DRAFT For Comments (January 17, 2003)

Preliminary analysis of the speciated $PM_{2.5}$ and PM_{10} data at Whiteface Mountain and the Bronx (IS 52), 2001-2002

Kevin Civerolo and Gopal Sistla
New York State DEC
Division of Air Resources
Bureau of Air Research
625 Broadway, 2nd Floor
Albany, New York 12233-3259 USA

Introduction

One of the challenges facing fine particulate modeling efforts as part of the SIP process is the need to assess model performance and its associated limitations. Even though the $PM_{2.5}$ NAAQS is based on mass, the models predict individual components (sulfates, nitrates, carbon species, etc.) and, therefore, the model assessment should focus on these components rather than simply on the mass itself (USEPA, 2000). Thus, it is important to understand how the measurements of PM mass and species are obtained when comparisons are to be made with model predictions, since model simulations are used for developing mitigation measures aimed at meeting and maintaining the $PM_{2.5}$ NAAQS.

The current generation of models such as CMAQ, CAMx and others predict not only the fine particulate components and total $PM_{2.5}$ mass, but also the inhalable particulate (IP) fraction corresponding to aerodynamic diameter <10 μm. In this preliminary analysis, we examined the PM_{10} and $PM_{2.5}$ database consisting of measured mass and some of the speciated components at two sets of collocated monitors in New York state, in their utility for use in model assessment applications.

Database

The database consists of PM_{10} and $PM_{2.5}$ mass, as well as the corresponding sulfate (SO_4) and nitrate (NO_3) fractions covering the 2001-2002 period measured at IS52 in the Bronx and at the lodge level of Whiteface Mountain. The Bronx monitor is located is an urban area while the Whiteface Mountain monitor is at a remote, rural, elevated site. The PM_{10} monitors are operated following EPA guidelines on a one-in-six-day sampling schedule, while the $PM_{2.5}$ monitors follow a one-in-three-day schedule.

The filters were processed using routine procedures including their handling, storing and transport. The number of samples varied from about 60 at Whiteface Mountain to about 77 at Bronx, with the added restriction that the $PM_{2.5}$ and PM_{10} data considered are from the same day. In the case of PM_{10} the filter media is quartz, of which a part is used to obtain the SO_4 and NO_3 concentrations via colorimetry. The $PM_{2.5}$ sampler consists of a Teflon filter analyzed for mass and elements, a nylon filter for SO_4 and NO_3 concentrations obtained via ion chromatography (IC), and a quartz filter for carbon analysis.

It should be noted that in the case of PM_{10}, the samples were not refrigerated and, as such, high volatilization losses of some of the species such as NO_3 are expected to occur. In the case of $PM_{2.5}$, neither the mass nor the ion data were subject to blank signal adjustment. The $PM_{2.5}$ data were quality-assured with the following validity codes:

- laboratory environmental criteria out of limits
- laboratory holding times exceeded
- cation/anion total charge ratio out of limits
- laboratory error
- outlier invalidated by QAO based on level 1 check

In the case of PM_{10}, the data below the detection limit were not used in this analysis. It should be noted that while this is not an issue at the Bronx site, roughly 25-30% of the PM_{10} NO_3 data at Whiteface Mountain were below the detection limit. In this study we considered two sets of data comprising of (a) all quality-assured data regardless of the validity flag, and (b) only those data that were not flagged.

Analysis and discussion of the PM data

In this study, $PM_{2.5}$ and PM_{10} mass and speciated components are hereafter denoted as "fine" and "IP," respectively, and the statistical estimates were made for the following ratios.

- fine NO_3/fine mass
- fine SO_4/fine mass
- IP NO_3/IP mass
- IP SO_4/IP mass
- fine NO_3/IP NO_3
- fine SO_4/IP SO_4
- fine mass/IP mass

Tables 1-4 list the statistical summary estimates for the two sites. Following are a few of the observations that can be made based upon these summaries. At the urban Bronx site, NO_3 is about 14% of the total fine mass, while at the rural Whiteface Mountain site NO_3 is only about 3-8% of the fine mass. The SO_4 fraction of the fine particulate mass is slightly higher at Whiteface Mountain (~30%) compared to the Bronx (~24%). These results appear to be essentially unchanged when <u>all</u> of the data, including the screened data, were used. For reference, the statistical summary of the absolute concentrations of fine and IP mass and species at these two sites are included in Appendix A (see Tables A.1 and A.2).

In terms of the IP data, the fractions of NO_3 and SO_4 to the total mass were about 6% and 30%, respectively, at Whiteface Mountain. While the NO_3 fraction at the Bronx was also about 6%, the SO_4 fraction was only about 22% at this site. Since volatilization losses of NO_3 from the high-volume sampler filters can be large, caution must be exercised with these results.

Occasionally the fine-to-IP ratios of NO_3, SO_4, and mass are greater than unity. While such a ratio has no physical meaning, the data show that such ratios do occur. This may be due to sampling uncertainty, losses, etc, and it only takes 1 or 2 very high ratios to skew the statistics, as well. For example, at Whiteface Mountain on February 7, 2002, the ratio of fine-to-IP NO_3 was 34.9. All other data on this day appear to be valid; the IP NO_3 mass was 0.1 $\mu g\ m^{-3}$ while that for fine NO_3 mass was 3.49 $\mu g\ m^{-3}$. This may be an illustration of huge losses from the high-volume sampler and a high blank signal in the case of the fine filter. For SO_4 and PM mass, it appears that the fine mass fractions account for about 80-90% of the IP mass on average, with both ratios being slightly higher at Whiteface Mountain.

It should also be noted that in theory one could estimate the coarse fraction as the difference between the IP and fine. However, in this study such a step was not taken because the measurements were made with different instrumentation, and in some instances, the fine mass was found to exceed the IP mass at both locations. Also, in this study we did not perform any assessment of the organic carbon (OC), elemental or "black" carbon (EC), and elemental concentrations since there are no corresponding IP data.

Comparison with the IMPROVE network

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) network is a multi-agency program which tracks particulate and haze levels at federally protected Class I areas in mostly rural settings. Since the late 1980s, the IMPROVE program has reported 24-hour average (twice per week or every three days) fine particulate and IP mass on Teflon filters, as well as the fine particulate ion, carbon, and elemental fractions. Therefore, a similar analysis of the fine-to-IP ratios can be performed using these data.

We considered the data from 12 rural sites (Pennsylvania, New York, New Jersey, and New England) and one urban (Washington, DC) IMPROVE monitor through May 2002. Note that some of the time records are 10-15 years long, while some are <2 years, and only the data above the minimum detectable limits were used. Table 5 lists the basic statistics for the $PM_{2.5}/PM_{10}$ ratio at these 13 sites. Similar to the New York data, the statistical summaries of the absolute fine and IP mass concentrations at each site are presented in Appendix A (see Tables A.3 and A.4).

The mean ratios are generally in the 0.60-0.75 range, with the lowest mean ratio at Brigantine (0.52) and the highest mean ratios at Pinnacle (0.74) and Connecticut Hill (0.70). Measurement uncertainty, at times, may cause this ratio to exceed unity. Observed ratios >1, having no physical meaning, were observed at eight of the 13 sites – Acadia (9 times out of 1379 total data points), Brigantine (1 time out of 966 total data points), Connecticut Hill (1 time out of 135 total data points), Lye Brook (20 times out of 819 total data points), Mohawk Mountain (1 time out of 79 total data points), Moosehorn (7 times out of 729 total data points), Proctor (1 time out of 144 total data points), and Washington, DC (11 times out of 1265 total data points). Combined, only 51 of 5516 times did the ratio exceed unity. Of these 51 points, the ratio exceeded 1.1 only three times – Lye Brook (twice) and Acadia (once). The observed fine and IP levels on these three days were rather low, ~2 $\mu g\ m^{-3}$. Also, 36 of the 51 high ratios occurred during the colder months, October through April.

Since the fine and IP mass are collected on Teflon filters with similar sampling conditions, the ratio of fine-to-IP mass rarely exceeds unity at these eastern US, and never by more than about 20%. That the ratio can occasionally exceed unity, especially at low concentrations, is not unexpected since the reported precision and accuracy of the measurements are at least ±5% (IMPROVE, 2002). However, it appears that the IMPROVE fine and IP measurements are more consistent than the New York data, which are obtained on different filters, with different flow conditions and sampling schedules.

Summary

In this analysis, we examined various ratios rather than the absolute levels. Even at collocated stations the ratio of fine and IP data gives rise to the values that are > 1, suggesting that it is important to ensure the validity of the data before utilizing such data in any model assessment. Unlike national monitoring programs such as IMPROVE, which report both fine and IP mass using nearly identical procedures, the DEC fine particulate monitoring network does not measure IP; rather, IP is measured with different methods at some these sites. An end-user interested in performing PM model evaluation might be inclined to use both the $PM_{2.5}$ data and the collocated IP data, even though these networks were established at different times, with different sampling, handling, and analysis protocols. The fact that the fine particulate and IP monitors are collocated does not necessarily ensure that the data are internally consistent. We suggest that the NO_3 data from the high-volume IP samplers be flagged as questionable. Since there is a need to compare both the IP and fine particulate concentrations in model assessment work, it is recommended that these measurement programs, both in New York and the other NESCAUM and MANE-VU states, should consider adopting common/similar monitoring platforms, protocols and procedures for sample handling as well as chemical component analysis.

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References

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USEPA (2000), Guidance for demonstrating attainment of air quality goals for $PM_{2.5}$ and regional haze (Draft), available at http://www.epa.gov/scram001/guidance/guide/draft_pm.pdf.

Table 1. Statistical summary of various ratios at the Whiteface Mountain site, 5/2001 - 7/2002. The valid flagged $PM_{2.5}$ data **are** included.

	fine NO_3/ fine PM	fine SO_4/ fine PM	IP NO_3/ IP PM	IP SO_4/ IP PM	fine NO_3/ IP NO_3	fine SO_4/ IP SO_4	fine PM/ IP PM
mean	0.078	0.292	0.057	0.316	2.346	0.966	0.849
median	0.037	0.279	0.059	0.300	0.900	0.786	0.767
minimum	0.005	0.009	0.009	0.049	0.125	0.070	0.354
maximum	0.485	0.515	0.200	0.800	34.900	10.512	2.820
standard deviation	0.092	0.115	0.041	0.157	5.793	1.405	0.387
N	60	60	38	54	35	49	50

Table 2. Statistical summary of various ratios at the Whiteface Mountain site, 5/2001 - 7/2002. The valid flagged $PM_{2.5}$ data **are not** included.

	fine NO_3/ fine PM	fine SO_4/ fine PM	IP NO_3/ IP PM	IP SO_4/ IP PM	fine NO_3/ IP NO_3	fine SO_4/ IP SO_4	fine PM/ IP PM
mean	0.080	0.298	0.057	0.316	2.346	1.012	0.860
median	0.033	0.313	0.059	0.300	0.900	0.803	0.756
minimum	0.005	0.009	0.009	0.049	0.125	0.070	0.354
maximum	0.485	0.515	0.200	0.800	34.900	10.512	2.820
standard deviation	0.102	0.122	0.041	0.157	5.793	1.534	0.402
N	45	40	38	54	35	41	37

Table 3. Statistical summary of various ratios at the Bronx site, 1/2001 - 7/2002. The valid flagged $PM_{2.5}$ data **are** included.

	fine NO_3/ fine PM	fine SO_4/ fine PM	IP NO_3/ IP PM	IP SO_4/ IP PM	fine NO_3/ IP NO_3	fine SO_4/ IP SO_4	fine PM/ IP PM
mean	0.135	0.236	0.074	0.219	2.470	0.872	0.805
median	0.142	0.245	0.053	0.218	1.775	0.860	0.798
minimum	0.016	0.020	0.003	0.022	0.055	0.040	0.071
maximum	0.265	0.355	0.748	0.400	11.500	2.200	1.612
standard deviation	0.067	0.073	0.090	0.067	2.116	0.246	0.248
N	73	73	77	77	72	72	70

Table 4. Statistical summary of various ratios at the Bronx site, 1/2001 - 7/2002. The valid flagged $PM_{2.5}$ data **are not** included.

	fine NO_3/ fine PM	fine SO_4/ fine PM	IP NO_3/ IP PM	IP SO_4/ IP PM	fine NO_3/ IP NO_3	fine SO_4/ IP SO_4	fine PM/ IP PM
mean	0.138	0.244	0.074	0.219	2.473	0.860	0.803
median	0.144	0.250	0.053	0.218	1.750	0.859	0.797
minimum	0.016	0.103	0.003	0.022	0.055	0.040	0.478
maximum	0.265	0.355	0.748	0.400	11.500	2.200	1.458
standard deviation	0.067	0.061	0.090	0.067	2.130	0.241	0.195
N	68	64	77	77	71	68	65

Table 5. Statistical summary of the ratio of fine particulate to IP mass ratios at selected IMPROVE sites in the eastern US.

site	mean	median	minimum	maximum	standard deviation	N
Pinnacle SP, NY	0.743	0.760	0.277	0.992	0.142	136
Connecticut Hill, NY	0.740	0.744	0.304	1.019	0.138	135
Acadia NP, ME	0.620	0.627	0.00	1.119	0.189	1379
Moosehorn NWR, ME	0.626	0.627	0.130	1.076	0.170	729
Proctor Maple RF, VT	0.690	0.699	0.346	1.019	0.137	144
Lye Brook, VT	0.715	0.730	0.176	1.189	0.169	819
Great Gulf, NH	0.618	0.639	0.111	0.993	0.169	363
Mohawk Mt., CT	0.702	0.695	0.136	1.029	0.155	79
Quabbin Reservoir, MA	0.687	0.679	0.211	0.955	0.136	128
Arendtsville, PA	0.686	0.696	0.181	0.928	0.142	133
MK Goddard SF, PA	0.720	0.723	0.300	0.953	0.111	136
Brigantine NWR, NJ	0.524	0.526	0.027	1.023	0.169	966
Washington, DC	0.715	0.724	0.00	1.057	0.141	1265

Appendix A. Statistical summaries of the New York and IMPROVE particulate data. All valid data, assembled from common sampling days, are included in these summaries unless otherwise specified.

Table A.1. Statistical summary of fine particulate and IP NO_3, SO_4, and mass ($\mu g\ m^{-3}$) at the Whiteface Mountain site, 5/2001 – 7/2002.

site	mean	median	minimum	maximum	standard deviation	N
Fine NO_3, all valid flagged $PM_{2.5}$ data are included	0.52	0.16	0.00	3.90	0.85	62
Fine NO_3, valid flagged $PM_{2.5}$ data are not included	0.52	0.16	0.00	3.90	0.85	62
Fine SO_4, valid flagged $PM_{2.5}$ data are included	2.55	1.18	0.08	17.87	3.59	62
Fine SO_4, valid flagged $PM_{2.5}$ data are not included	2.85	1.39	0.08	17.87	3.84	52
Fine mass, valid flagged $PM_{2.5}$ data are included	9.40	5.10	1.49	126.99	17.03	61
Fine mass, valid flagged $PM_{2.5}$ data are not included	11.34	5.98	1.62	126.99	19.14	36
IP NO_3	0.29	0.30	0.10	0.90	0.17	38
IP SO_4	2.54	1.55	0.60	20.30	3.16	54
IP mass	8.27	5.50	1.00	36.00	7.30	56

Table A.2. Statistical summary of fine particulate and IP NO_3, SO_4, and mass ($\mu g\ m^{-3}$) at the Bronx site, 1/2001 – 7/2002.

site	mean	median	minimum	maximum	standard deviation	N
Fine NO_3, valid flagged $PM_{2.5}$ data are included	2.54	1.94	0.07	8.69	2.13	75
Fine NO_3, valid flagged $PM_{2.5}$ data are not included	2.51	1.93	0.07	8.69	2.13	74
Fine SO_4, valid flagged $PM_{2.5}$ data are included	3.94	3.20	0.18	12.18	2.42	75
Fine SO_4, valid flagged $PM_{2.5}$ data are not included	3.99	3.17	0.18	12.18	2.46	70
Fine mass, valid flagged $PM_{2.5}$ data are included	17.43	14.32	1.20	81.96	12.00	73
Fine mass, valid flagged $PM_{2.5}$ data are not included	17.60	13.88	5.23	81.96	12.14	66
IP NO_3	1.67	0.90	0.20	24.70	2.95	77
IP SO_4	4.53	3.70	1.10	15.20	2.68	77
IP mass	21.10	17.00	8.00	91.00	11.99	77

Table A.3. Statistical summary of fine particulate mass (μg m^{-3}) at selected IMPROVE sites in the eastern US.

site	mean	median	minimum	maximum	standard deviation	N
Pinnacle SP, NY	9.27	6.66	1.64	54.56	8.08	136
Connecticut Hill, NY	8.40	6.25	1.52	52.49	7.16	135
Acadia NP, ME	6.68	5.14	0.00	45.58	5.39	1441
Moosehorn NWR, ME	5.61	4.63	0.59	31.42	3.73	742
Proctor Maple RF, VT	6.79	5.28	0.52	32.90	5.15	287
Lye Brook, VT	6.82	4.95	0.00	43.20	6.03	966
Great Gulf, NH	6.45	4.58	0.58	37.22	5.27	395
Mohawk Mt., CT	6.30	5.14	0.94	25.61	4.37	79
Quabbin Reservoir, MA	7.33	5.73	0.78	29.09	5.65	131
Arendtsville, PA	11.40	9.15	1.93	38.88	7.09	133
MK Goddard SF, PA	11.22	8.59	1.94	50.09	8.54	136
Brigantine NWR, NJ	11.11	9.43	0.00	60.55	6.66	1064
Washington, DC	16.76	15.14	0.00	56.32	8.49	1341

Table A.4. Statistical summary of IP mass (μg m^{-3}) at selected IMPROVE sites in the eastern US.

site	mean	median	minimum	maximum	standard deviation	N
Pinnacle SP, NY	12.20	9.69	2.26	54.88	8.94	136
Connecticut Hill, NY	11.04	8.77	2.22	52.94	7.97	136
Acadia NP, ME	10.98	8.99	0.92	88.47	8.01	1403
Moosehorn NWR, ME	8.97	7.97	1.20	40.07	4.94	742
Proctor Maple RF, VT	8.55	6.94	0.71	36.20	6.20	144
Lye Brook, VT	9.20	7.34	0.45	51.77	6.81	853
Great Gulf, NH	10.38	8.66	0.76	53.36	7.48	370
Mohawk Mt., CT	9.47	8.05	1.28	33.82	6.60	79
Quabbin Reservoir, MA	10.27	8.78	0.88	33.54	6.65	128
Arendtsville, PA	17.02	14.91	2.48	46.81	9.25	136
MK Goddard SF, PA	15.10	12.36	3.24	55.84	9.87	136
Brigantine NWR, NJ	22.07	19.30	2.27	144.08	12.64	978
Washington, DC	23.50	21.14	4.02	73.80	10.71	1280