

# Predicting near real-time PM<sub>2.5</sub> Concentrations from Continuous Mass and Species Measurements in New York City

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## **Introduction**

Near real-time PM<sub>2.5</sub> data are used by State and Local Air Quality Monitoring Agencies to notify the public about actual air quality conditions and to assist in the preparation of PM<sub>2.5</sub> forecasts for periods 1 to 3 days in the future. The public is becoming more aware of air quality in their areas and the new lower Daily Ambient Air Quality standard for PM<sub>2.5</sub> makes it likely that the Air Quality Index (AQI) levels will also be lowered. This will make it likely that State and Local Air Monitoring Agencies will have to forecast more PM<sub>2.5</sub> concentrations that are near or above the levels where public health warnings have to be issued. These warnings which are based on projected FRM concentrations have to be as accurate as possible.

The NYSDEC primarily uses the R&P 1400ab TEOM to determine the near real-time concentration of PM<sub>2,3</sub> at more than 25 locations in New York State. The data that the NYSDEC uses for PM<sub>2,3</sub> notifications and to send to the EPA's AirNow website are adjusted with a non linear regression to more closely resemble the FRM (AAAR Feb, 2005 17PH-28). Since most State and Local Agencies do not adjust their TEOM data, the TEOM ata used in these examples has not been adjusted. The measurements from the TEOM are biased with respect to the filter based FRM particularly in colder seasons when the FRM retains more mass than the heated sensor (50°C) on the TEOM. This bias can be more significant in urban areas where contributions from volatile "fresh emissions" tend to be larger.

The NYSDEC operates a site in New York City with collocated filter based daily FRM and 1/3 day speciation, continuous sulfate, nitrate and OC/EC analyzers. Data from these continuous speciation instruments can be used to calculate a more accurate near real-time approximation of a FRM measurement than a TEOM.

## Site Description

The monitoring site is located in the South Bronx, New York City at Intermediate School 52, 681 Kelly Street. It is impacted by several major nearby highways, Hunts Point produce market with significant truck traffic and LaGuardia airport which lies a few km to the south east. In this area the population density is greater than 12,000/km<sup>2</sup> and approximately 90% of the population live within less than half a mile of a major roadway. The site is host to data collection for several health studies and is one of the two primary sites in New York City where continuous PM<sub>2.5</sub> species data is collected.



## **PM Speciation Instruments and Data Calculations**

### TECO 5020 Sulfate Particulate Analyzer

PM<sub>2.5</sub> Sharp Cut Cyclone (1 LPM total flow), Na<sub>2</sub>CO<sub>3</sub> denuder for removal of SO<sub>2</sub> and acid gases Quartz oven at 1000°C with SS rod for reduction of SO<sub>4</sub> to SO<sub>2</sub> Teflon filter on inlet of SO<sub>3</sub> analyzer (pulsed fluorescence), 5 minute zero cycle followed by 10 minute sample

cycle, Calibration: SO<sub>2</sub> analyzer with NIST traceable gas standard



then normalized to the STN filter data using monthly regression slopes similar to that shown. This  $SO_4$  data is then adjusted to account for ammonium ion (assumes aerosol is neutral).



Average 24-hr SUNSET vs STN Filter OC

#### Sunset Labs OC/EC Carbon Aerosol Analyzer

PM<sub>25</sub> Sharp Cut Cyclone (8 LPM), Parallel plate denuder with charcoal impregnated strips or Monolith 47 minute sample collection on quartz filter, Analysis using NIOSH 5040 protocol

Detection: NDIR detection of CO<sub>2</sub> Calibration: NIST traceable CH<sub>4</sub> gas standard

Hourly Organic Carbon data is adjusted using average of hourly blanks collected over a 24-48 hr period with a teflon filter on inlet. To convert to organic mass, OC is scaled by a factor of 1.5 which accounts for additional elements as discussed by Bae et al. Atmos. Env., 2006.

#### R&P 8400N Nitrate Analyzer

 $PM_{2.5}$  sharp cut cyclone; Humidified impaction followed by flash volatilization to  $NO_x$  10 minute cycle time, 1 LPM sample flow, Analysis by API NO\_x analyzer.



Filter Samplers FRM: R&P 2025 Partisol (Filters weighed by RTI) Speciation: R&P 2300 (Filters analyzed by RTI: STN protocol) Speciation: IMPROVE protocol (Filters analyzed by IMPROVE labs)

# Sum of Species and TEOM Mass compared to FRM

# Episode in Summer



	LOW	3011 01	11510	I LOM IO	3011110						
	(50°C)	SPECIES	ug/m <sup>3</sup>	FRM	FRM		TEOM	SUM of	FRM	TEOM to	SUM to
6/2006	7.4	6.9	9.0	-16.9%	-23.2%	_	(50°C)	SPECIES	ug/m <sup>3</sup>	FRM	FRM
/2006	21.8	22.1	22.5	-3.0%	-1.7%	2/14/2006	16.3	22.0	22.9	-28.7%	-4.2%
3/2006	36.5	39.5	38.7	-5.6%	2.2%	2/15/2006	27.3	32.6	34.1	-19.9%	-4.2%
9/2006	36.9	41.6	40.2	-8.1%	3.6%	2/16/2006	33.5	39.9	44.7	-25.0%	-10.8%
)/2006	14.5	18.3	17.0	-14.4%	7.4%	2/17/2006	5.6	9.0	8.3	-32.6%	8.8%
/2006	10.8	12.2	12.2	-11.3%	0.2%	Average over 2/14 - 2/17:			-26.6%	-2.6%	
Average over 6/16 - 6/21			-9.9%	-1.9%		-					

# Results

6/16 6/17 6/18 6/19 6/20 6/21

> Collocated TEOM (50° C), Sum of Species and FRM data from the Bronx, NY site are compared for a summer and a winter episode in 2006. The Sum of Species includes (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, EC, OM, NO<sub>3</sub> and particle bound water associated with (NH<sub>2</sub>)<sub>2</sub>SO<sub>4</sub>. The Sum of Species does not account for elemental mass. In both episodes, the 24hr integrated mass measured by the FRM exceeded the AQI level of 100:(Unhealthy for Sensitive Groups). The results from the FRM, TEOM and the calculated Sum of Species all track each other but there are significant biases.

> The TEOM underestimates the sum of species for much of the summer episode from June 18 onwards and for almost the entire winter episode. The TEOM is biased low compared to the FRM by 5 to 15% for the summer episode and 20 to 30% for the winter episode. With the exception of June 16 the sum of species and FRM agree within 5 to 10% for the summer and winter episodes. During the summer episode sulfate dominates the mass and organic matter account for 35-45%. During the winter episode, organic matter, sulfate and nitrate contribute roughly equally to the mass.

## **Implications**

The near real-time species data provide a more accurate estimate of the FRM measurements than the TEOM 1400ab operated at 50° C. This is significant because it is expected that the AQI levels will be adjusted downward to reflect the new lower daily  $PM_{2,5}$  standard. State and Local Air Monitoring Agencies will have to forecast  $PM_{2,5}$  concentrations on a more frequent basis that are very close to or exceed the levels requiring public health notices. It is important that these forecasts are accurate so the public is not misinformed about air quality conditions that could cause them to change their behavior and thus their exposure or their potential contributions to emission reduction programs.

Continuous speciation analyzers are becoming more widely available as technology improves. This equipment provides data on time scales from minutes to several hours and this data is generally correlated with filter based data to provide a reference to the FRM. It is likely that adjusted data from continuous speciation instruments can be more closely correlated with the FRM than the newest automated  $PM_{2.5}$  instruments that are seeking FEM status. This is due to the fact that when using near real-time speciation data, only the species such as nitrate and organic carbon that are partially retained by the FRM have to be adjusted. Since the new continuous mass instruments cannot identify individual components of  $PM_{2.5}$  they will not be able to predict the amount of a PM matrix that will be retained in the FRM measurement. It is possible that an area's attainment status could be affected by the accuracy of one of the new automated  $PM_{2.5}$  instruments if they are able to attain FEM equivalency.

Continuous speciation data is also being used by health researchers who are concerned with the short and long term effect on health indicators of specific components of  $PM_{2,5}$  rather than just total  $PM_{2,5}$  mass. These researchers are often less concerned with correlations to the FRM than with the actual amount of PM components present in the environment. The highly time resolved continuous speciation data can also assist in the interpretation of short term environmental effects on human physiology.

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**Episode in Winter**