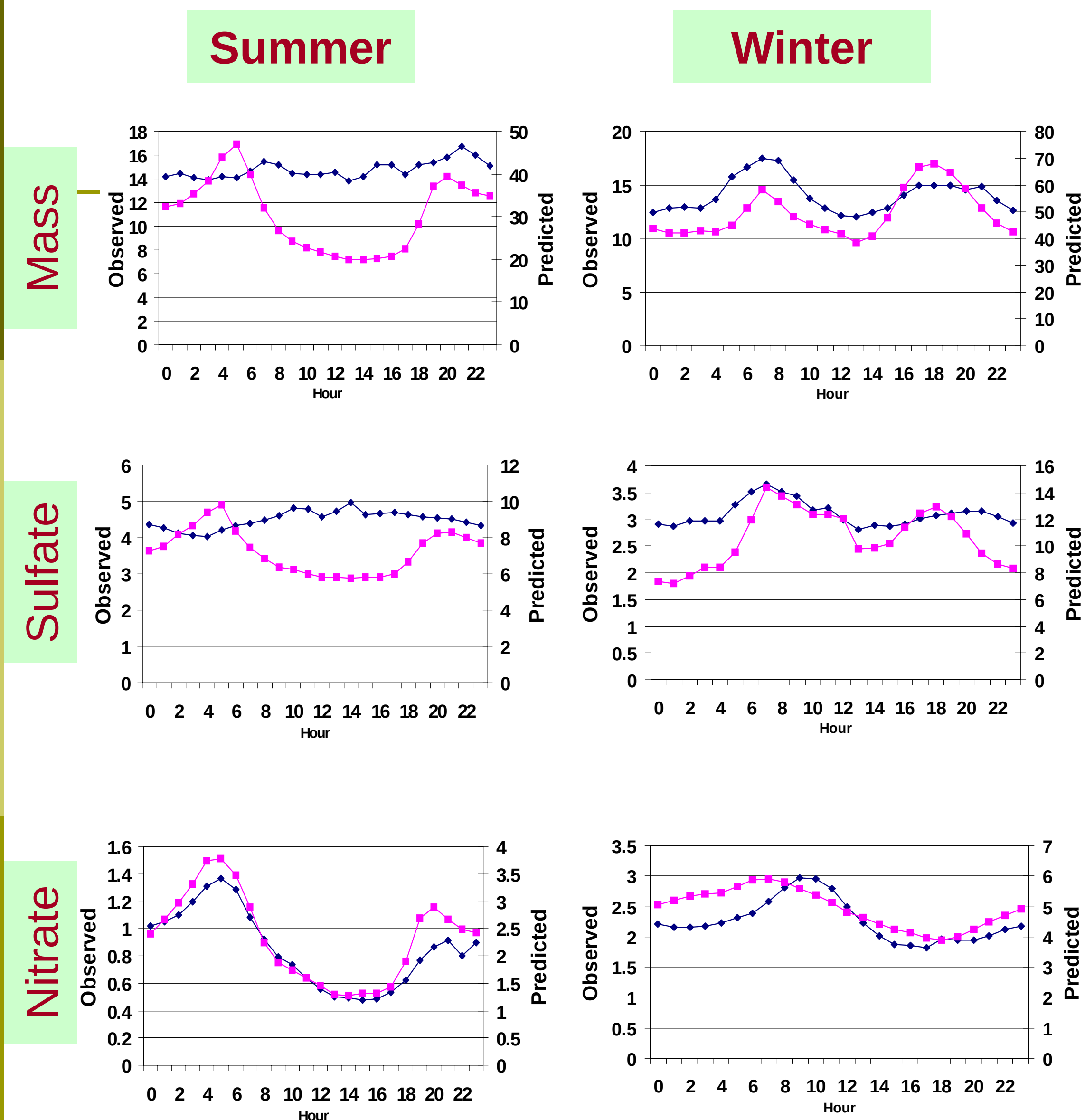
Comparison based on STN data

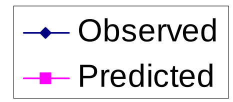
- Primary PM emissions appear to be over-estimated for the 3 urban monitors in New York City, as illustrated by significant over-predictions of EC.

- 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





(All concentrations are in µg/m³)

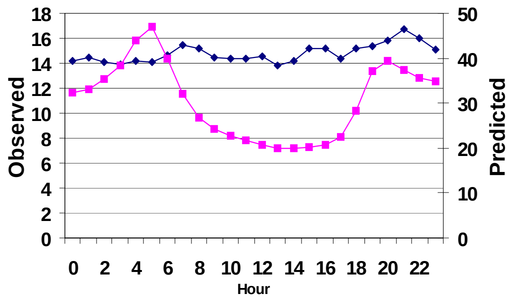
Note the use of different scales between Observed and Predicted Concentrations

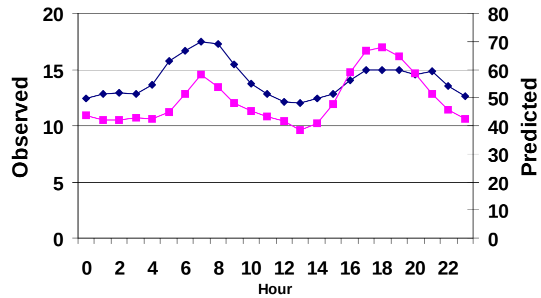
Predicted and Observed Diurnal Profiles at IS52, Bronx, NY

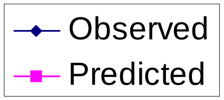
Summer

Winter

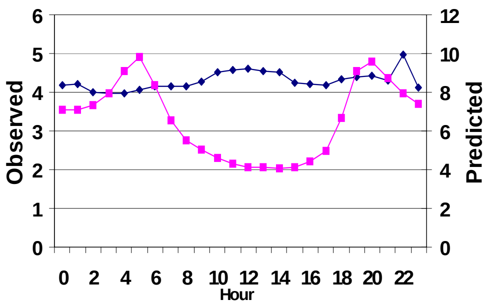
Mass

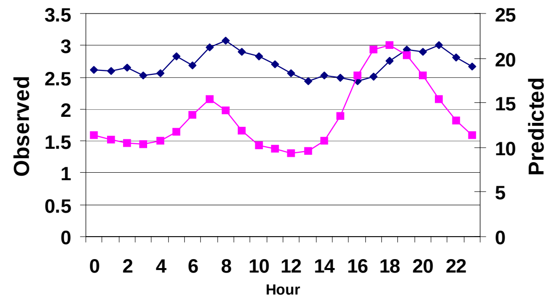




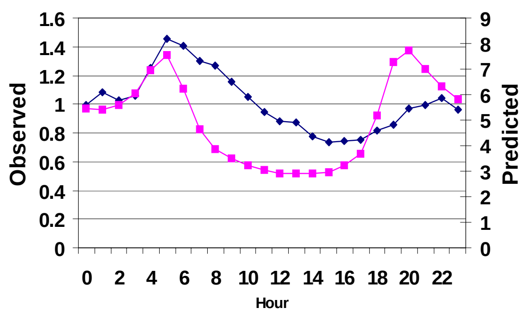


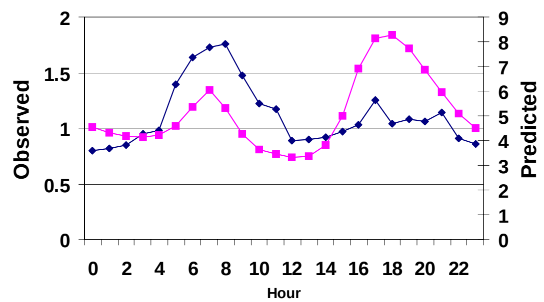
Org. Matter





EC





(All concentrations are in µg/m^3)

Note the use of different scales between Observed and Predicted Concentrations

Comparison based on Continuous data

- 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 $PM_{2.5}$ 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

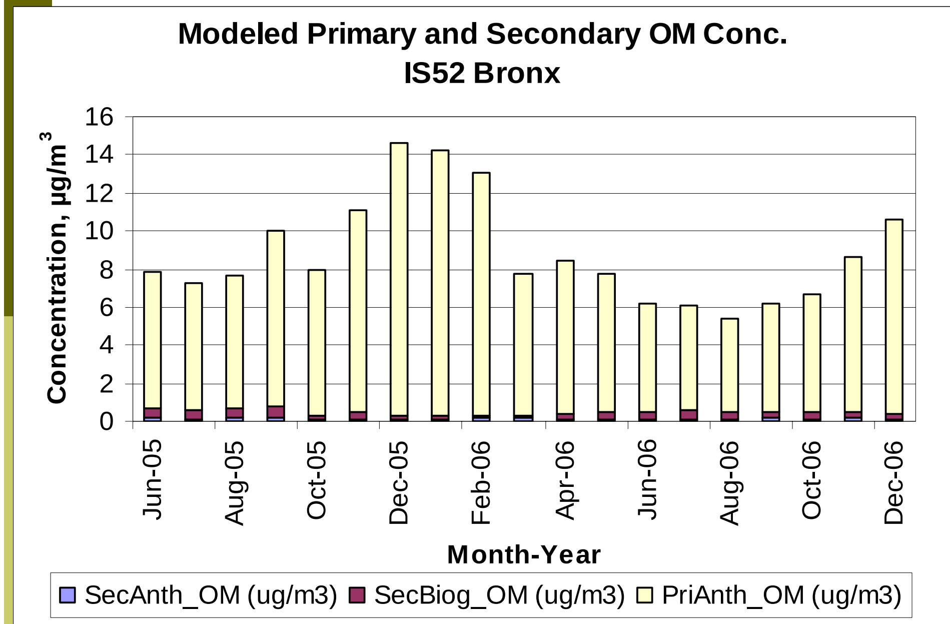
- The non-capture of the overall diurnal pattern in summer for the species other than nitrate suggests the need for a closer examination of the speciation used in the emissions inventory and their temporal allocation

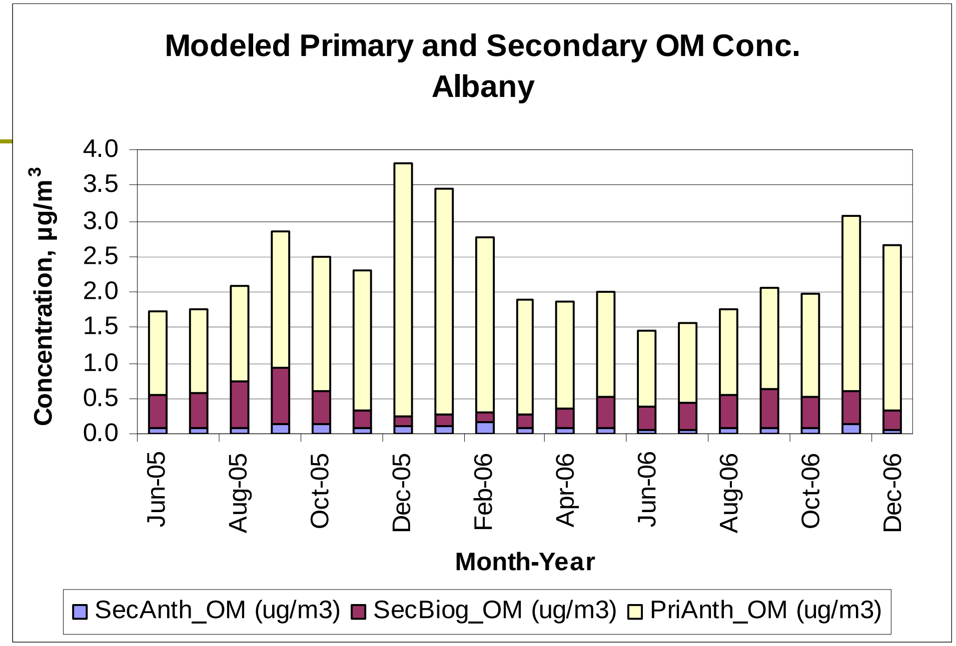
What Does Model-Predicted Organic Matter (OM) Show?

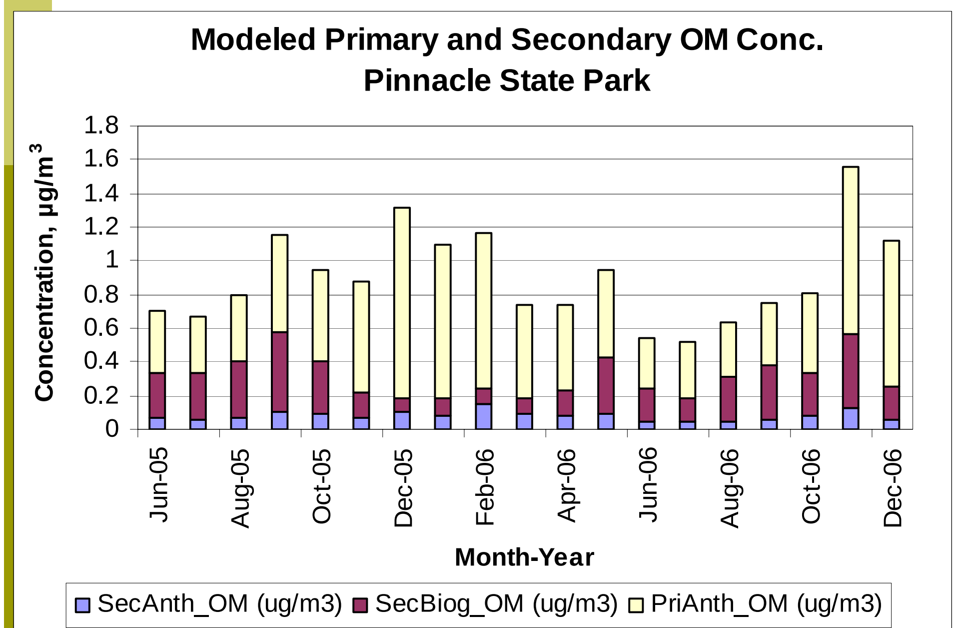
- Modeled OM is combination of contributions from
  - primary and secondary anthropogenics, and
  - secondary biogenics

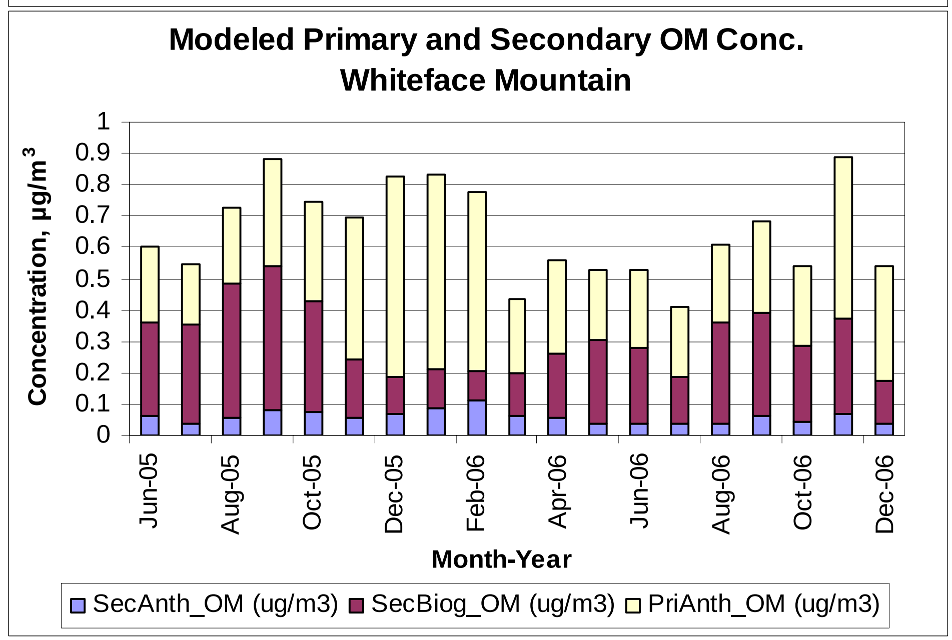
- We calculated model-predicted hourly average concentrations of OM at
  - Urban (IS52)
  - Suburban (Albany)
  - Rural (Pinnacle State Park)
  - Remote (Whiteface Mountain)

CMAQ-predicted Primary and Secondary Organic Concentrations









Modeled Ratio of SOA to OM

Site	**Summer/Fall**	**Winter**
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?

- 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

- 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

- We would like to express our thanks to the Bureau of Air Quality Surveillance staff for providing the measured $PM_{2.5}$ mass and species concentrations.