Appendix B 2

LADCO Winter Nitrate Study (Draft)

Table 4-1:Summary Statistics for Milwaukee Site During WNS (All Hours). Table Contains Revised Data Only

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
PM2.5	µg m^{-3}	17.1	11.4	2142	-2.9	5.5	8.7	14.4	22.7	32.7	72.7
NOx	ppb	22.7	23.3	2033	5.0	5.0	10.0	17.0	29.0	43.0	304.0
Temp	C	-2.7	7.5	2160	-23.6	-12.1	-8.3	-2.5	2.5	6.3	24.2
Wind Speed	m/s	3.0	1.3	2160	0.3	1.3	2.0	3.0	3.8	4.7	8.0
Wind Direction	Degrees	NA	NA	2160	0			see wind rose			360
NOy	ppb	26.5	24.3	1849	2.1	7.8	12.8	19.9	32.9	48.1	342.4
O3	ppb	22.2	10.7	2135	2.0	7	14	23	31	35	53
NO	ppb	6.6	15.8	2105	-1.0	0.0	1.0	2.0	7.0	13.0	254.0
NO2	ppb	16.3	10.1	2105	2.0	5.0	9.0	14.0	23.0	31.0	57.0
SO4	µg m^{-3}	2.03	1.57	1668	-0.50	0.49	0.97	1.72	2.80	3.81	14.53
NO3	µg m^{-3}	4.35	4.37	1742	-0.20	0.49	1.17	3.03	6.18	10.09	35.48
NH4	µg m^{-3}	2.13	1.73	1793	0.01	0.39	0.85	1.75	2.96	4.14	11.35
NH3	ppb	2.27	1.84	1683	0.29	0.61	0.97	1.71	3.00	4.74	18.48
TNO3	µg m^{-3}	5.57	5.20	1604	-0.80	0.78	1.72	3.96	7.90	13.07	42.17
TNH3	µg m^{-3}	3.28	2.61	1575	-0.51	0.49	1.31	2.82	4.70	6.64	18.62
HNO3	ppb	0.49	1.02	1604	-0.60	-0.14	0.02	0.24	0.60	1.28	14.13
Dry Bulb Temp	C	-2.90	7.48	2159	-24.25	-12.01	-8.30	-2.83	2.20	6.00	23.30
Wet Bulb Temp	C	-4.75	6.79	2159	-24.65	-13.21	-9.80	-4.54	0.42	3.55	14.20
RH (Mitchell Airport)	0-100	64.4	13.6	2159	22.0	47.0	55.1	64.6	73.7	83.0	98.5
Pressure	mbar	991.9	9.6	2159	964.3	979.2	985.3	992.1	999.8	1004.7	1013.8
Rainfall	mm/hr	0.08	0.43	2160	0.0	0.00	0.00	0.00	0.00	0.00	6.86
PM2.5, 24 hr	µg m^{-3}	18.3	11.0	29	4.2	4.9	10.3	17.2	21.1	39.0	49.7
NO3, 24 hr	µg m^{-3}	4.9	4.4	28	0.5	0.7	2.2	3.4	6.4	13.3	17.4
SO4, 24 hr	µg m^{-3}	2.2	1.2	28	0.8	1.0	1.4	2.0	2.8	4.0	5.9
NH4, 24 hr	µg m^{-3}	2.3	1.8	28	0.4	0.4	1.0	2.0	3.0	5.0	8.0
EC[a]	µg m^{-3}	0.52	0.69	28	0.12	0.1	0.3	0.4	0.5	0.8	4.0
OC[a]	µg m^{-3}	5.1	7.9	28	1.2	1.9	2.3	3.1	5.1	6.8	45.1
EC/OC[a]	Unitless	0.11	0.04	28	0.04	0.05	0.08	0.11	0.14	0.16	0.20
EC[b]	µg m^{-3}	0.39	0.20	27	0.12	0.1	0.3	0.4	0.5	0.7	0.83
OC[b]	µg m^{-3}	3.6	1.8	27	1.2	1.9	2.2	3.1	5.1	6.3	7.8
EC/OC[b]	Unitless	0.11	0.04	27	0.04	0.05	0.07	0.12	0.14	0.16	0.20
NH3	ppb	1.9	1.0	27	0.7	0.9	1.2	1.6	2.4	3.1	5.3
HNO3	ppb	0.3	0.2	27	0.09	0.1	0.15	0.21	0.35	0.5	0.83
SO2	ppb	0.7	1.1	28	0.09	0.12	0.17	0.33	0.92	1.66	5.02

[a] includes Jan 22 OC and EC values

[b] does not include Jan 22 OC and EC values. While the OC and EC statistics change significantly, the EC/OC ratio on Jan 22 (0.09) is similar to the mean (0.11) and median (0.11) ratios, so the overall mean, median, and distribution stay almost unchanged.

Table 4-2. Summary Statistics for Mayville Site During WNS (All Hours). Table Contains Revised Data Only

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
PM2.5	µg m^{-3}	11.7	8.8	2148	-2.7	2.9	5.2	9.6	16.4	23.6	63.1
PM2.5b	µg m^{-3}	11.5	9.4	1979	-6.3	2	4.9	9.31	16.1	24.7	62.8
SO2	ppb	1.5	1.2	2019	0.1	0.4	0.8	1.3	2.0	3.0	13.8
Temp	Deg C	-5.3	8.4	2160	-28.3	-15.5	-11.7	-5.4	1	5.6	21.4
Wind Speed	m/s	3.9	6.1	2160	-49.6	2.0	3.1	4.3	5.9	7.3	11.3
Wind Direction	Degrees	NA	NA	2160	0			see wind rose			360
RH	0-100	72.2	14.4	2160	30.0	53.0	62.0	72.0	83.0	93.0	96.0
Dew Point	Deg C	-9.7	8.5	2160	-32.2	-21.0	-16.2	-9.3	-3.2	1.2	9.2
NOy	ppb	6.3	4.6	2075	1.1	2.4	3.3	5.3	7.9	11.5	57.2
O3	ppb	30.8	7.6	2038	0	21.0	26.0	31.0	36.0	39.0	58.0
SO4	µg m^{-3}	2.20	1.7	1809	-0.5	0.4	1.0	1.9	3.1	4.3	10.1
NO3	µg m^{-3}	3.3	3.6	1816	-0.2	0.2	0.6	2.0	4.6	7.9	27.3
NH4	µg m^{-3}	2.1	1.8	1800	0.0	0.4	0.7	1.5	2.9	4.3	12.6
NH3	ppb	2.4	2.2	1990	0.3	0.6	0.8	1.7	3.0	5.2	16.2
TNO3	µg m^{-3}	4.8	3.6	1679	-0.2	1.1	2.1	3.6	7.2	9.9	22.1
TNH3	µg m^{-3}	3.3	2.2	1673	0.5	1.1	1.6	2.6	4.5	6.4	12.1
HNO3	ppb	0.2	0.5	1679	-0.9	-0.2	-0.1	0.1	0.4	0.8	4.9
Dry Bulb Temp	Deg C	-5.0	8.3	2157	-28.6	-15.4	-11.3	-5.2	1.31	5.17	20.9
Wet Bulb Temp	Deg C	-6.5	7.6	2157	-28.8	-16.1	-12.3	-6.5	-0.5	3.1	14.1
RH	0-100	69.2	12.3	2157	27.3	52.4	60.6	69.0	78.2	85.9	95.9
Pressure	mbar	987.6	9.6	2157	960.2	974.5	981.0	987.9	995.0	1000.7	1010.0
PM2.5, 24 hr	µg m^{-3}	15.8	8.9	30	4.2	6.9	9.9	14.4	17.5	32.2	38
NO3, 24 hr	µg m^{-3}	4.9	4.1	27	0.6	1.3	1.8	3.5	6.5	11.9	14.4
SO4, 24 hr	µg m^{-3}	2.25	0.9	27	0.9	1.2	1.6	2.0	2.8	3.3	4.8
NH4, 24 hr	µg m^{-3}	2.2	1.6	27	0.1	0.6	1.2	1.7	3.1	4.6	6.3
EC, 24 hr	µg m^{-3}	0.3	0.2	28	0.1	0.1	0.1	0.3	0.4	0.5	0.6
OC, 24 hr	µg m^{-3}	3.2	2.1	28	1.1	1.2	1.9	2.9	4	5.4	11.8
NH3, 24 hr	ppbv	2.2	1.7	27	0	0.7	1.0	1.7	3.3	4.5	7.6
EC/OC	Unitless	0.09	0.03	27	0.01	0.04	0.07	0.09	0.12	0.13	0.14
HNO3, 24 hr	ppbv	0.2	0.1	27	0	0.06	0.08	0.2	0.2	0.4	0.5
SO2, 24 hr	ppbv	0.4	0.4	27	0	0.1	0.2	0.3	0.5	0.9	2.2

Table 4-3. Summary Statistics for Jefferson St. Site (Atlanta, GA) (All Hours).

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
SO4	µg m^{-3}	2.6	1.7	2391	-0.1	0.81	1.4	2.2	3.2	4.6	15.2
NO3	µg m^{-3}	1.4	1.4	2357	-0.1	0.2	0.4	1.1	2.0	3.0	10.9
NH4	µg m^{-3}	1.3	0.9	2460	-0.01	0.4	0.8	1.2	1.7	2.4	6.3
HNO3	ppb	0.3	0.2	2207	-0.1	0.06	0.1	0.2	0.3	0.5	2.0
NH3	ppb	1.1	0.8	2323	0.02	0.4	0.6	1.0	1.5	2.1	6.2
O3	ppb	19.7	12.4	2529	-0.8	1.6	8.3	18.7	27.6	35.5	57.7
CO	ppb	306.2	238.6	2444	104.1	162.6	191.8	233.8	311.8	491.3	2265.9
SO2	ppb	3.1	6.1	2463	0	0.3	0.7	1.5	3.2	8.4	86.3
NO	ppb	17.2	44.8	2525	0.01	0.4	1.1	3.4	10.7	37.3	397.4
NO2	ppb	16.7	10.5	2512	1.2	5.4	8.6	13.8	22.4	32.3	61.8
NOx	ppb	32.6	46.7	2511	1.6	6.6	10.7	17.5	33.2	62.2	431.1
NOy	ppb	35.4	53.6	2523	1.9	7.4	11.6	18.3	34.1	69.2	422.0
Wind Speed	m/s	2.0	1.1	2535	0.07	0.7	1.2	1.9	2.7	3.5	5.6
Wind Direction	Degrees	212	91	2538	1.	see wind rose					360
Temperature	Deg C	9.2	7.2	2542	-11.7	-1.3	3.6	8.7	13.8	17.6	27.6
RH %	Unitless	66.7	23.8	2541	17.11	32.9	46.7	67.0	88.6	98.2	101.4
Station Pressure	mbar	985.6	6.3	2540	964.5	977.6	982.8	986.6	989.9	993.1	1002.21
Solar Radiation	W m-2	125.8	204.1	2542	-1.0	0.2	0.3	0.8	147.0	494.5	801.4
Rainfall	mm	57.3	43.8	2539	0	0	1.52	24.13	63.5	119.1	173.4
PM2.5	µg m^{-3}	11.7	6.8	2463	1.3	4.7	6.8	10.3	15.2	21.3	51.0
BC	µg m^{-3}	0.7	0.7	1732	0	0.18	0.34	0.56	0.91	1.43	6.19
TC	µg m^{-3}	4.5	3.9	2324	0.2	1.5	2.0	3.3	5.7	9.8	36.8
OC	µg m^{-3}	4.2	3.7	1589	0.1	1.2	1.8	3.1	5.4	9.4	35.3
BC / OC	Unitless	0.18	0.12	1613	0.04	0.10	0.13	0.18	0.25	0.34	1.9

Table 4-4. Summary Statistics for Yorkville, GA (All Hours)

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
SO4	µg m^{-3}	2.33	1.54	2729	-0.21	0.66	1.19	2.07	3.13	4.30	10.46
NO3	µg m^{-3}	1.04	1.15	2773	-0.06	0.12	0.26	0.69	1.44	2.32	10.32
NH4	µg m^{-3}	1.15	0.74	2778	0	0.34	0.63	1.05	1.49	2.05	5.98
HNO3	ppb	0.28	0.26	2846	-0.05	0.04	0.11	0.20	0.37	0.62	2.05
NH3	ppb	2.06	3.41	2810	0.09	0.3	0.66	1.21	2.32	4.11	68.69
O3	ppb	31.62	11.57	2869	-0.04	16.41	24.15	31.97	39.05	45.70	68.40
CO	ppb	176.34	44.48	2642	82.52	129.67	148.77	168.91	195.22	230.63	452.33
SO2	ppb	1.54	2.71	2864	-0.01	0.10	0.34	0.88	1.86	3.36	59.07
NO	ppb	0.40	1.32	2877	-0.05	-0.01	0	0.02	0.25	1.01	25.26
NO2	ppb	3.08	3.17	2875	0.13	0.67	1.11	2.02	3.79	6.983	31.12
NOx	ppb	3.5	4.0	2874	0.2	0.7	1.2	2.2	4.3	7.4	43.1
NOy	ppb	4.8	4.3	2874	0.21	1.5	2.2	3.5	5.9	9.3	45.1
Wind Speed	m/s	3.4	1.6	2888	0.2	1.4	2.2	3.3	4.5	5.6	10.5
Wind Direction	Degrees	217	92	2891	0	114	149	212	305	338	360
Temperature	Degree C	8.1	7.1	2893	-13.3	-1.8	3.2	8.6	13.8	16.8	25.3
RH %	Unitless	70.0	23.2	2895	19.8	37.8	50.2	70.4	92.5	100.3	103.0
Station Pressure	mbar	972.4	6.3	2879	951.6	963.6	969.4	973.4	976.5	989.4	988.9
Solar Rad	W m^{-2}	128.3	215.4	2896	0	1.0	1.1	1.5	162.5	512.0	926.5
Rainfall	mm	27.11	32.60	2889	0	0	2.03	10.67	41.15	82.80	120.40
PM 2.5	µg m^{-3}	11.0	5.9	2651	1.2	4.8	7.2	9.9	13.6	18.5	59.4
BC	µg m^{-3}	0.3	0.3	2626	0.01	0.1	0.1	0.2	0.4	0.6	2.2
TC	µg m^{-3}	2.4	2.1	2848	0.1	0.8	1.2	1.9	3.0	4.9	22.0
OC	µg m^{-3}	2.2	1.9	2574	0.01	0.7	1.1	1.7	2.6	4.2	19.8
BC / OC	Unitless	0.16	0.37	1872	0.03	0.07	0.09	0.13	0.17	0.24	15.8

4.3 Episode Identification

Episodes were defined as periods where the smoothed $PM_{2.5}$ hourly (7 hour running average) concentration exceeded 27 μg m^{-3} for 4 or more consecutive hours. The detailed procedure for episode identification and the detailed episode list can be found in appendix 1. A low threshold was selected for episodes (27 threshold instead of 35 or 35.5 μg m^{-3} and 4 hour duration rather than 24 hour duration) to increase the number of episodes isolated for study. The rationale behind this is that the meteorology and chemistry contributing to PM levels of 27-35.5 μg m^{-3} may be very similar to that causing full 24 hour values in excess of 35.5. Alternate thresholds of 26, 28, etc. would serve the same purpose.

The Milwaukee site had the highest number of episodes (13), while the Mayville site had 7 episodes. All episodes that occurred at Mayville also had a concurrent Milwaukee episode. Therefore episodes could be classified as "shared" between the two sites or "Milwaukee only." The exact start and end times of shared episodes were not identical.

The urban Atlanta site (Jefferson St.) experienced 6 episodes using the same episode definition, and the rural Atlanta site (Yorkville) experienced 2 episodes. Similar to the Wisconsin sites, episodes were either shared or urban only. There were no rural only episodes.

The episodes are shown in a $PM_{2.5}$ time series for the Wisconsin sites, and in a $PM_{2.5}$ time series for the Georgia sites.

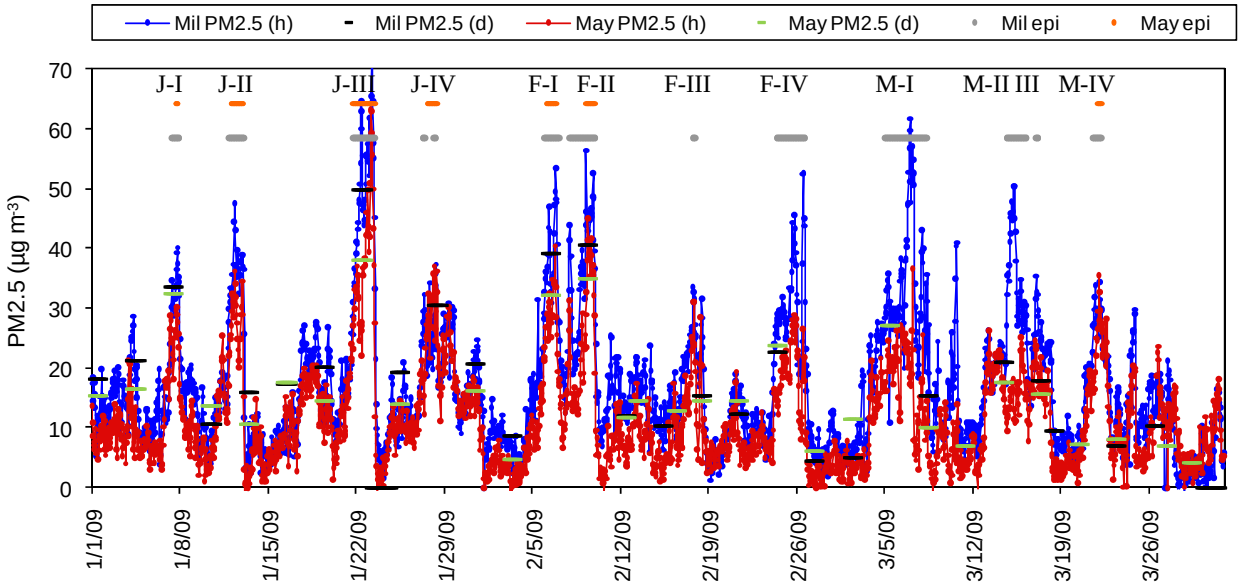


Figure 4-5. Hourly and daily $PM_{2.5}$ at the Wisconsin sites. Blue (hourly) and black (24 hr) PM2.5 concentrations are shown for Milwaukee. Red (hourly) and green (daily) PM2.5 concentrations are for Mayville. Grey and orange bands indicate hours that have been designated as episode hours. Grey is for Milwaukee while orange is for Mayville. The episode number is indicated above the episode bands, with J-I being Jan-I, F-I for Feb-I, and M-I for Mar-I.

Similar figure for Jeff St / Yorkville under preparation.

Table 4-5. Summary table for Wisconsin episodes – see appendix 1 for more detail

			Milwaukee		Mayville	
Episode Name	Start Day	End Day	Peak 7hr $PM_{2.5}$	Avg. $PM_{2.5}$ during period	Peak 7hr $PM_{2.5}$	Avg. $PM_{2.5}$ during period
JAN-I	7-Jan	7-Jan	36.4	33.6	30.1	29.0
JAN-II	11-Jan	13-Jan	40.1	36.1	36.2	28.7
JAN-III	21-Jan	23-Jan	64.5	50.3	55.0	37.9
JAN-IV	27-Jan	27-Jan	28.1	28.9		
JAN-V	27-Jan	28-Jan	31.4	31.4	32.3	30.5
FEB-I	5-Feb	7-Feb	47.0	37.6	34.3	30.7
FEB-II	7-Feb	10-Feb	47.5	35.4	40.3	36.9
FEB-III	17-Feb	17-Feb	29.8	30.3		
FEB-IV	24-Feb	26-Feb	41.9	31.3		
MAR-I	5-Mar	8-Mar	54.6	33.8		
MAR-II	14-Mar	16-Mar	47.2	35.5		
MAR-III	17-Mar	17-Mar	30.8	31.6		
MAR-IV	21-Mar	22-Mar	30.0	29.4	29.8	29.8

Table 4-6. Summary table for Atlanta episodes – see appendix 1 for more detail

			Atlanta		Yorkville	
Episode Name	Start Day	End Day	Peak 7hr $PM_{2.5}$	Avg. $PM_{2.5}$ during period	Peak 7hr $PM_{2.5}$	Avg. $PM_{2.5}$ during period
JAN-A	22-Jan	23-Jan	32.5	33.7		
JAN-B	26-Jan	26-Jan	28.8	28.6		
FEB-A	7-Feb	7-Feb	30.0	30.6		
FEB-B	8-Feb	10-Feb	31.9	27.3	31.2	29.0
FEB-C	24-Feb	26-Feb	38.1	32.2	46.2	31.9
MAR-A	10-Mar	11-Mar	28.8	29.1		

4.4 Diurnal Patterns

A complete printout of diurnal averaged patterns for both the Atlanta and Wisconsin sites can be found in the appendix. Some representative patterns are repeated here and discussed in subsequent sections.

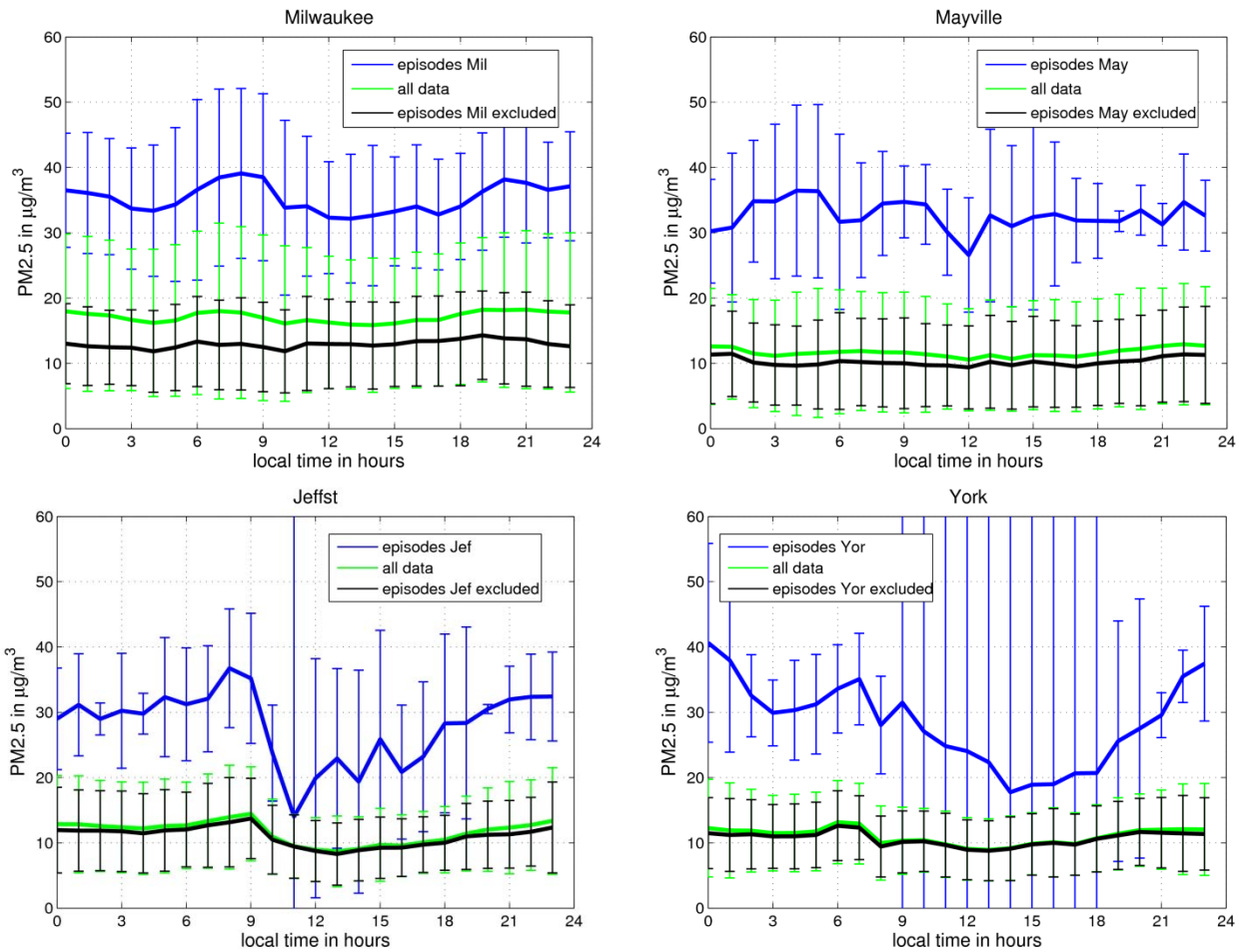


Figure 4-6. Diurnal pattern for $PM_{2.5}$ in urban sites (left), rural sites (left), Wisconsin sites (top) and Georgia sites (bottom).

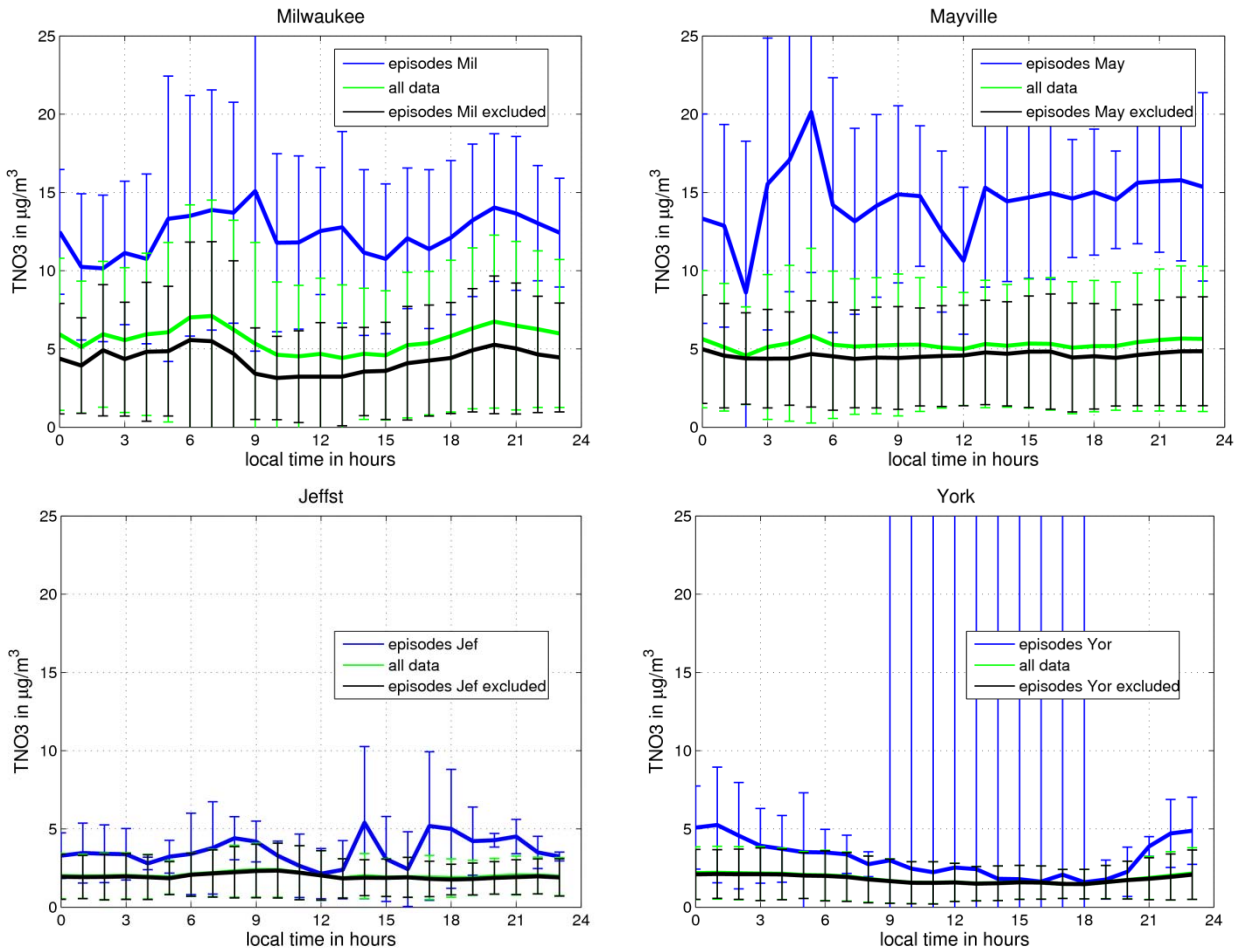


Figure 4-7. Diurnal pattern for total nitrate in urban sites (left), rural sites (left), Wisconsin sites (top) and Georgia sites (bottom).

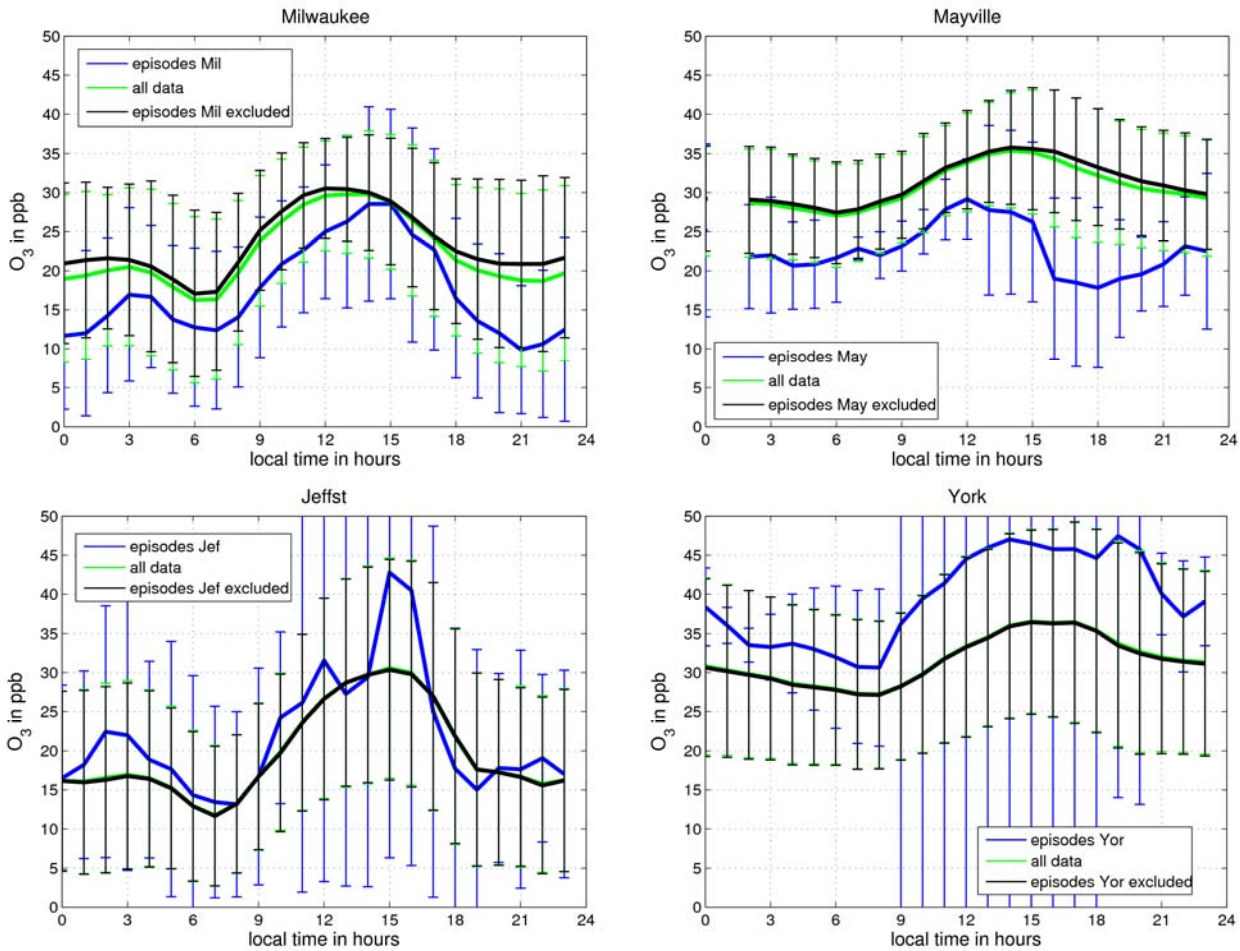


Figure 4-8. Diurnal pattern for ozone in urban sites (left), rural sites (left), Wisconsin sites (top) and Georgia sites (bottom).

4.5 Aerosol Composition

Appendices contains detailed figures and tables of aerosol and gas composition during the overall study period, during episodes, during non-episodes, and during individual episodes. The appendix also includes values for the OC/EC ratio, information on mass balance closure, and values for the degree of sulfate neutralization, gas ratio, and adjusted gas ratio. In this section, the results are reported graphically, and average episode (rather than episode specific) chemical composition is shown.

Due to the different hours with missing data (either from flagged hourly data or from 1 in 3 day sampling), there are different numbers of hours available for different studies of relative composition. Accordingly, three composition analysis were completed:

- Analysis 1 – Inorganic aerosol composition, using all simultaneous hours where SO_4, NO_3, NH_4, and $PM_{2.5}$ were available.
- Analysis 2 – inorganic aerosol composition plus OC and EC (carbonaceous compounds).
- Analysis 3 – inorganic aerosol plus inorganic gas (NH_3 and HNO_3) composition analysis.

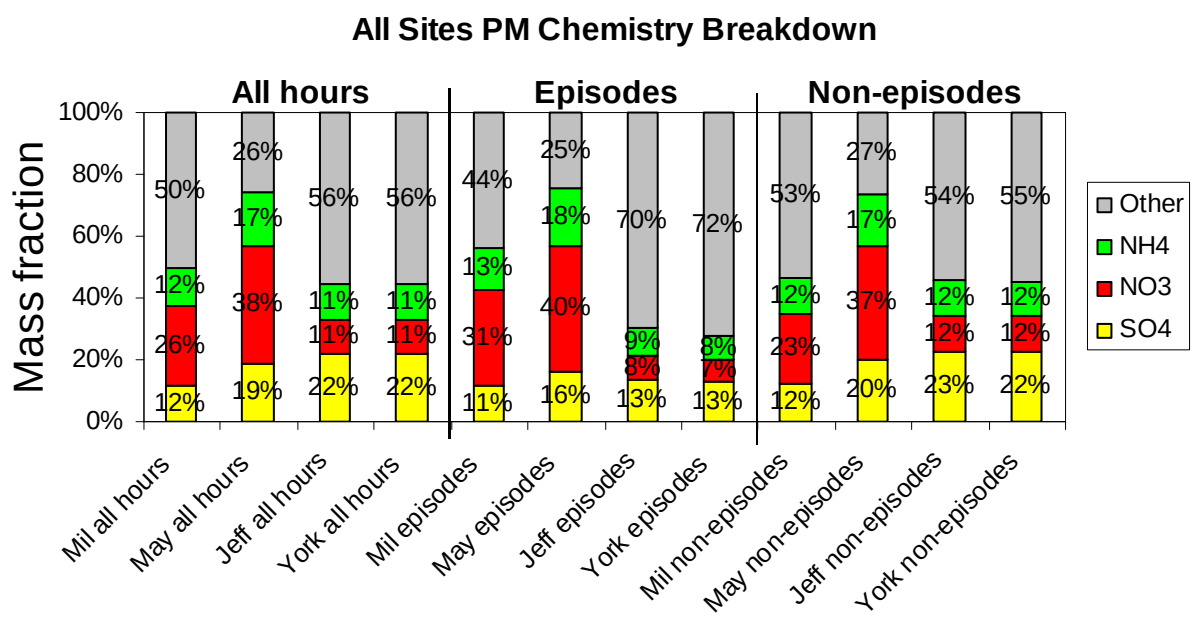


Figure 4-9. Basic chemical composition analysis, using mean values for all hours with available SO4, NH4, NO3, and PM2.5 values.

Figure 4-9 shows that the other (mainly OC) contribution is very important at both urban sites,

and at Yorkville. Nitrate is much more important at the WNS study than at the SEARCH sites.

The second type of chemical composition analysis pulls in available OC and EC data, showing that (at most sites) the other can be accounted for by the measured organic matter (OC x 1.4 OM/OC ratio) and EC. The mass balance at Mayville does not close as well as at the other sites.

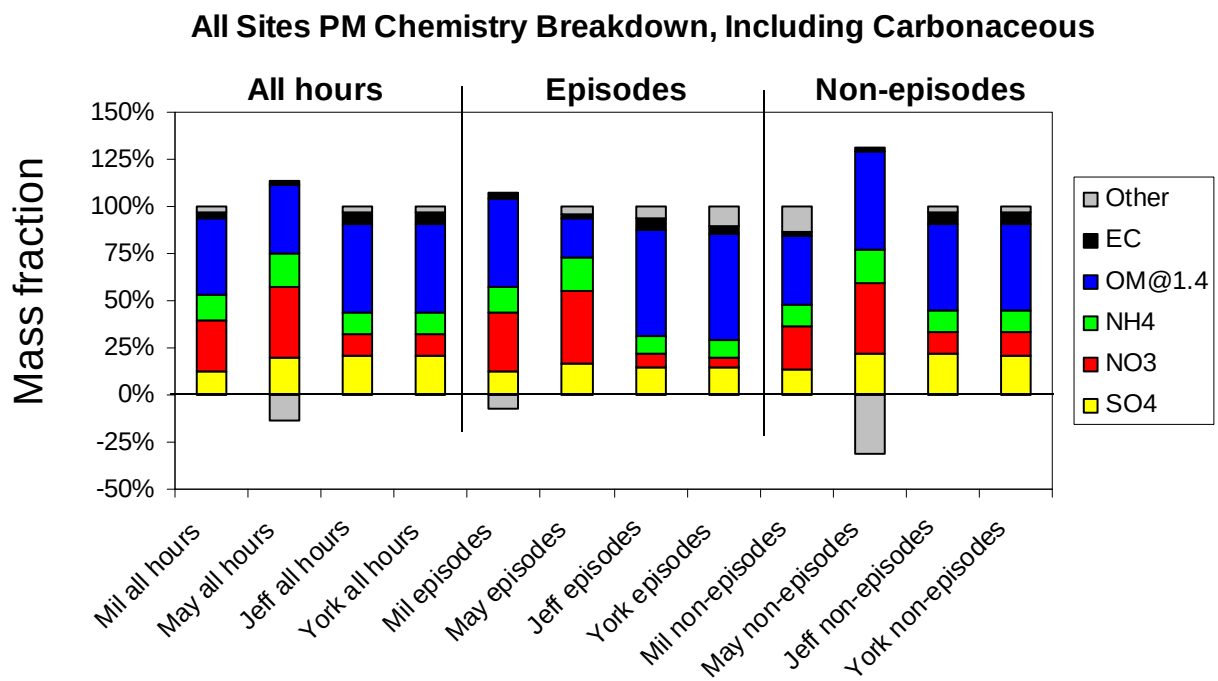


Figure 4-10. Chemical composition analysis, using mean values for all hours with available SO_4, NH_4, NO_3, OC, EC and $PM_{2.5}$ values.

Having OC and EC values allows calculation of the OC/EC ratio, which is an indicator of the source of the OC. Secondary OC gives rise to high OC/EC ratios, assuming the primary OC/EC ratio remains constant.

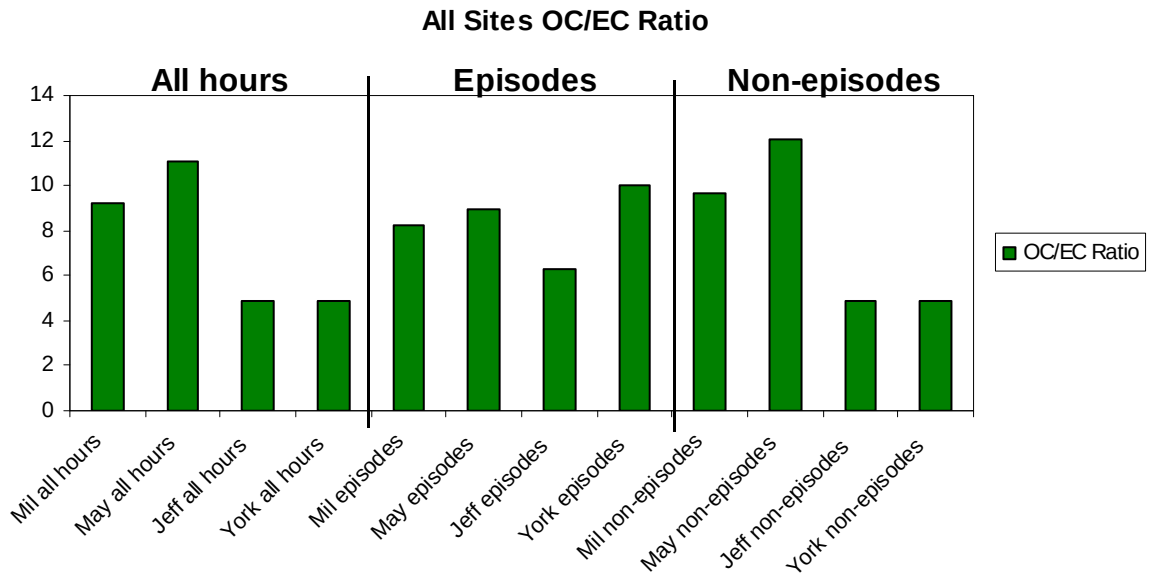


Figure 4-11. OC/EC ratio. Note: instrumentation is consistent between Milwaukee and Mayville, and between Jefferson St. and Yorkville, but not necessarily between the Wisconsin and SEARCH sites.

The third type of chemical composition analysis includes NH3 and HNO3 gases.

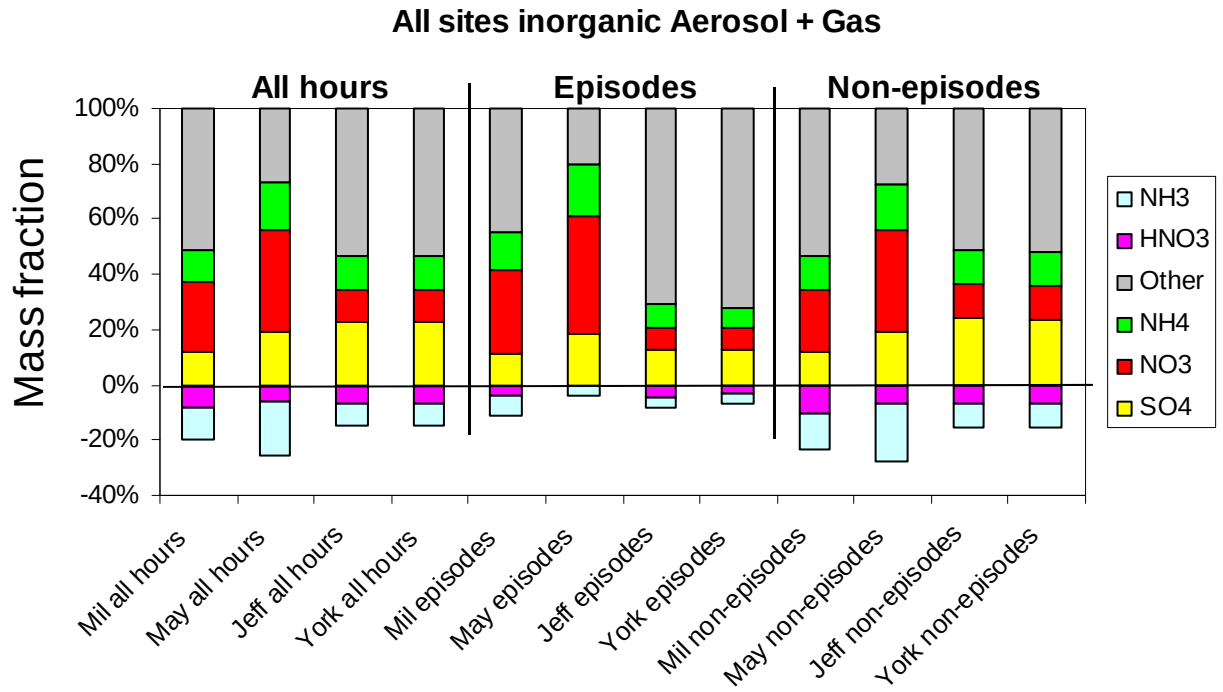


Figure 4-12. Chemical composition analysis including inorganic gases, using mean values for all hours with available SO_4, NH_4, NO_3, HNO_3, NH_3 and $PM_{2.5}$ values.

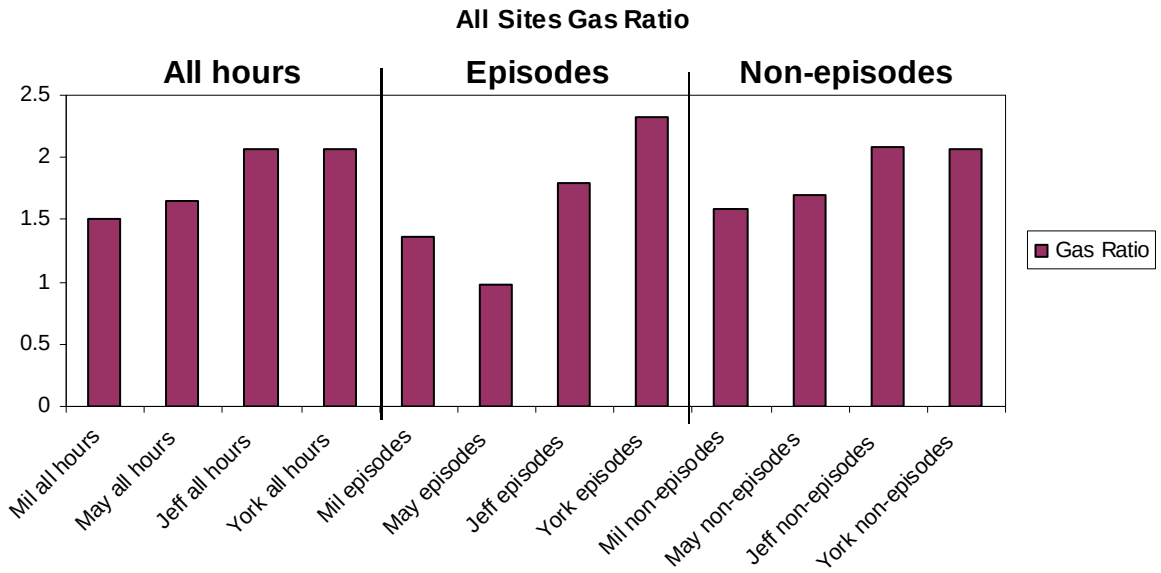


Figure 4-13. Gas ratio for the four sites during episode and non episode periods.

By examining the enrichment or enhancement ratios of compounds (the ratio of the concentration during episodes to that during non-episode periods), some insight can be gained toward what sources become more prevalent (on a relative basis) during episodes. The results of this calculation are shown in Table 4-7.

Table 4-7. Enhancement ratios for key chemical compounds

	SO_4	NO_3	NH_4	OC	EC	HNO_3	NH_3	TNO_3	TNH_3	$PM_{2.5}$
Milwaukee[a]	2.53	3.64	3.02	3.72	3.84	1.05	1.33	2.70	2.25	2.65
Milwaukee[b]	2.59	3.94	3.03	4.28	4.45	1.72	1.10	3.36	2.17	2.71
Milwaukee[c]	2.19	2.68	2.57	1.73	1.91	0.41	1.09	1.57	1.67	2.32
Milwaukee[d]	2.59	3.94	3.03	1.37	1.99	1.72	1.10	3.36	2.17	2.71
Mayville	2.91	4.05	3.73	1.38	1.91	< 1	0.57	2.73	1.84	3.33
Jefferson St.	1.52	1.81	1.96	2.92	2.30	1.74	1.08	1.77	1.56	2.58
Yorkville	1.48	1.65	1.76	2.78	1.47	1.33	1.05	1.57	1.48	1.31

[a]Milwaukee enhancement – all episode hours versus all non-episode hours – including Jan 22 OC and EC outliers
[b]Milwaukee enhancement – "both site" episodes; only counting episodes with 7 or more hours of OC data; including the Jan 22 OC and EC outliers
[c]Milwaukee enhancement – "Milwaukee only" episodes; only counting episodes with 7 or more hours of OC data.
[d]Milwaukee enhancement – "both site" episodes; only including episodes with 7 or more hours of OC data; excluding the Jan 22 OC and EC outliers

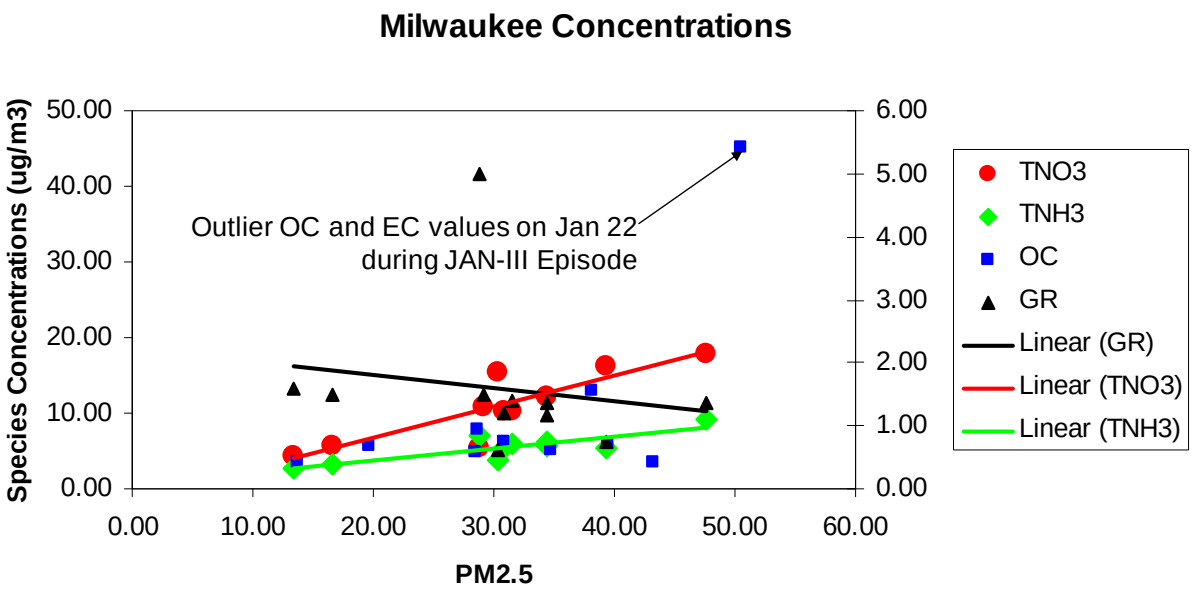
From the enhancement ratios (which are the mean concentration during episodes divided by the mean concentration during non-episodes) one can get a sense of the source or aerosol types that are most "characteristic" of an episode. A qualitative ranking of the enhanced species

can be found in table 4-8.

Table 4-8. Conclusions drawn from enhancement ratios

Site	Comment (#1 being most enhanced / #5 being least enhanced)
Milwaukee (all episodes, including the high OC and EC readings of Jan 22)	
	#1 EC; #2 OC; #3 Total nitrate; #4 Sulfate; #5 Total Ammonia
Milwaukee "both site" episodes versus Milwaukee only episodes – analysis including the Jan 22 high OC / EC sample	
Both site episodes	- same ordering as "all episodes" case above
Milwaukee only episodes	- #1 sulfate; #2 EC; #3 OC; #4 Total ammonia; #5 Total nitrate
Milwaukee "both site" episodes versus Milwaukee only episodes – analysis excluding the Jan 22 high OC / EC sample	
Both site episodes	- Milwaukee (both site episodes): #1 Total nitrate; #2 Total sulfate; #3 Total ammonia; #4 EC; #5 OC
Milwaukee only episodes	- Milwaukee only episodes: #1 sulfate; #2 EC; #3 OC; #4 Total ammonia; #5 Total nitrate.
Mayville	#1 Total sulfate; #2 Total Nitrate; #3 EC; #4 Total Ammonia; #5 OC
Jefferson St.	#1 OC; #2 EC; #3 Total nitrate; #4 Total ammonia; #5 sulfate
Yorkville	1 OC; #2 Total nitrate; #3 & #4 (tied) Total ammonia and sulfate; #5 EC

The shifting of the PM chemistry as $PM_{2.5}$ increases can be seen in the following figures, which graph various PM composition indicators for different episodes, for all episodes, for all hours, and for non-episodes.



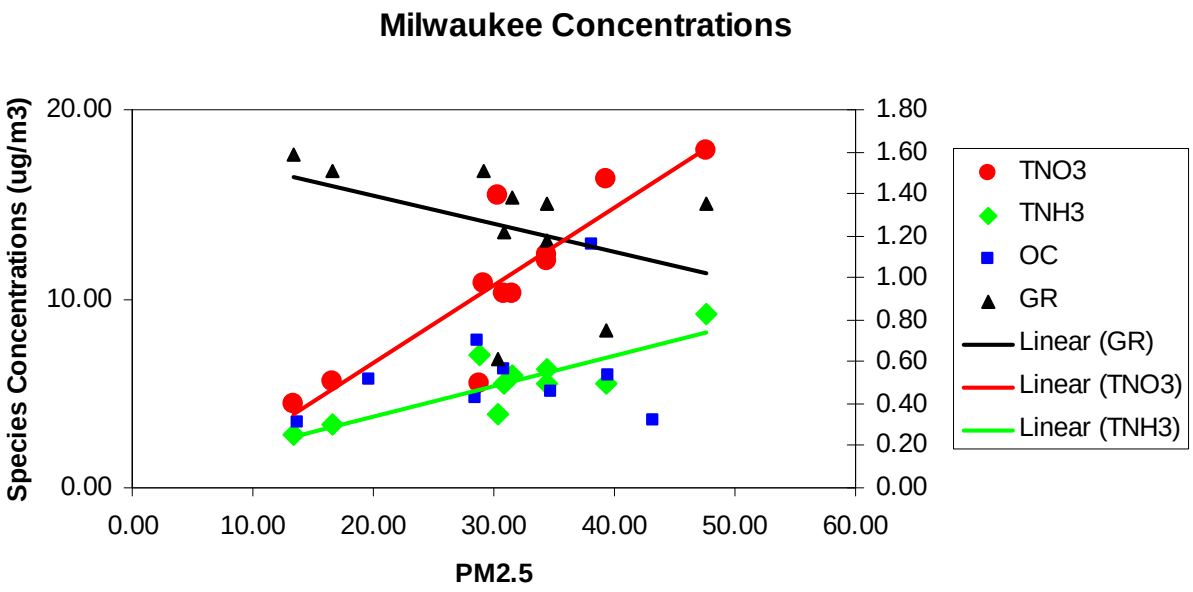


Figure 4-14. Total nitrate, total ammonia, OC, and gas ratio as a function of $PM_{2.5}$ for various periods in the Milwaukee dataset. Top figure has outlier gas ratio and OC/EC values, while bottom figure has these excluded. Lines are linear fits. Gas ratio decreases slightly with increasing $PM_{2.5}$, reflecting greater enhancement of nitrate than of ammonia.

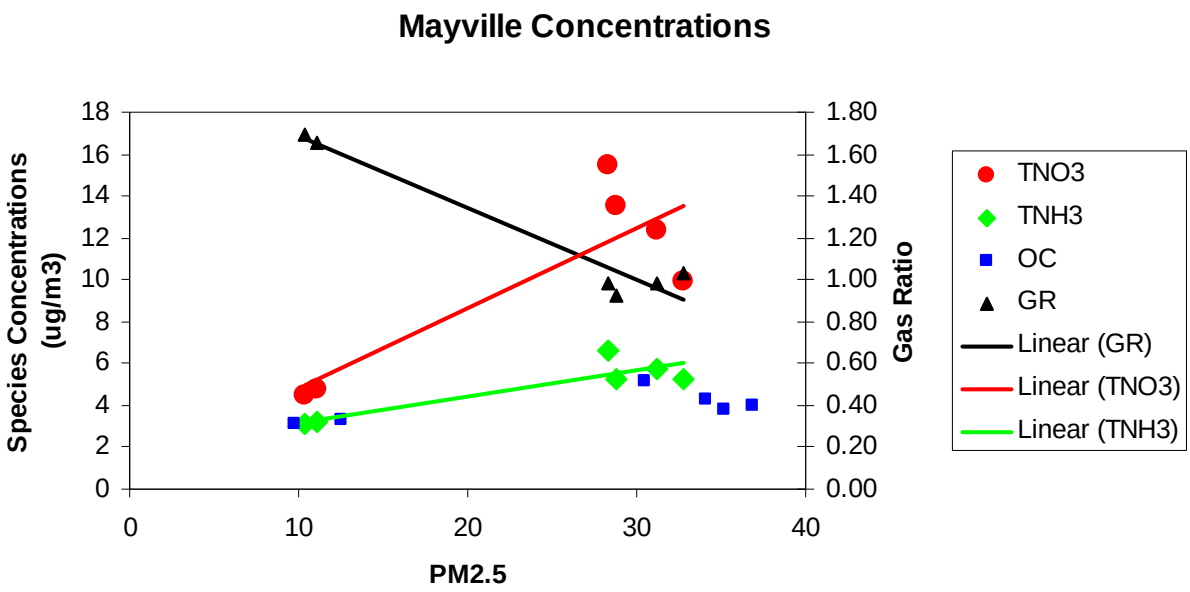


Figure 4-15. Total nitrate, total ammonia, OC, and gas ratio as a function of $PM_{2.5}$ for various periods in the Mayville dataset. Gas ratio decreases slightly with increasing $PM_{2.5}$, reflecting greater enhancement of nitrate than of ammonia.

Bill Adamski has completed an analysis of historical speciation data with a focus on OC and EC, and this will be integrated into a final report.

4.6 Conclusions that can be drawn from concentrations, diurnal patterns, and site-to-site comparisons

- Mean and episode conditions at the Georgia sites display a slightly more distinctive diurnal pattern with a peak at 09:00 and a minimum at 13:00. Elevated PM during episodes is most pronounced during nighttime hours. In Wisconsin sites, the diurnal patterns for $PM_{2.5}$ are very flat during episodes and non-episodes, with a slight (a few microgram per m^3) increase at Milwaukee during episodes at 8 AM. This contrast suggests that variations in $PM_{2.5}$ in Wisconsin are not caused so much by diurnal changes in boundary layer height and wind speed, but rather by regional meteorology. Another possibility is that boundary layer and wind speeds remain low during daytime hours of episodes.
- Nitrate is not much involved in Georgia wintertime episodes.
- Despite comparable O_3 levels (22 ppb mean in Milwaukee, 20 ppb mean in Atlanta) and

comparable NO_2 levels (16 ppb in Milwaukee, 17 ppb in Atlanta), the total nitrate levels in Milwaukee are, on average, 2.5 times higher than in Atlanta. This is likely due to more favorable nighttime conversion from NO_2 to nitrate in Milwaukee, and from the higher lifetime of aerosol nitrate relative to nitric acid gas (on average 91% aerosol fraction for nitrate in Milwaukee, versus 62% aerosol fraction in Atlanta).

- The total ammonia level in Atlanta is 2.1 μg m^{-3}, with 61% in the aerosol phase. For Milwaukee, the total ammonia level is 3.3 μg m^{-3}m with 64% in the aerosol phase.
- Milwaukee only episodes are characterized by strongest enhancements in sulfate, EC, and OC.
- At both Mayville and Milwaukee sites the OC/EC ratio decreases on average during episodes. This suggests that primary OC is driving the OC increases rather than secondary, although the data is sparse and somewhat noisy.
- Gas ratios, an indicator of ammonia availability, are higher at the Georgia sites (~2) than in Wisconsin sites (1.0-1.7). Georgia sites have no consistent change in the gas ratio during episodes.
- Gas ratios, an indicator of ammonia availability, decreased slightly as $PM_{2.5}$ increased at these sites (although within the margin of error at Milwaukee), possibly suggesting a slight decrease in ammonia availability during episodes due to reduced regional transport. The gas ratios in Mayville were slightly higher than in Milwaukee (e.g. 1.7 vs. 1.5 for all study hours) during non-episodes although this is within the margin of experimental error. During episodes, the ordering switched, with the gas ratios at 1.0 (Mayville) and 1.35 (Milwaukee).
- Gas ratios decrease slightly as $PM_{2.5}$ increases at Wisconsin sites (although within margin of error) possibly suggesting a slight decrease in ammonia availability during episodes.
- The Jan-V and Feb-II episodes in Milwaukee were the most ammonia limited, with gas ratios of 0.61 and 0.75, respectively. Both Jan-V and Feb-II occurred at both sites. In Mayville, the Jan-V and Feb-II episodes did not have sufficient data to calculate the gas ratio.
- The Mar-I (Milwaukee only) episode had atypically high ammonia availability.
- Sulfate at WNS sites shows a peak during daytime, presumably from OH-driven sulfate production.
- Ammonia has a flat diurnal pattern, but has slightly higher average levels during the late

afternoon.

- Milwaukee ozone has a minimum from 6-7 AM from titration by NO. Mean ozone is 31 ppb in Mayville and 22 ppb in Milwaukee, a difference of 41%.
- Milwaukee episodes tend to be 5 degrees warmer than climatological mean conditions. Mayville episodes are also warmer than the climatological mean, but warmer in the afternoon (relative to climatological mean) than the morning.
- Despite being warmer, episodes in Wisconsin have 10% higher relative humidity than average.
- NO_y values are much higher at the urban site (26 ppb) than at the rural site (6 ppb). The main difference being in NO due to NO_x sources in Milwaukee.

5. METEOROLOGICAL AND HISTORICAL CONTEXT FOR THE 2009 LADCO WNS

5.1 METEOROLOGY

The 2009 WNS took place during a winter that featured considerable departures from 1971-2000 climatology of Southeastern Wisconsin. January was 2.72 ºC colder than normal and much drier, with only 48% of the climatological average of 47 mm of precipitation in eight days of measurable precipitation. In particular, the 21-day period from 18 January to 8 February had only a trace (0.25 mm) of precipitation and two days of measurable snowfall at Milwaukee, and featured four pollution episodes. February and March were slightly warmer than normal (+0.94 ºC and +0.67 ºC, respectively) with unusually high precipitation (39% and 42% above normal). More than half of the 0.96 m of snowfall recorded at Milwaukee General Mitchell Airport during the three-month study period occurred in March (0.50 m). Milwaukee had snow cover in SNODAS assimilated for all 31 days in January, 18 days in February, and 10 days in March, consistent with reports at the airport (31, 14, and 7 days, respectively).

Fine particle episodes during the WNS all began under similar synoptic conditions, characterized by an approaching high level ridge/surface low pressure system moving into the region, bringing warm, moist, stagnant air. These findings from the 2009 WNS conform to the existing LADCO conceptual model of $PM_{2.5}$ episodes throughout the year (LADCO, 2009) and the empirical Classification and Regression Tree for Midwestern daily average $PM_{2.5}$ concentrations.

Local conditions during episodes were consistent with this synoptic context. Figure 5-1 and 5-2 show daily average time series of observed temperature and relative humidity at the Mayville and Milwaukee sites, augmented with daily surface pressure observations at Fond du Lac County and Milwaukee General Mitchell airports. Falling surface pressure and increases in temperatures and relative humidity coincident with the arrival of a low pressure system were the primary local signals for the initiation of a wintertime episode. Mayville experienced the same local meteorological changes as Milwaukee during the Milwaukee-only episodes, even when local fine particle concentrations were not high enough to qualify as an episode.

Meteorological conditions during events were distinct from the rest of the study period (Table 5-1). Local episodes at both sites were defined throughout primarily by high relative humidity, low pressure, lower visibility, and lighter, more southerly winds.

There was never any liquid precipitation at either site on the first day of an episode or on the preceding day, although snow commonly accompanied episodes. Nine of the thirteen episodes concluded with rain (two), snow (four), or a combination (three) in SNODAS, often accompanying frontal systems. However, the strongest event (1/21-1/23) concluded without precipitation. Thus, while rainout cleared the air after most episodes, it was not as necessary for the termination of an event as the passage of a frontal system advecting the polluted air away. Snow cover was an important source of ambient moisture, enhancing particle growth and increasing aerosol mass during many of the events. Only the last three episodes in March occurred without snow on the ground. All four episodes in February and the first in March began on days with at least 0.5” of snow cover at both sites, and all of them completely melted the snow at Milwaukee. These were among the most severe and long-lived episodes sampled during the WNS, including four of the five most severe events. All February and March days without snow cover occurred after fine particle episodes with consecutive days of temperatures above freezing. Thus, melting and sublimation of snowpack during particle events featuring a warm, stagnant, shallow boundary layer provided a source of moisture that contributed to event severity.

Winds at Milwaukee, more than precipitation or snow cover, help explain why the two days that otherwise met the general criteria for fine particle episodes did not generate a strong event. On 1/17, despite a strong drop in pressure, rising temperatures, and high RH, hourly wind average speeds up to 4.56 m/s prevented $PM_{2.5}$ concentrations from building beyond 27 μg/m^3. On 2/21, high winds (averaging 4.12 m/s throughout the day and reaching 5.95 m/s), prevented $PM_{2.5}$ from reaching 20 μg/m^3. The absence of snowpack and 5.5” of snowfall may have further contributed. In both of these cases, winds were from the south, as during episodes, but were abnormally strong. Likewise, winds explain why Chicago did not experience a strong local fine particle event during the peak of the strongest episode at Mayville and Milwaukee on 1/22, when 24 hour average $PM_{2.5}$ concentrations were 69.7 μg/m^3 and 50.4 μg/m^3, respectively. Chicago

had similar temperature, pressure, and relative humidity throughout the episode, but with wind speeds twice as high as Milwaukee that day.

The impacts of actinic flux on rates of photochemical reactions has been hypothesized as a potential factor in wintertime particle events, but the lack of local observations of insolation made this factor difficult to address conclusively. The study sites are more than 100 km from the nearest site with direct insolation data, the University of Wisconsin Extension Automated Weather Observation Network station at Arlington, Wisconsin. Half-hourly insolation at this site was dramatically lower during Milwaukee episodes, by 30-50% in the mornings and by 10% at the noon daily maximum (Appendix 5-1), but similar during the afternoon. Visibility statistics at Milwaukee (Appendix 5-2) generally agree. As the decreases in insolation during episodes are greater than the extinction caused by aerosols at these concentrations, results suggest lower photolysis rates during fine particle episodes due to adsorption and scattering by clouds. Co-located photometer and ceilometer observations may be useful additions to future studies.

Table 5-1. Hourly meteorological conditions averaged by fine particle episode status, January 1/1—3/31 2009.

Site	Location	Variable	Units	Mayville Episode Hours	Milwaukee Episode Hours	No Episode	All Hours
Mayville	Site	Temperature	ºC	-6.36	-0.21	-5.21	-5.28
		Wind speed	m/s	3.75	3.84	3.98	3.96
		Wind direction	º	199.95	194.21	215.49	214.55
		RH	%	83.82	79.27	71.42	72.18
	KFLD Airport	Visibility	km	9.49	11.91	14.76	14.44
		RH	%	79.40	76.55	68.51	69.17
		Dry bulb	ºC	-6.61	-0.68	-4.93	-5.03
		Wet bulb	ºC	-7.46	-2.10	-6.44	-6.50
		Dew point	ºC	-9.69	-4.55	-10.10	-10.08
		Pressure	hPa	983.73	984.62	987.83	987.58
Milwaukee	Site	Temperature	ºC	-4.23	1.37	-3.61	-2.72
		Wind speed	m/s	2.33	2.30	3.11	2.97
		Wind direction	º	225.76	201.52	229.79	224.72
	MKE Airport	Visibility	km	7.29	8.69	14.01	13.05
		RH	%	74.93	72.84	62.60	64.44
		Dry bulb	ºC	-4.62	0.71	-3.69	-2.90
		Wet bulb	ºC	-5.74	-1.00	-5.56	-4.75
		Dew point	ºC	-8.54	-3.87	-10.14	-9.02

Pressure	hPa	988.24	989.18	992.50	991.91

5.2 AIRMASS BACK TRAJECTORIES

Air mass back trajectories from the Mayville and the Milwaukee sites were analyzed using the NOAA HYSPLIT model from January 1st to April 3rd, 2009 by D. Kenski at LADCO. 3-hourly meteorology input for trajectory calculations was taken from 40 km resolution NOAA Eta Data Assimilation System (EDAS). Starting times of back trajectories were 6 am, noon, 6 pm and midnight. Figures 5-4 to 5-9 show composite plots of back trajectories at 0, 500, and 1000 m in each month. Red dot trajectories indicate periods with $PM_{2.5}$ episodes at both sites, green dots for Milwaukee-only episodes, and blue dots for clean periods. Back trajectories that started closest to the first hour of a $PM_{2.5}$ episode were chosen for the analysis, in order to highlight conditions that initiated episodes.

Winds blew mostly from the west and northwest in January, and episodes typically occurred in airmasses originating to the west and west-southwest at low wind speeds. In February, winds from the south and north-northwest prevailed. Most episodes happened under southerly wind conditions, with airmasses that had recently passed over Illinois and Indiana. In March, wind most often blew from the north, but episodes were still defined by southerly winds.

The frequencies of airmass passage over neighboring states and regions (Figure 5-3) were analyzed for episode and non-episode periods in each month (Figures 5-10 and 5-11). Airmasses coming from Canada and Minnesota, associated with fast-moving high pressure systems, were usually correlated with lower $PM_{2.5}$ levels. Higher $PM_{2.5}$ concentrations occurred with winds from Iowa, especially in January, but this was more an indication of the approach of a surface low-pressure system than a suggestion of Iowa as a source of fine particle loading during events. Based on trajectory analysis, there was no evidence that Mayville episodes were ever due directly to air polluted during passage over Milwaukee; these conditions occurred only eight times out of 1,030 cases for the three months, and never during episodes.

5.3 WINTER FINE PARTICLE EPISODES, 2002—2008

The level of episodic $PM_{2.5}$ particle pollution in Wisconsin during the WNS study period was above historical average levels. This has been investigated in two ways. First, a database of daily FRM and IMPROVE $PM_{2.5}$ mass values for the U.S. for the period Jan 2001 – Mar 2009 was assembled. This was then used to make a daily smoothed (kriged) $PM_{2.5}$ surface for the upper Midwest. Then on a pixel-by-pixel basis, this smoothed surface was used to calculate an episode index for the period. The episode index for a given cell is as follows:
INDEX = $\sum \max[0, (PM_{2.5} - 27)]$ where the sum is over multiple days and the units of this are in ug m^{-3} days. Accumulation of this quantity to 62 μg m^{-3} days is necessary (but not sufficient) for a 98th percentile concentration of 35.5 μg m^{-3}. Figure 5-12 shows this index for the months of Jan-Mar for the years 2001-2009, and for the WNS study period. The black line shows the 62 μg m^{-3} day threshold. Note the change in colorscale for the two figures.

A second way of looking at it is to use the same index, but to look at individual site concentrations. This avoids any artifacts that the spatial smoothing might impose on the data. On average, Jan-Mar episode activity is higher at Milwaukee than at Mayville (64 vs. 34), a ratio of 1:9. During the 2009 WNS, the ratio of the episode indicator was similar, but episode activity was elevated at both locations (151 at Milwaukee for 2009 and 80 for Mayville at 2009). Looking at the figures, it can be seen that high episode activity years are 2009, 2005, and 2001. 2008 is moderate in Milwaukee but clean in Mayville. These are in qualitative agreement with the yearly Kriged surfaces in appendices, but further comparison is needed at specific grid cells to verify that the Kriging is sufficiently faithful in grid cells with measurement datapoints.

Figure 5-13 shows that the Wisconsin sites were more polluted than other sites such as Bondville, IL, Lake Sugema, IA, and Boundary Waters MN. These sites are all shown together using actual IMPROVE or EPA $PM_{2.5}$ data (not Kriged data) for the entire cold weather season (Nov-Mar).

REFERENCES

Lake Michigan Air Directors Consortium (2009). Conceptual Model of PM2.5 Episodes in the Midwest.

Figures

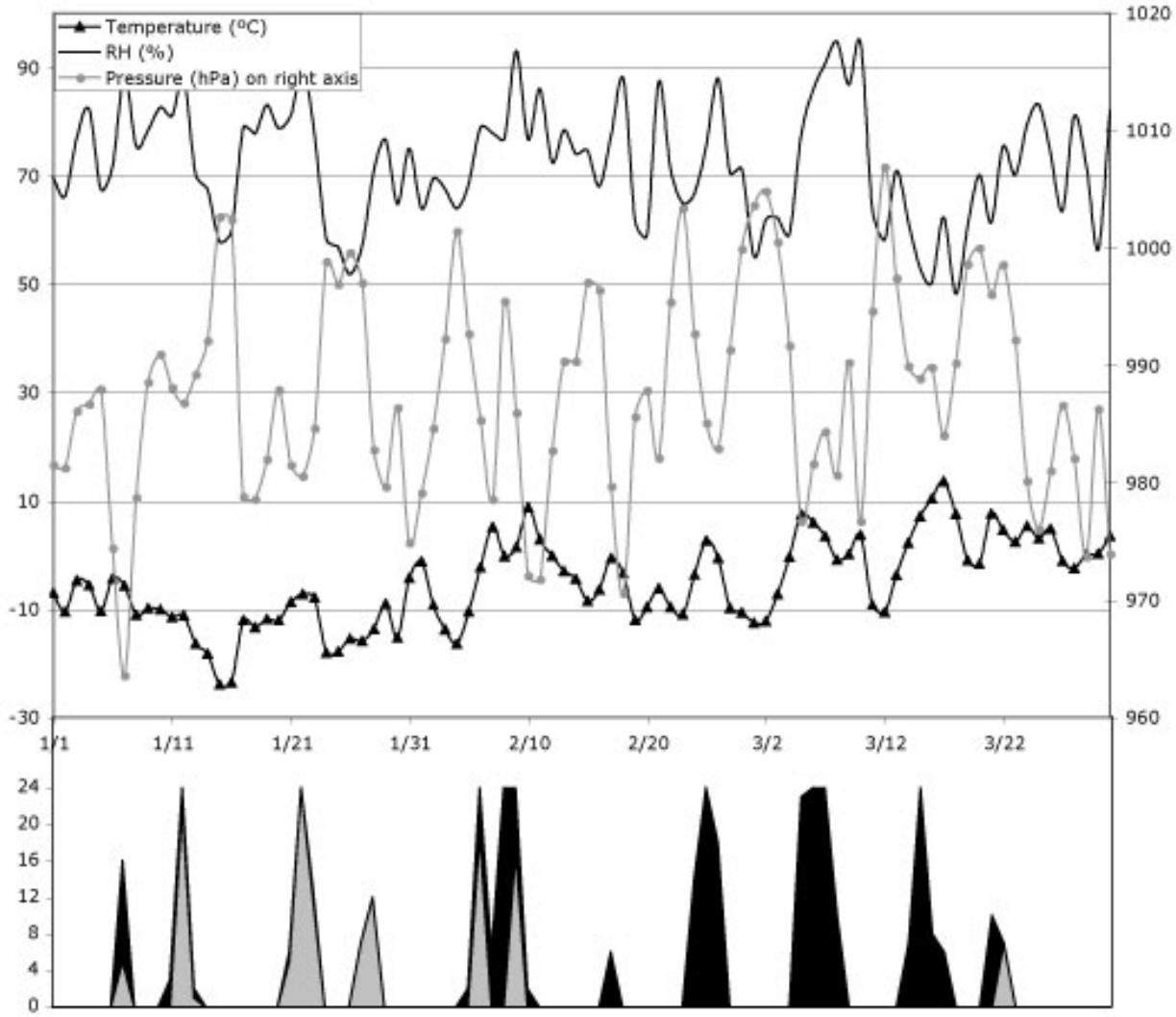


Figure 5-1. Mayville daily average temperature, relative humidity, and surface pressure, along with daily number of episode hours at Milwaukee (black) and Mayville (gray).

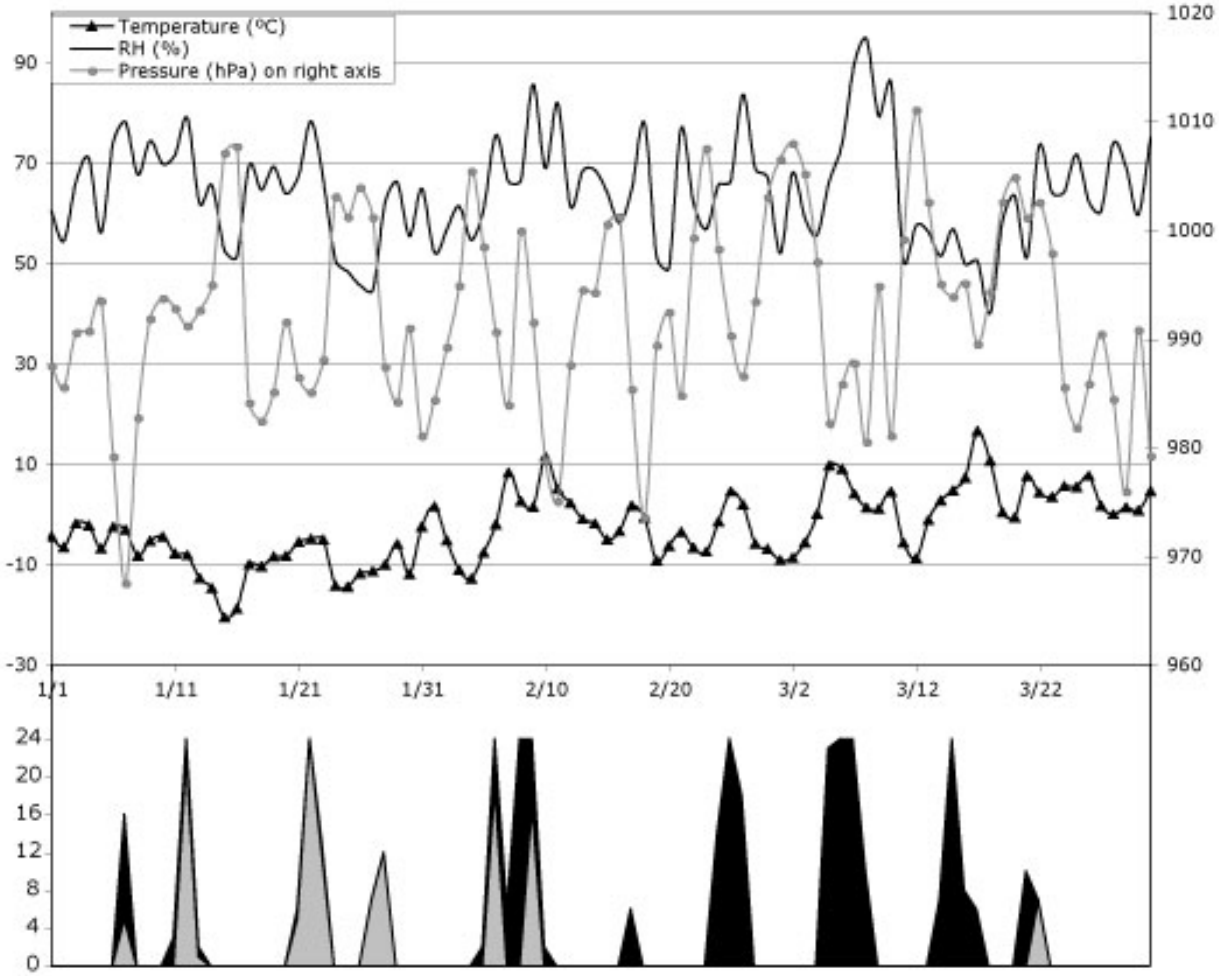


Figure 5-2. Milwaukee daily average temperature, relative humidity, and surface pressure, along with daily number of episode hours at Milwaukee (black) and Mayville (gray).

Figure 5-3. Regions to calculate frequency of air mass passes. States boundaries and US boundaries are used for the outside of the regions.

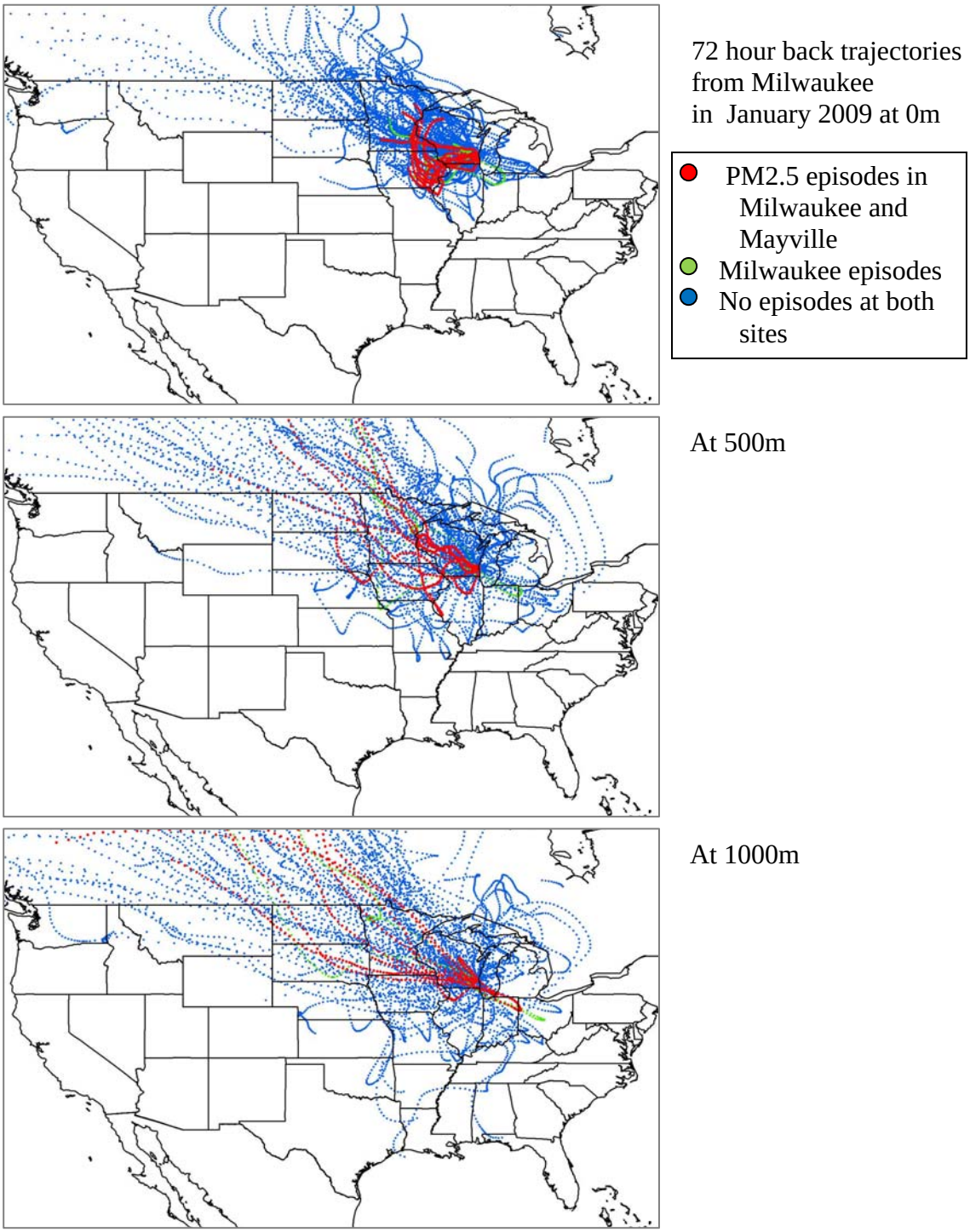


Figure 5-4. 72 hour back trajectories from the Milwaukee site in January 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.

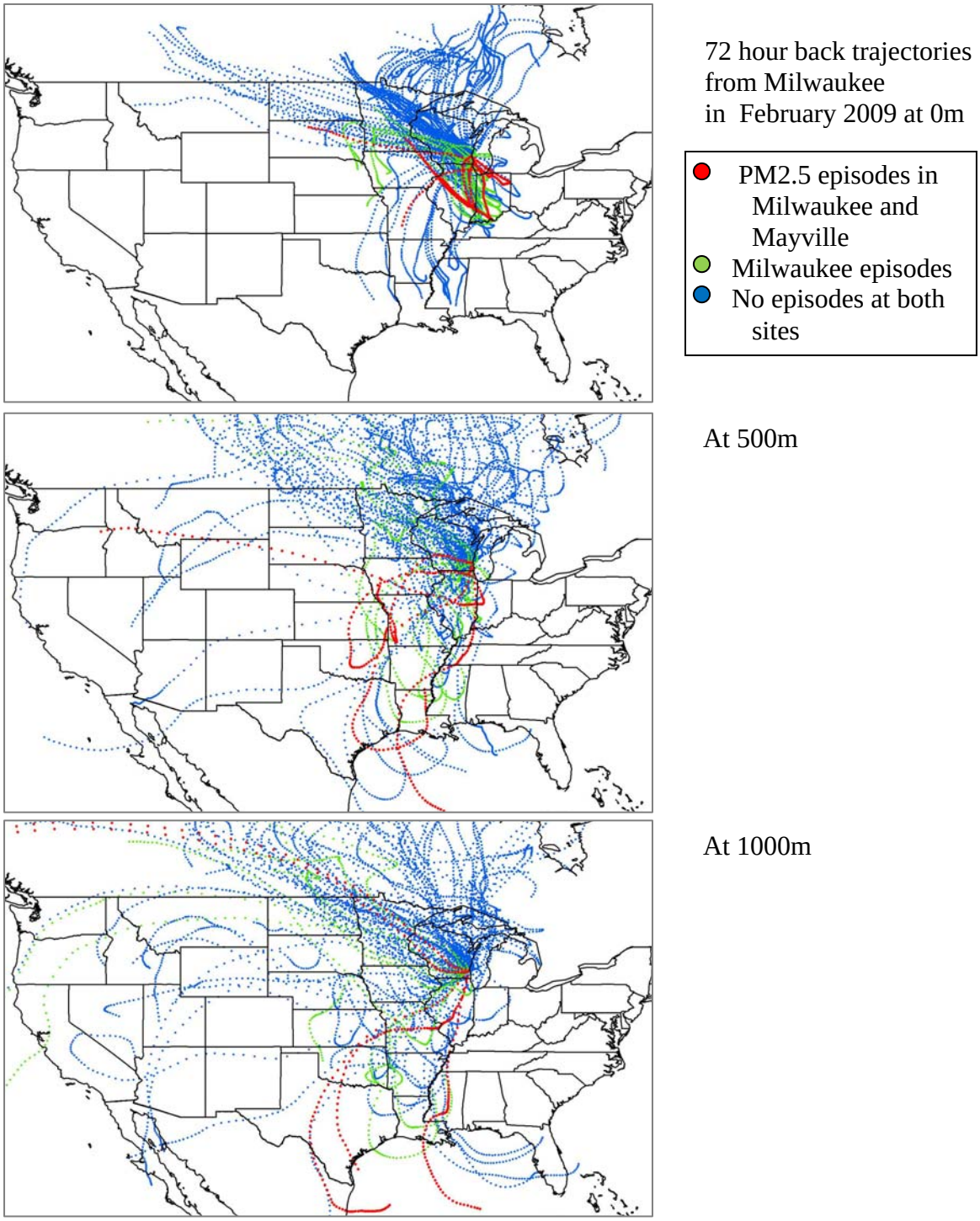


Figure 5-5. 72 hour back trajectories from the Milwaukee site in February 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.

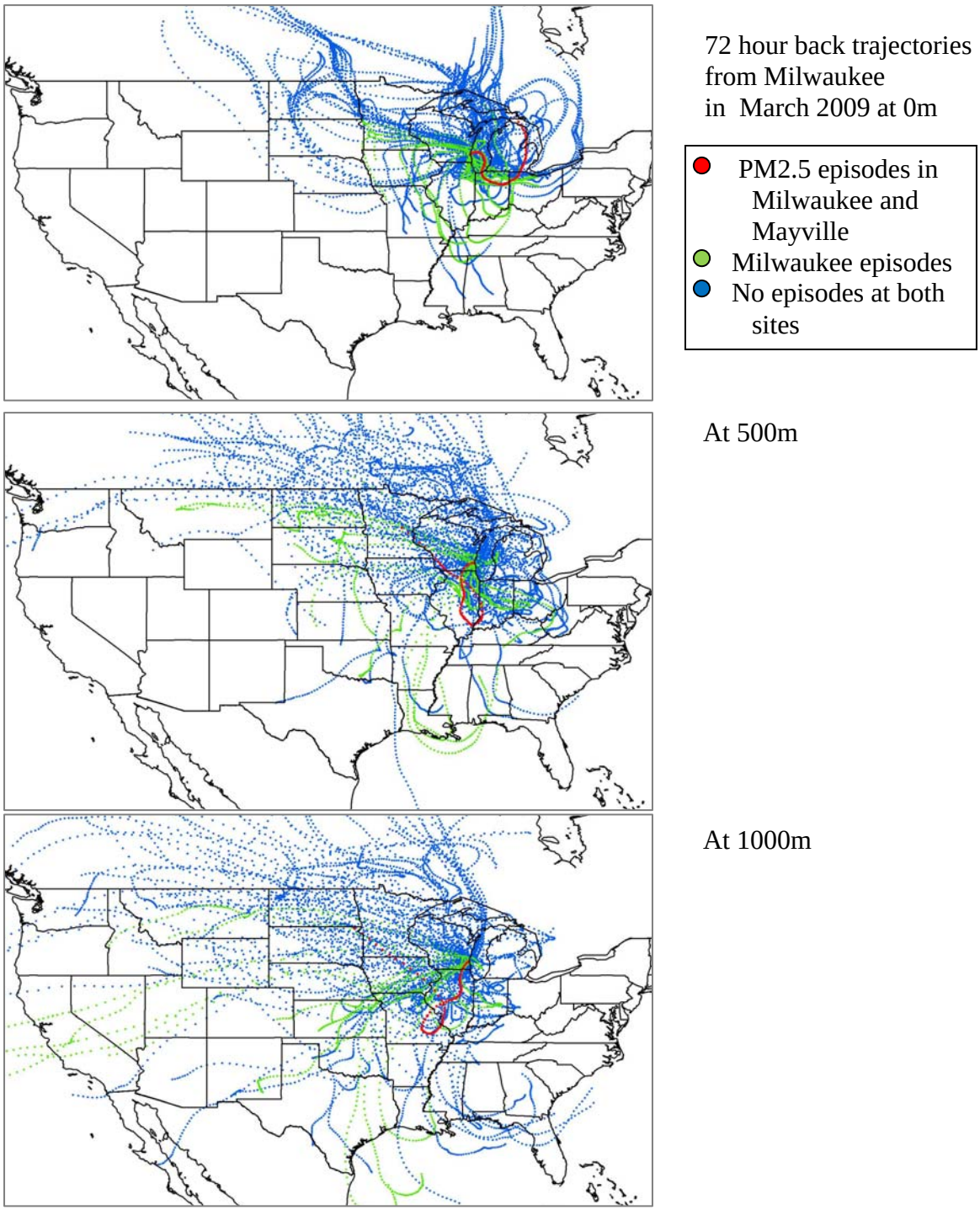


Figure 5-6. 72 hour back trajectories from the Milwaukee site in March 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.

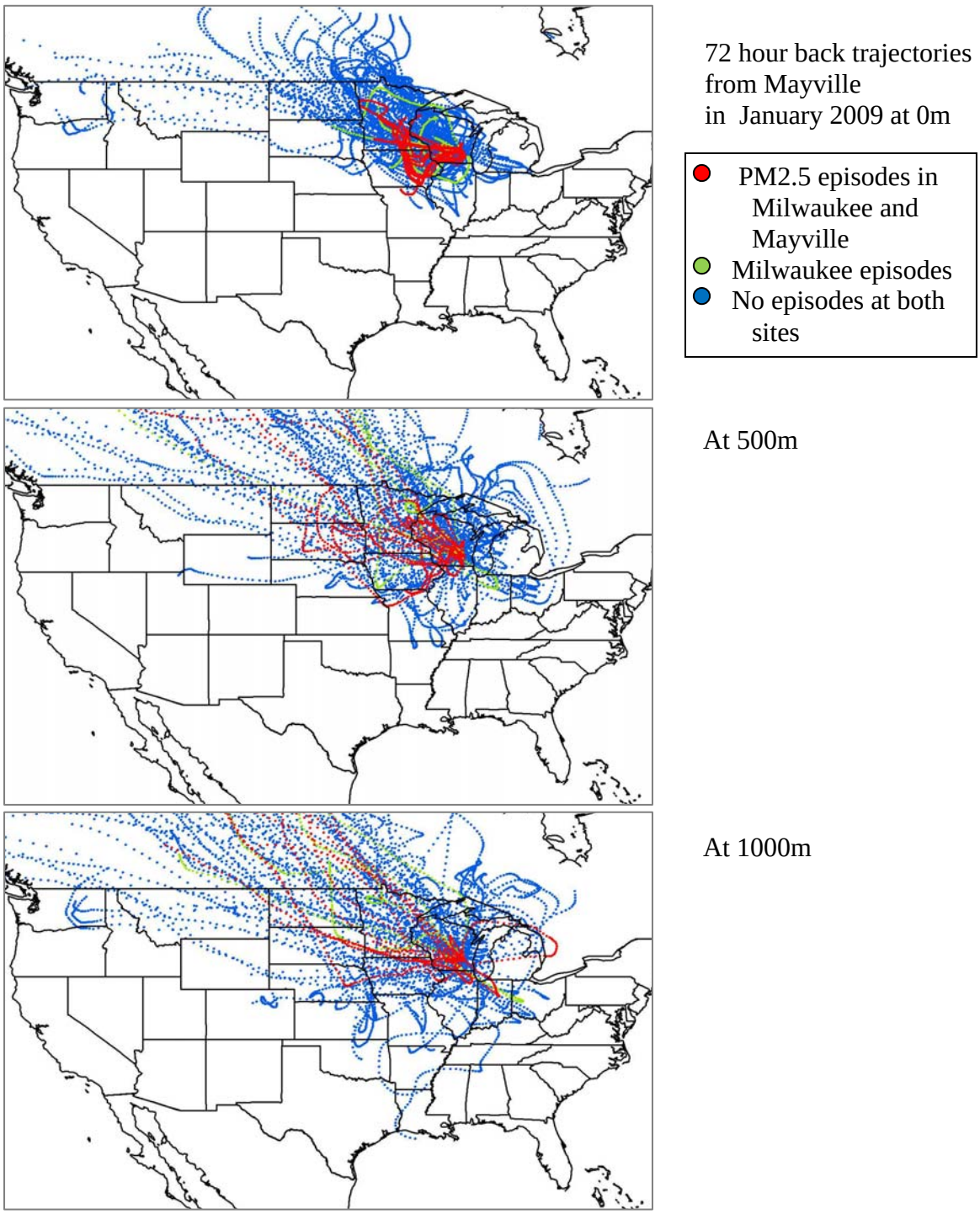


Figure 5-7. 72 hour back trajectories from the Mayville site in January 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.