TSD- 3a

Analysis of Ambient $PM_{2.5}$ Mass and Speciation

for the New York Metropolitan Area through 2006

Bureau of Air Quality Analysis and Research

Division of Air Resources

New York State Department of Environmental Conservation

Albany, NY 12233

December 14, 2007

Introduction

With the promulgation of the annual and daily $PM_{2.5}$ national ambient air quality standards (NAAQS) in 1997, the New York State Department of Environmental Conservation (NYSDEC) initiated monitoring this pollutant on a statewide basis beginning in 1998/1999. A majority of the monitoring efforts to date have involved 24-hour, filter-based Federal Reference Method (FRM) samplers. Most of the FRM samplers operate on a 1-in-3-day schedule, although a few monitors operate on a daily basis. Also, as per network design requirements, several FRM sites have collocated duplicate samplers.

The $PM_{2.5}$ NAAQS is mass-based, but ambient $PM_{2.5}$ has a complex morphology and chemical composition. In order to obtain information on species composition, the NYSDEC also has operated Speciation Trends Network (STN) monitors at several locations across the state. Similar to the FRM network, the STN samplers operate on a 1-in-3-day schedule. The STN program provides for the concentration of major ions, carbon compounds, and trace elements, which generally constitute the bulk of $PM_{2.5}$ mass.

Although time series of ambient $PM_{2.5}$ mass and species are relatively short compared to other criteria pollutants, such as ozone, it is nonetheless important to examine temporal and seasonal trends in the data, in addition to characterize current ambient levels. Here we present such trends on a composite basis over the New York portion of the New York City $PM_{2.5}$ non-attainment area (NYC NAA), corresponding to Bronx, Kings, Nassau, New York, Orange, Queens, Richmond, Suffolk and Westchester Counties. All data used in this analysis are publicly available on the NYSDEC Division of Air Resources' ambient $PM_{2.5}$ monitoring website (please see http://www.dec.ny.gov/chemical/8539.html).

FRM data

Table 1 lists the site locations and sampling periods between 1999-2006 for all FRM monitors in the three NYSDEC sub-regions that cover parts of the NYC NAA: Region 1 (Long Island; 6 sites), Region 2 (New York City; 19 sites), and Region 3 (Lower Hudson River Valley; 3 sites). The analysis included Dutchess County for completeness, even though it is not part of the NYC NAA area. Seven of the Region 2 sites have collocated duplicate monitors. Three of the sites also operated daily for at least part of the time. A map of the FRM locations is shown in Figure 1.

Figure 2 displays the composite average FRM mass by NYSDEC region, using all valid data from 1999-2006. The averages presented in Figure 2 do not represent design values for attainment/regulatory purposes; however, the annual NAAQS of 15 $\mu g\ m^{-3}$ is shown for reference. This figure illustrates that on average, $PM_{2.5}$ is higher in Region 2 than the surrounding areas. Whereas the average levels in New York City range from about 13-15 $\mu g\ m^{-3}$, the average levels in the surrounding counties is about 10-12 $\mu g\ m^{-3}$.

One other feature evident in Figure 2 is that $PM_{2.5}$ levels in the most recent few years are generally lower than levels measured in 1999-2001.

Figure 3 displays the composite seasonal/quarterly variations in FRM mass by NYSDEC region, again using all valid data from 1999-2006. In Regions 1 and 3 there appears to be a warm season maximum; this corresponds to the time of maximum photochemical activity and secondary particulate formation. In Region 2 the $PM_{2.5}$ levels are high in during both the warm and cold seasons. The high levels during the colder months are likely indicative of local sources in the New York City, such as space heating, as well as the effects of large urban emissions being mixed through a shallow atmospheric boundary layer.

Tables 2 and 3 display the annual average and 98^{th} percentiles of FRM mass, respectively, from 2000-2006. Only those years with at least 75% valid samples are included in these tables. Note that some of the values presented in Tables 2 and 3 correspond to years that do not necessarily have four complete quarters. Similar to Figure 2, Table 2 indicates than on an average basis $PM_{2.5}$ levels are generally lower in the most recent years compared to earlier years. In particular, average $PM_{2.5}$ levels in 2006 were generally the lowest in this seven-year period. The 98^{th} percentiles presented in Table 3 are related to the daily $PM_{2.5}$ NAAQS, which consists of the average of the 98^{th} percentile values over three consecutive years. Currently the daily NAAQS is 65 $\mu g\ m^{-3}$, and Table 3 shows that all sites in the New York metropolitan area have been well below this level.

Table 4 lists the linear trends in $PM_{2.5}$ mass at longest-running sites FRM sites in the New York metropolitan area. These sites operated from 1999/2000 through 2006, and the trends reported in Table 4 are based on quarterly average values at each site. Only those quarters with at least 10 valid data points were included in the linear trend estimates. Consistent with the composite averages presented earlier, $PM_{2.5}$ mass appears to be decreasing at each of these longest-running sites, by ~0.1-0.5 $\mu g\ m^{-3}\ yr^{-1}$.

STN data

Table 5 lists the site locations and sampling periods of the STN monitors. Each of these sites is collocated with an FRM monitor. The STN samplers collect five ions – sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), potassium (K), and sodium (Na) – nearly 50 trace elements, and various carbon species – elemental carbon (EC) and organic carbon (OC). For this analysis, we assume that $PM_{2.5}$ is primarily composed of only SO_4, NO_3, NH_4, EC, OC, and major crustal species (major oxides of Al, Ca, Fe, Si, and Ti; e.g. US EPA, 2007), and hereafter refer to the sum of these species as the "reconstructed mass." Although the $PM_{2.5}$ NAAQS is strictly mass-based, here we attempt to approximate the average species composition of the ambient $PM_{2.5}$ in NYC.

We adjusted the OC value by subtracting a constant, monitor-specific blank, and applying a multiplicative factor of 1.8 to account for the non-carbon composition (O, H, etc.). In various EPA documents, a blank of 1.40 $\mu g\ m^{-3}$ for MetOne SASS instruments

(Canal Street Post Office, N.Y. Botanical Gardens) and 0.93 μg m^{-3} for R&P 2300 ACCU instruments (I.S. 52, Queens College II/P.S. 219) is assumed (e.g., http://www.epa.gov/airtrends/aqtrnd03/pdfs/2_chemspecofpm25.pdf). We then calculated the composite average of each of these components across all four STN sites for all valid data points, as well as for just the winter (December-February) and summer (June-August) periods.

Figure 4 displays the annual, wintertime, and summertime average major $PM_{2.5}$ speciation levels. On an overall annual basis, SO_4 and OC account for about 27% and 35%, respectively, of the reconstructed mass in New York City, roughly twice the contribution of NO_3. During the winter months, OC is the largest contributor to the reconstructed mass (34%), while SO_4 and NO_3 also account for about 20%. The relative importance of NO_3 is higher during the winter months because NO_3 volatilization is much lower during the colder months. During the summer months, SO_4 and OC levels are considerably higher than during the winter months, and account for about 70% of the reconstructed mass. The smallest components of reconstructed mass correspond to EC and crustal mass (~4-8%). On average, the reconstructed mass in New York City is about 18.2 μg m^{-3} during the summer months, and about 15.2 μg m^{-3} during the winter months.

Summary

The FRM data collected across the New York metropolitan area over the past seven years suggest that $PM_{2.5}$ levels are generally higher in the core urban areas compared to the surrounding suburban counties. While this is a rather short time period, it appears that $PM_{2.5}$ levels have been decreasing across the entire metropolitan area since the early 2000's. In terms of species composition, SO_4 and OC are the most important species, especially during the summer months, while NO_3 is also an important species during the winter months. It appears that emissions control programs that target precursors of SO_4, NO_3, and OC will be needed to further reduce $PM_{2.5}$ levels across the metropolitan area.

Reference

United States Environmental Protection Agency (US EPA), 2007. Guidance on the use of models and other analyses for demonstrating attainment of air quality goals for ozone, $PM_{2.5}$, and regional haze. Office of Air Quality Planning and Standards, 253 pp., EPA-454/B-07-002.

Table 1. Listing of FRM sites, 1999-2006. Some locations have primary ("P") and duplicate ("D") samplers. Dates with an asterix denote daily sampling for at least part of the period.

NYSDEC Region	Site Name	County	Dates
1	Eisenhower Park	Nassau	1/1999 – 12/1999
1	Hempstead	Nassau	1/1999 – 12/2006
1	Briarcliffe	Nassau	2/2000 – 3/2003
1	Roslyn	Nassau	7/2000 – 3/2003
1	Roslyn Heights	Nassau	1/1999 – 3/2000
1	Babylon	Suffolk	1/1999 – 12/2006
2	Mabel Dean H.S.	New York	1/1999 – 6/2001*
2	J.H.S. 45	New York	P: 1/2000 – 12/2006 D: 1/2006 – 12/2006
2	P.S. 59	New York	P: 1/1999 – 12/2006 D: 1/1999 – 12/2005
2	P.S. 19	New York	10/2001 – 12/2006
2	Canal Street Post Office	New York	P: 1/1999 – 12/2006 D: 8/1999 – 9/2001
2	I.S. 155	Bronx	P: 1/1999 – 7/1999 D: 1/1999 – 7/1999
2	Morrisania II	Bronx	1/1999 – 12/2006
2	N.Y. Botanical Gardens	Bronx	1/1999 – 12/2006
2	I.S. 52	Bronx	P: 9/1999 – 12/2006* D: 9/1999 – 12/2006
2	Greenpoint	Kings	P: 1/1999 – 12/2000 D: 1/1999 – 7/1999
2	P.S. 321	Kings	1/1999 – 3/2003
2	P.S. 314	Kings	4/2000 – 1/2003
2	J.H.S. 126	Kings	1/2001 – 12/2006
2	Queensboro Community College	Queens	1/1999 – 12/2000
2	P.S. 29	Queens	P: 7/1999 – 1/2003 D: 8/1999 – 1/2003
2	P.S. 214	Queens	4/2000 – 3/2003
2	Queens College II/P.S. 219	Queens	1/2001 – 4/2006*
2	Susan Wagner H.S.	Richmond	1/1999 – 12/2006
2	Port Richmond Post Office	Richmond	12/1999 – 12/2006
3	Poughkeepsie	Dutchess	7/1999 – 3/2003
3	Newburgh	Orange	2/2000 – 12/2006
3	Mamaroneck	Westchester	2/2000 – 12/2006

Table 2. Annual average $PM_{2.5}$ levels for sites with at least 75% valid samples in a given year, 2000-2006. Incomplete years are left blank.

Site Name	2000	2001	2002	2003	2004	2005	2006
Hempstead	12.29	12.86	11.35	12.37	11.28	12.38	10.91
Briarcliffe	12.73	12.44	11.27				
Roslyn		12.25	11.28				
Babylon	12.66	13.02	11.43	11.78	10.68	12.09	10.41
Mabel Dean H.S.	16.71						
J.H.S. 45 (P)	15.52	15.18	14.12	14.35	13.12	14.51	12.63
J.H.S. 45 (D)							12.77
P.S. 59 (P)	18.42	17.95	15.88		15.63	16.96	14.60
P.S. 59 (D)	18.38	18.01	16.22		15.76	16.81	
P.S. 19			15.62	15.94	15.10	15.59	13.79
Canal Street Post Office (P)	17.57	17.13	15.42	15.76	14.43	15.45	12.76
Canal Street Post Office (D)	17.36						
Morrisania II	16.73	15.92	15.34	15.58	14.39	16.38	14.40
N.Y. Botanical Gardens	14.30	14.35	13.46	13.35	12.80	13.87	12.72
I.S. 52 (P)	15.10	15.65	14.25	14.76	13.72	13.78	12.84
I.S. 52 (D)	15.35	14.74	14.46	14.82	13.53	14.82	12.88
Greenpoint	16.30						
P.S. 321	14.88	15.06	13.28				
P.S. 314		16.29	13.95				
J.H.S. 126		15.24	14.04	14.19	14.06	15.08	12.97
Queensboro Community College		13.04					
P.S. 29 (P)	14.08	13.52					
P.S. 29 (D)	13.86	13.73					
P.S. 214		14.00	13.11				
Queens College II/P.S. 219			12.78	13.48	12.16	12.18	
Susan Wagner H.S.	12.44	13.00	10.84		11.35	12.15	10.45
Port Richmond Post Office	14.31	14.46	13.83		13.33	14.36	12.03
Poughkeepsie	11.31	11.18	10.73				
Newburgh	11.90	11.58	11.07	11.84	10.48	12.14	9.81
Mamaroneck	12.62	12.93	11.76	12.14	11.33	12.46	11.11

Table 3. The 98th percentile of $PM_{2.5}$ levels for sites with at least 75% valid samples in a given year, 2000-2006. Incomplete years are left blank.

Site Name	2000	2001	2002	2003	2004	2005	2006
Hempstead	32.1	31.2	31.9	39.3	30.8	35.1	33.0
Briarcliffe	34.0	32.5	30.7				
Roslyn		32.2	30.3				
Babylon	31.8	34.1	30.9	38.8	30.9	34.3	31.9
Mabel Dean H.S.	42.9						
J.H.S. 45 (P)	40.8	35.8	35.5	46.2	38.0	36.6	37.6
J.H.S. 45 (D)							37.8
P.S. 59 (P)	41.7	40.4	35.6		41.1	40.1	40.7
P.S. 59 (D)	42.1	39.8	35.5		41.4	39.5	
P.S. 19			35.8	48.5	38.9	36.5	36.8
Canal Street Post Office (P)	41.4	38.2	33.6	46.2	39.1	39.5	35.9
Canal Street Post Office (D)	41.0						
Morrisania II	40.1	36.7	35.2	44.8	38.2	37.7	41.5
N.Y. Botanical Gardens	39.0	35.0	33.4	38.2	31.3	36.6	39.8
I.S. 52 (P)	40.5	38.9	40.6	39.1	33.9	36.8	38.7
I.S. 52 (D)	40.3	35.2	36.8	46.0	38.2	38.0	38.1
Greenpoint	41.7						
P.S. 321	42.0	34.6	31.2				
P.S. 314		36.5	31.9				
J.H.S. 126		34.9	33.8	46.2	36.9	38.1	37.7
Queensboro Community College		32.8					
P.S. 29 (P)	35.7	36.2					
P.S. 29 (D)	38.0	35.8					
P.S. 214		36.8	33.0				
Queens College II/P.S. 219			37.4	39.0	33.4	34.0	
Susan Wagner H.S.	33.0	31.4	24.3		33.5	32.1	32.0
Port Richmond Post Office	39.8	31.9	39.3		31.3	37.2	36.2
Poughkeepsie	30.8	27.6	31.2				
Newburgh	29.8	27.8	30.5	31.3	27.4	29.6	31.7
Mamaroneck	34.9	33.5	32.5	36.8	33.5	32.8	34.4

Table 4. Trends in $PM_{2.5}$ mass at the longest running FRM monitors, based on quarterly averages from 1999-2006, in $\mu g\ m^{-3}\ yr^{-1}$. Only those quarters with at least 10 valid samples are included in this trend estimate.

Site Name	Trend ($\mu g\ m^{-3}\ yr^{-1}$)
Hempstead	-0.12
Babylon	-0.34
J.H.S. 45	-0.42
P.S. 59	-0.30
Canal Street Post Office	-0.50
Morrisania II	-0.27
N.Y. Botanical Gardens	-0.15
I.S. 52 (P)	-0.33
I.S. 52 (D)	-0.23
Susan Wagner H.S.	-0.13
Port Richmond Post Office	-0.20
Newburgh	-0.20
Mamaroneck	-0.20

Table 5. Listing of Speciation Trends Network (STN) sites, 2000-2006. All sites are located in NYSDEC Region 2.

Site Name	County	Dates
Canal Street Post Office	New York	8/2002 – 12/2006
N.Y. Botanical Gardens	Bronx	2/2000 – 12/2005
I.S. 52	Bronx	1/2001 – 12/2006
Queens College II/P.S. 219	Queens	4/2001 – 12/2006

Figure 1. Map of FRM sites.

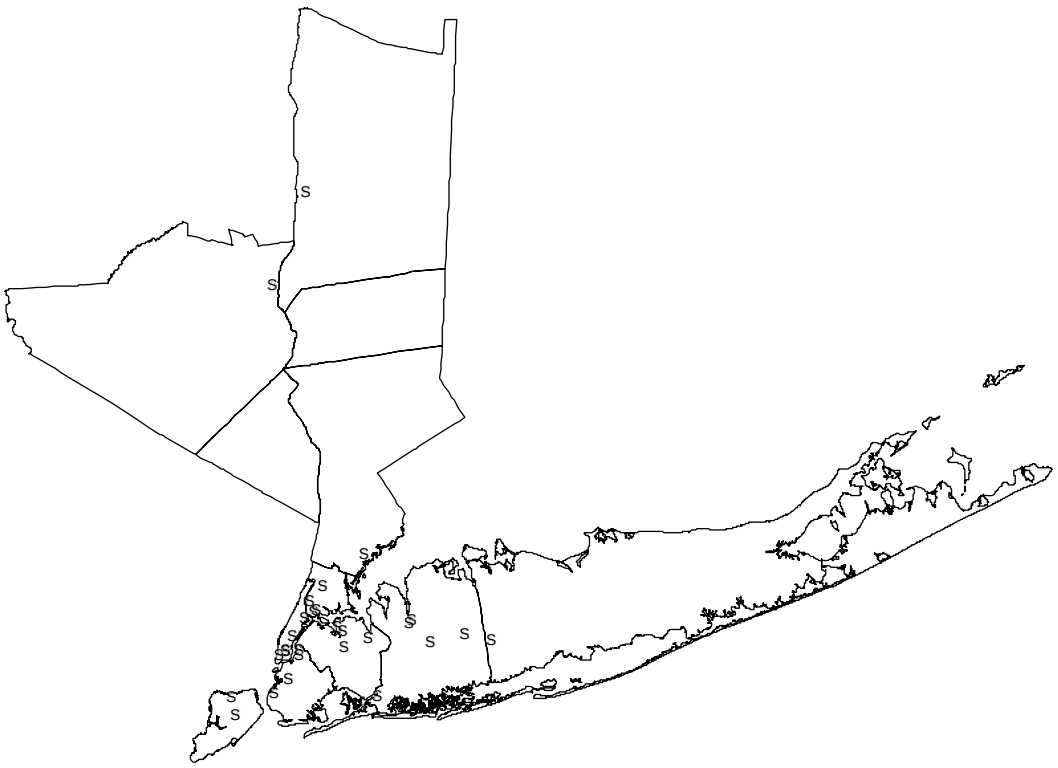

Figure 2. Annual average $PM_{2.5}$ mass at FRM sites by NYSDEC Region.

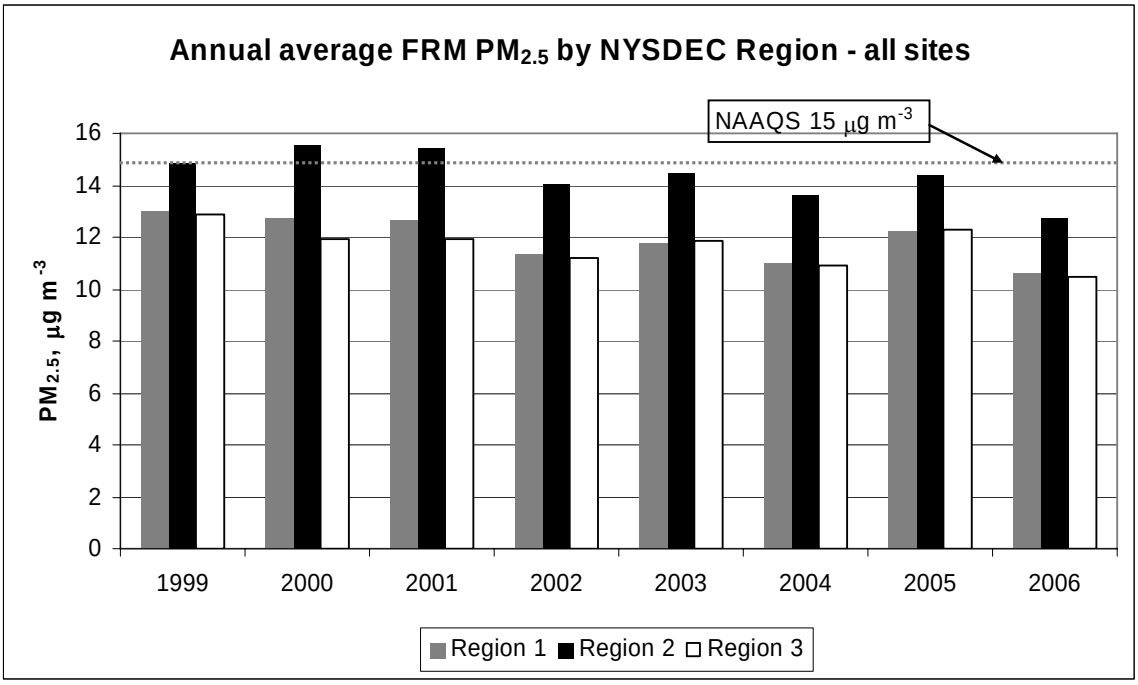

Figure 3. Seasonal variation in $PM_{2.5}$ mass at FRM sites, by NYSDEC Region.

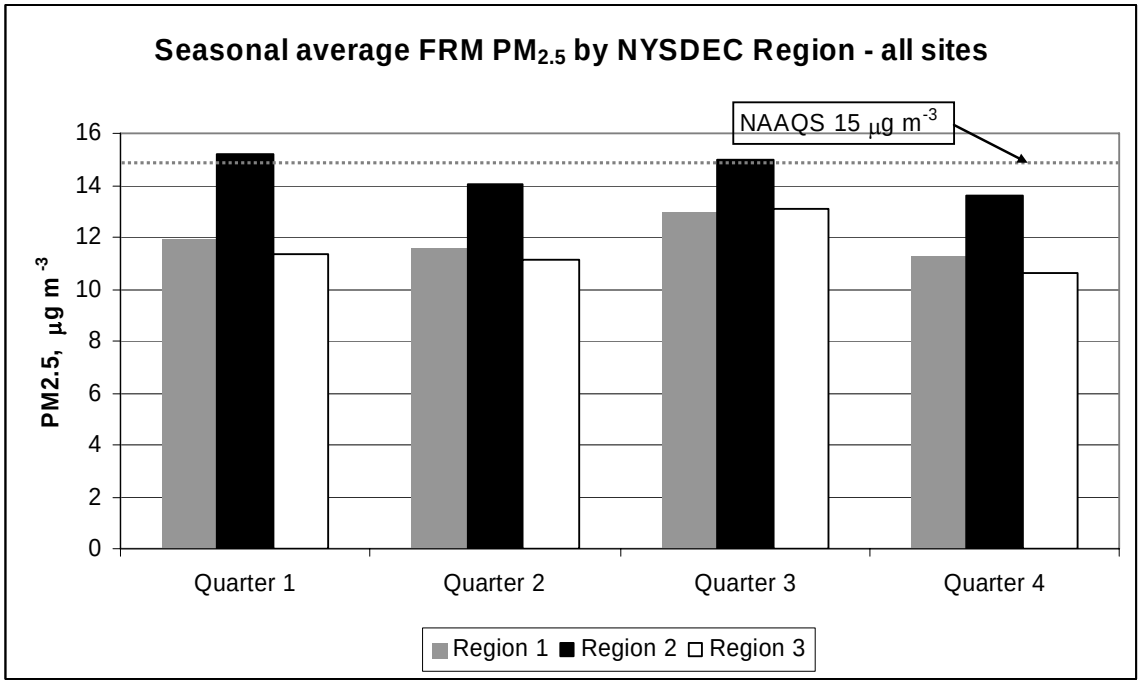

Figure 4. Average $PM_{2.5}$ speciation – annual, winter (DJF), and summer (JJA).