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**Supplementary Information File**

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Overview of the LADCO Winter Nitrate Study: Hourly Ammonia, Nitric Acid and  
PM<sub>2.5</sub> Composition at Urban and Rural Sites During PM<sub>2.5</sub> Episodes in the U.S.

Great Lakes Region

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**Table S1. Milwaukee Descriptive Statistics**

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
PM2.5	$\mu\text{g m}^{-3}$	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	$\mu\text{g m}^{-3}$	2.03	1.57	1668	-0.50	0.49	0.97	1.72	2.80	3.81	14.53
NO3	$\mu\text{g m}^{-3}$	4.35	4.37	1742	-0.20	0.49	1.17	3.03	6.18	10.09	35.48
NH4	$\mu\text{g m}^{-3}$	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	$\mu\text{g m}^{-3}$	5.57	5.20	1604	-0.80	0.78	1.72	3.96	7.90	13.07	42.17
TNH3	$\mu\text{g m}^{-3}$	4.28	2.10	1575	1.23	2.04	2.69	3.91	5.42	6.98	16.59
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	$\mu\text{g m}^{-3}$	18.3	11.0	29	4.2	4.9	10.3	17.2	21.1	39.0	49.7
NO3, 24 hr	$\mu\text{g m}^{-3}$	4.9	4.4	28	0.5	0.7	2.2	3.4	6.4	13.3	17.4
SO4, 24 hr	$\mu\text{g m}^{-3}$	2.2	1.2	28	0.8	1.0	1.4	2.0	2.8	4.0	5.9
NH4, 24 hr	$\mu\text{g m}^{-3}$	2.3	1.8	28	0.4	0.4	1.0	2.0	3.0	5.0	8.0
EC, <sup>a</sup> 24 hr	$\mu\text{g m}^{-3}$	0.52	0.69	28	0.12	0.1	0.3	0.4	0.5	0.8	4.0
OC, <sup>a</sup> 24 hr	$\mu\text{g m}^{-3}$	5.1	7.9	28	1.2	1.9	2.3	3.1	5.1	6.8	45.1
EC/OC <sup>a</sup>	Unitless	0.11	0.04	28	0.04	0.05	0.08	0.11	0.14	0.16	0.20
EC, <sup>b</sup> 24 hr	$\mu\text{g m}^{-3}$	0.39	0.20	27	0.12	0.1	0.3	0.4	0.5	0.7	0.83
OC, <sup>b</sup> 24 hr	$\mu\text{g m}^{-3}$	3.6	1.8	27	1.2	1.9	2.2	3.1	5.1	6.3	7.8
EC/OC <sup>b</sup>	Unitless	0.11	0.04	27	0.04	0.05	0.07	0.12	0.14	0.16	0.20
NH3, 24 hr	ppb	1.9	1.0	27	0.7	0.9	1.2	1.6	2.4	3.1	5.3
HNO3, 24 hr	ppb	0.3	0.2	27	0.09	0.1	0.15	0.21	0.35	0.5	0.83

<sup>a</sup> includes Jan 22 OC and EC values

<sup>b</sup> 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 S2. Mayville Descriptive Statistics**

Variable	Units	Mean	Std. Dev	n	Min	10th	25th	Median	75th	90	Max
PM2.5	$\mu\text{g m}^{-3}$	11.7	8.8	2148	-2.7	2.9	5.2	9.6	16.4	23.6	63.1
PM2.5b	$\mu\text{g m}^{-3}$	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	4.6	2.0	2135	0.22	2.1	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	$\mu\text{g m}^{-3}$	2.20	1.7	1809	-0.5	0.4	1.0	1.9	3.1	4.3	10.1
NO3	$\mu\text{g m}^{-3}$	3.3	3.6	1816	-0.2	0.2	0.6	2.0	4.6	7.9	27.3
NH4	$\mu\text{g m}^{-3}$	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	$\mu\text{g m}^{-3}$	4.8	3.6	1679	-0.2	1.1	2.1	3.6	7.2	9.9	22.1
TNH3	$\mu\text{g m}^{-3}$	4.0	2.6	1673	0.64	1.32	1.91	3.24	5.45	7.80	14.77
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	$\mu\text{g m}^{-3}$	15.8	8.9	30	4.2	6.9	9.9	14.4	17.5	32.2	38
NO3, 24 hr	$\mu\text{g m}^{-3}$	4.9	4.1	27	0.6	1.3	1.8	3.5	6.5	11.9	14.4
SO4, 24 hr	$\mu\text{g m}^{-3}$	2.25	0.9	27	0.9	1.2	1.6	2.0	2.8	3.3	4.8
NH4, 24 hr	$\mu\text{g m}^{-3}$	2.2	1.6	27	0.1	0.6	1.2	1.7	3.1	4.6	6.3
EC, 24 hr	$\mu\text{g m}^{-3}$	0.3	0.2	28	0.1	0.1	0.1	0.3	0.4	0.5	0.6
OC, 24 hr	$\mu\text{g m}^{-3}$	3.2	2.1	28	1.1	1.2	1.9	2.9	4	5.4	11.8
NH3, 24 hr	ppbv	2.3	1.6	27	0.4	0.8	1.1	1.9	3.2	4.2	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	0.21	0.17	27	0.06	0.06	0.10	0.16	0.23	0.34	0.9

**Table S3. Slopes, intercepts and confidence interval parameters**

Summary table of regression parameters derived from comparison of integrated and continuous samplers

Parameter	M (note 1)	B (note 1)	f (note 2)	$\epsilon$ (note 2)	Example confidence interval (Note 3)	Note
Milwaukee Total Nitrate	1.06	-0.62	0.19	1.03	5.64±2.16	
Mayville Total Nitrate	1.06	-0.11	0.22	0.91	3.91±1.75	
Milwaukee Total Ammonia	0.95	+0.31	0.17	0.59	3.91±1.23	
Mayville Total Ammonia	1.22	+0.02	0.24	0.68	3.99±1.46	
Milwaukee Sulfate	1.40	-0.33	0.37	0.55	2.43±1.28	
Mayville Sulfate	1.35	-0.16	0.67	1.05	2.51±2.38	
Milwaukee Nitrate	1.11	-0.05	0.09	0.26	5.16±0.68	
Mayville Nitrate	1.16	+0.45	0.18	0.67	4.83±1.35	
Milwaukee Ammonium	1.15	-0.12	0.18	0.39	2.49±0.80	
Mayville Ammonium	1.25	-0.21	0.23	0.41	2.20±0.86	
Milwaukee Ammonia	0.85	0.38	0.30	0.94	2.95±1.84	b, B, and $\epsilon$ in ppb
Mayville Ammonia	1.25	0.37	0.49	1.11	3.27±2.24	b, B, and $\epsilon$ in ppb

Note 1: M and B are the parameters for  $iCAMS_{corrected} = M(iCAMS_{raw}) + B$

Note 2: f and  $\epsilon$  are the parameters for an error model where errors contain a constant term and a term that is proportional to the measured values

Note 3: Confidence interval is shown at the mean measurement value, e.g. the 95% confidence interval of Milwaukee total nitrate at mean concentration levels runs from 5.64 – 2.16 (3.48  $\mu\text{g m}^{-3}$ ) to 5.64 + 2.16 (7.8  $\mu\text{g m}^{-3}$ ).

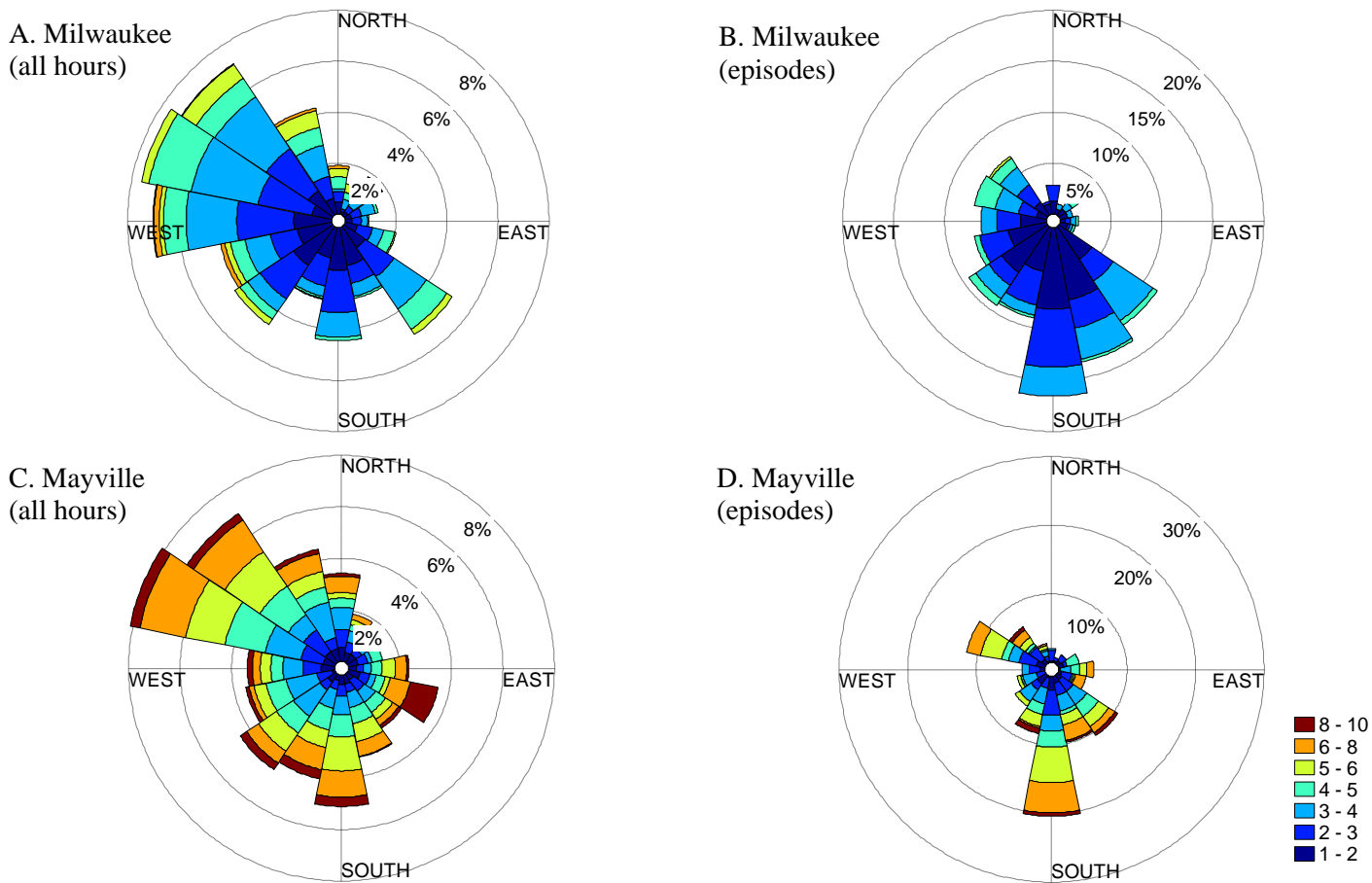


Figure S4. Wind rose for each site during the study. All wind roses use the same color scale which show wind speed in m/s, shown panel D.

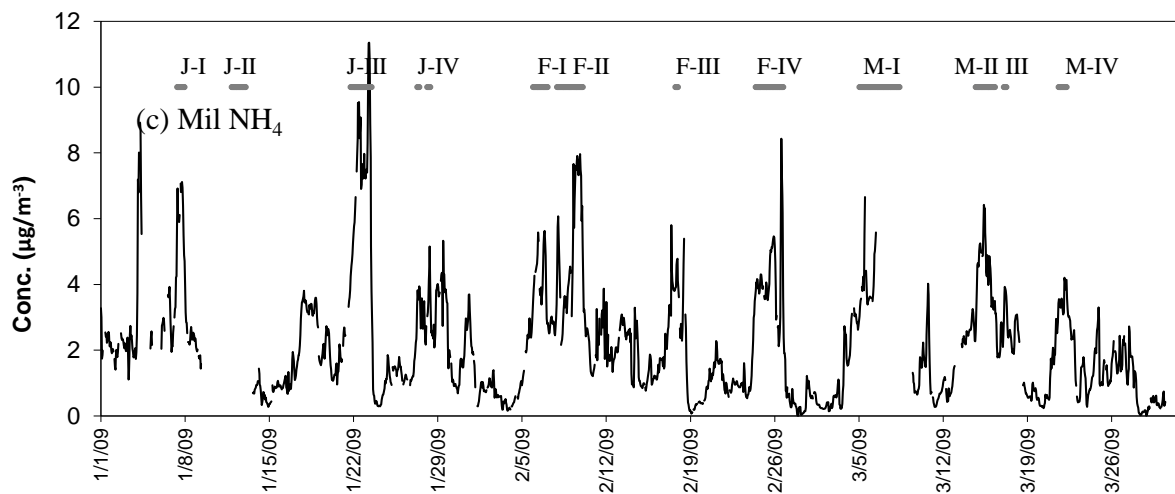
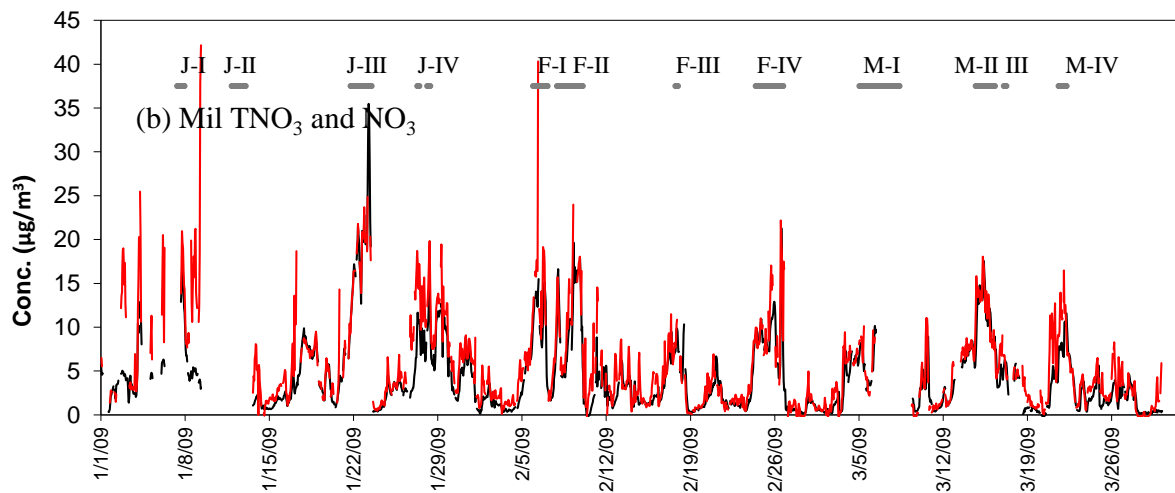
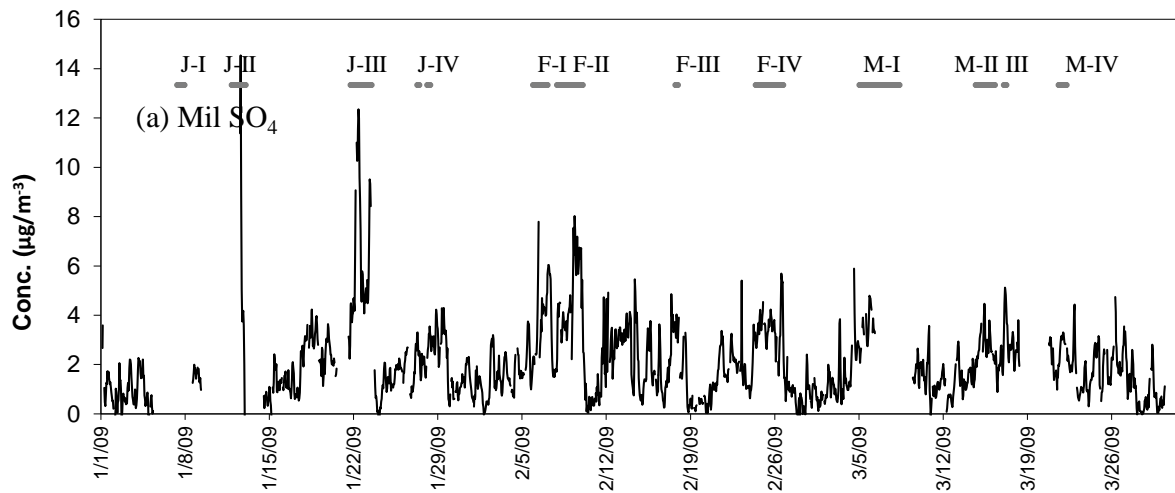


Figure S5. Hourly measurement time series at Milwaukee for (a)  $\text{SO}_4$ , (b)  $\text{NO}_3$  (black) and  $\text{HNO}_3(\text{g}) + \text{NO}_3(\text{p})$  in red, and (c)  $\text{NH}_4$

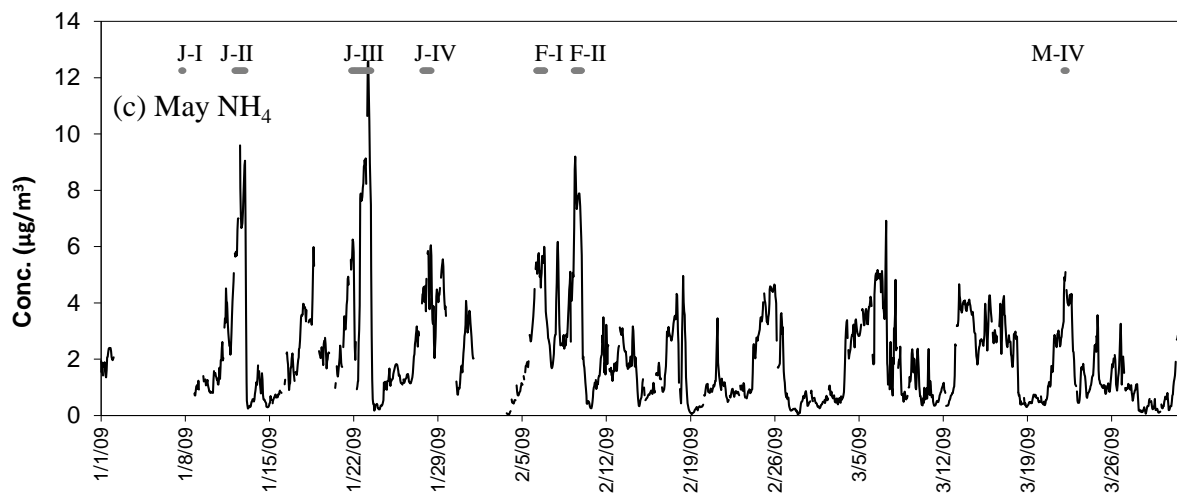
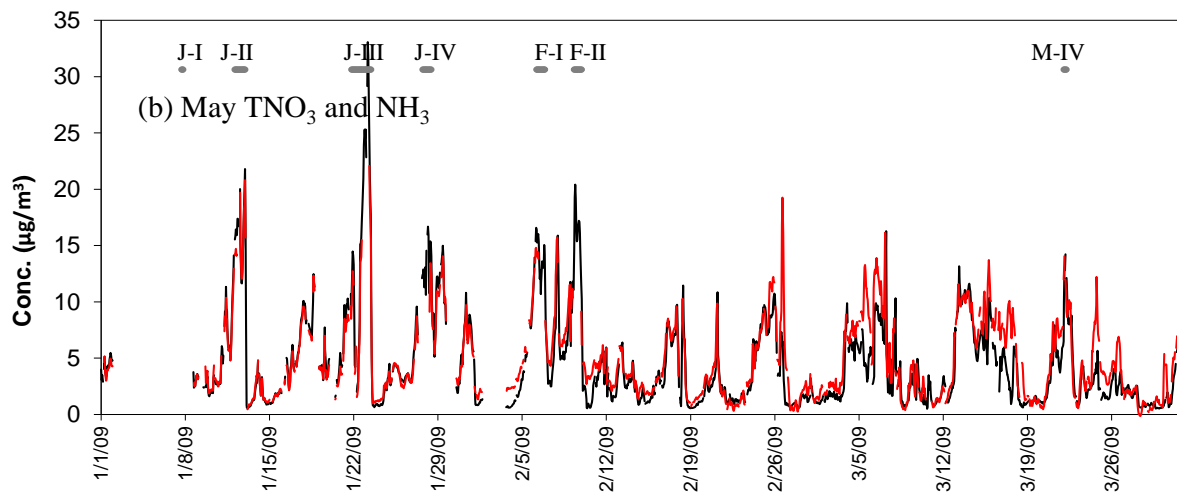
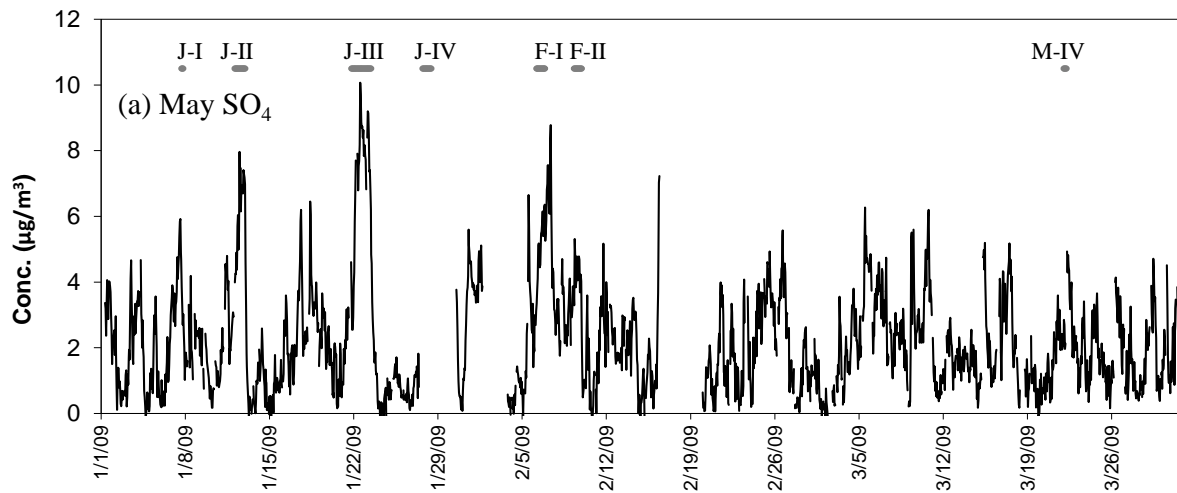


Figure S6. Hourly measurement time series at Mayville for (a)  $\text{SO}_4$ , (b)  $\text{NO}_3$  (black) and  $\text{HNO}_3(\text{g}) + \text{NO}_3(\text{p})$  in red, and (c)  $\text{NH}_4$

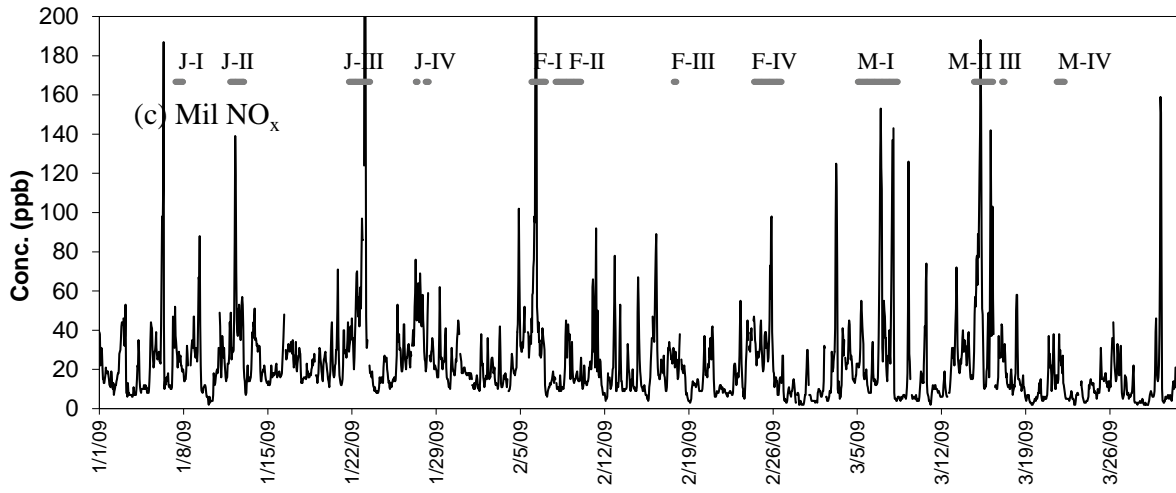
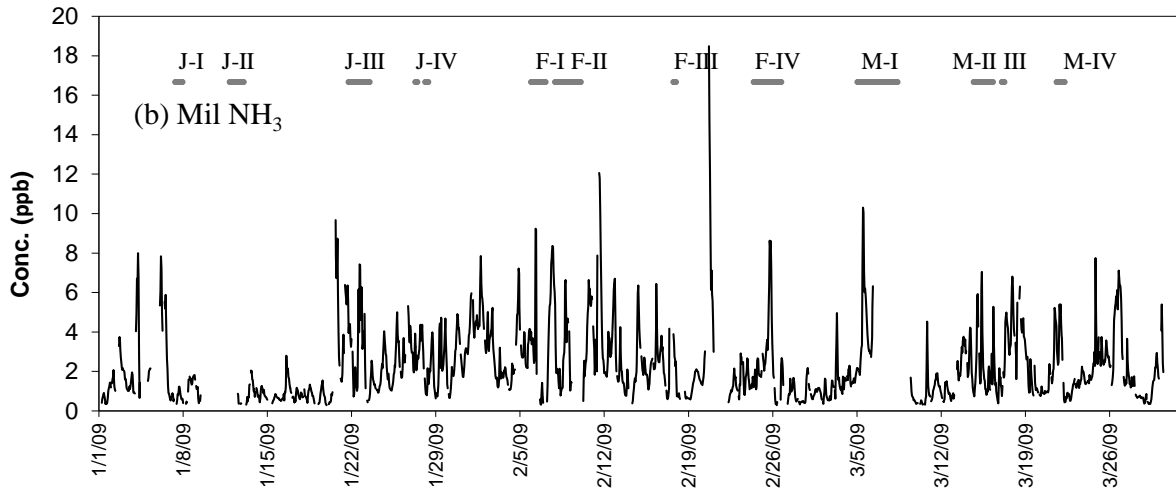
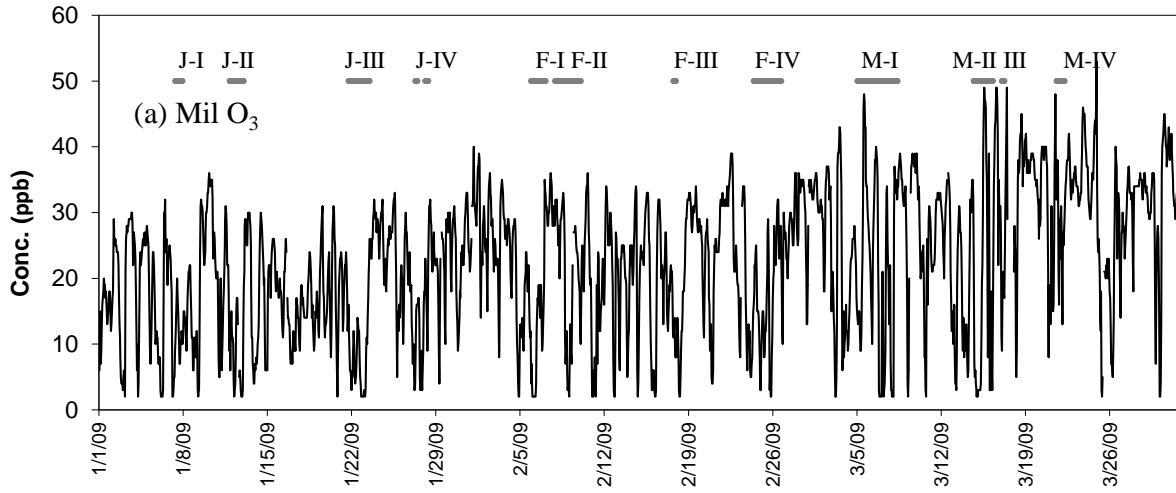


Figure S7. Hourly measurement time series at Milwaukee for (a) O<sub>3</sub>, (b) NH<sub>3</sub>, and (c) NO<sub>x</sub>



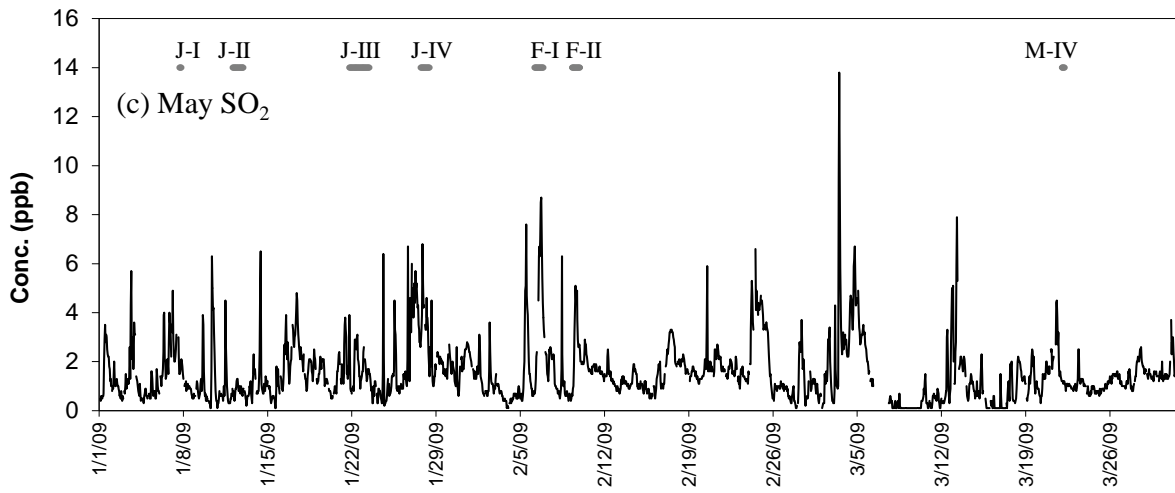
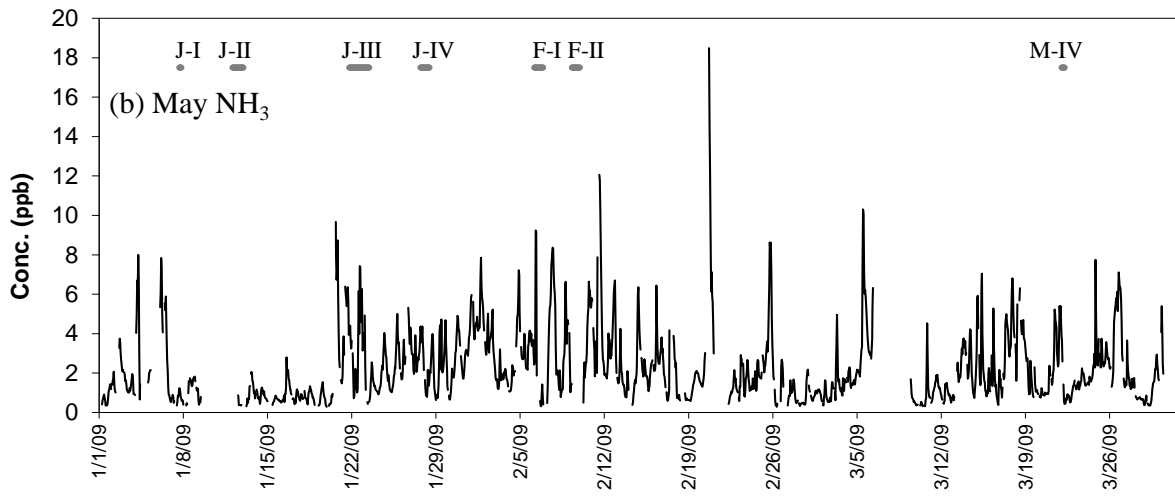
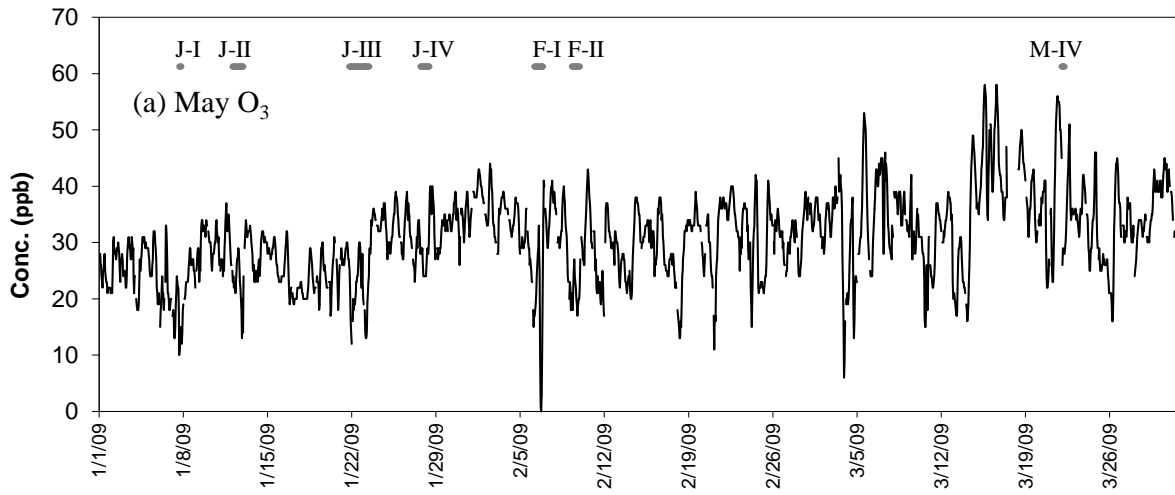


Figure S8. Hourly measurement time series at Mayville for (a) O<sub>3</sub>, (b) NH<sub>3</sub>, and (c) SO<sub>2</sub>