Appendix B 3

LADCO Winter Nitrate Study (Draft)

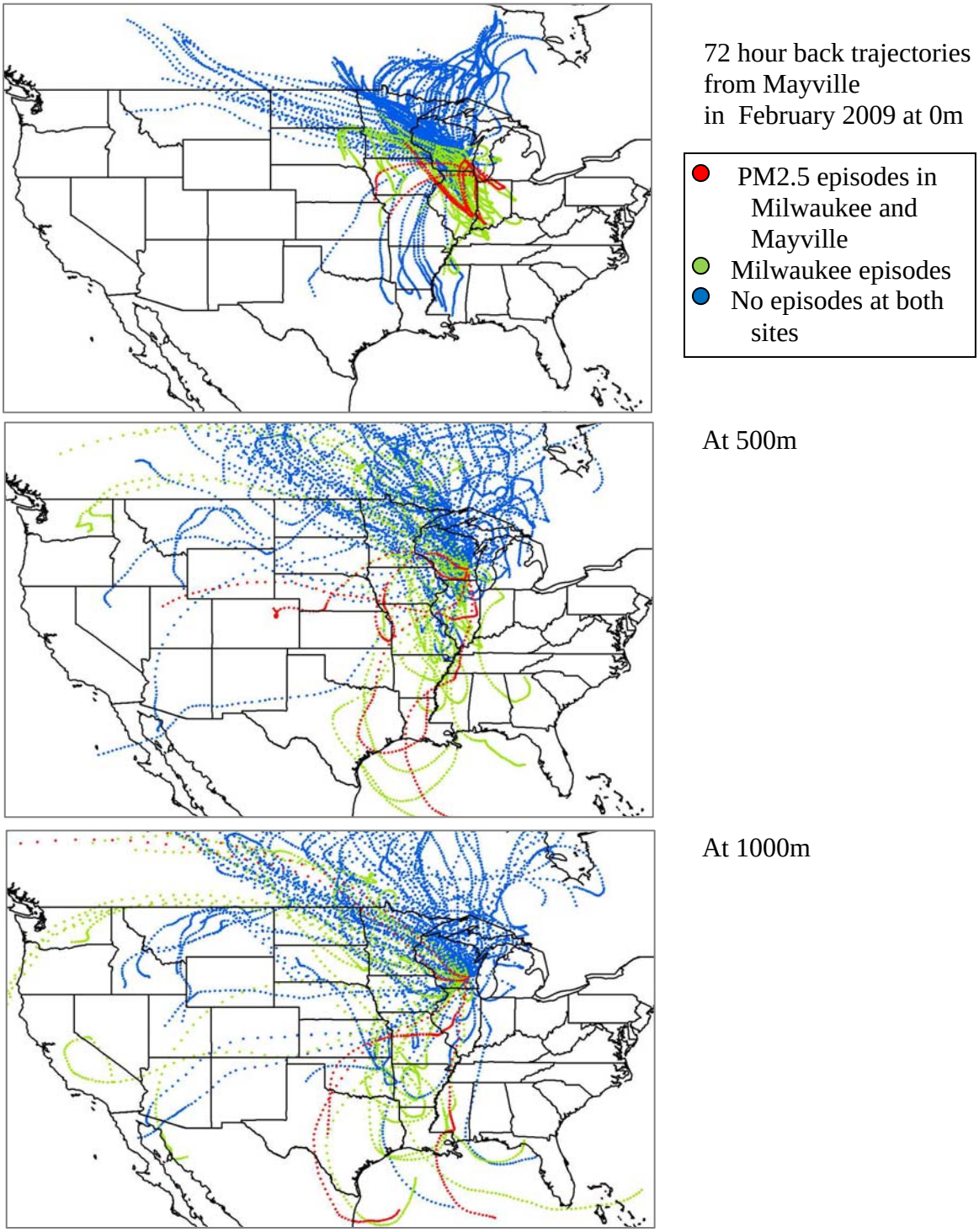


Figure 5-8. 72 hour back trajectories from the Mayville site in February 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.

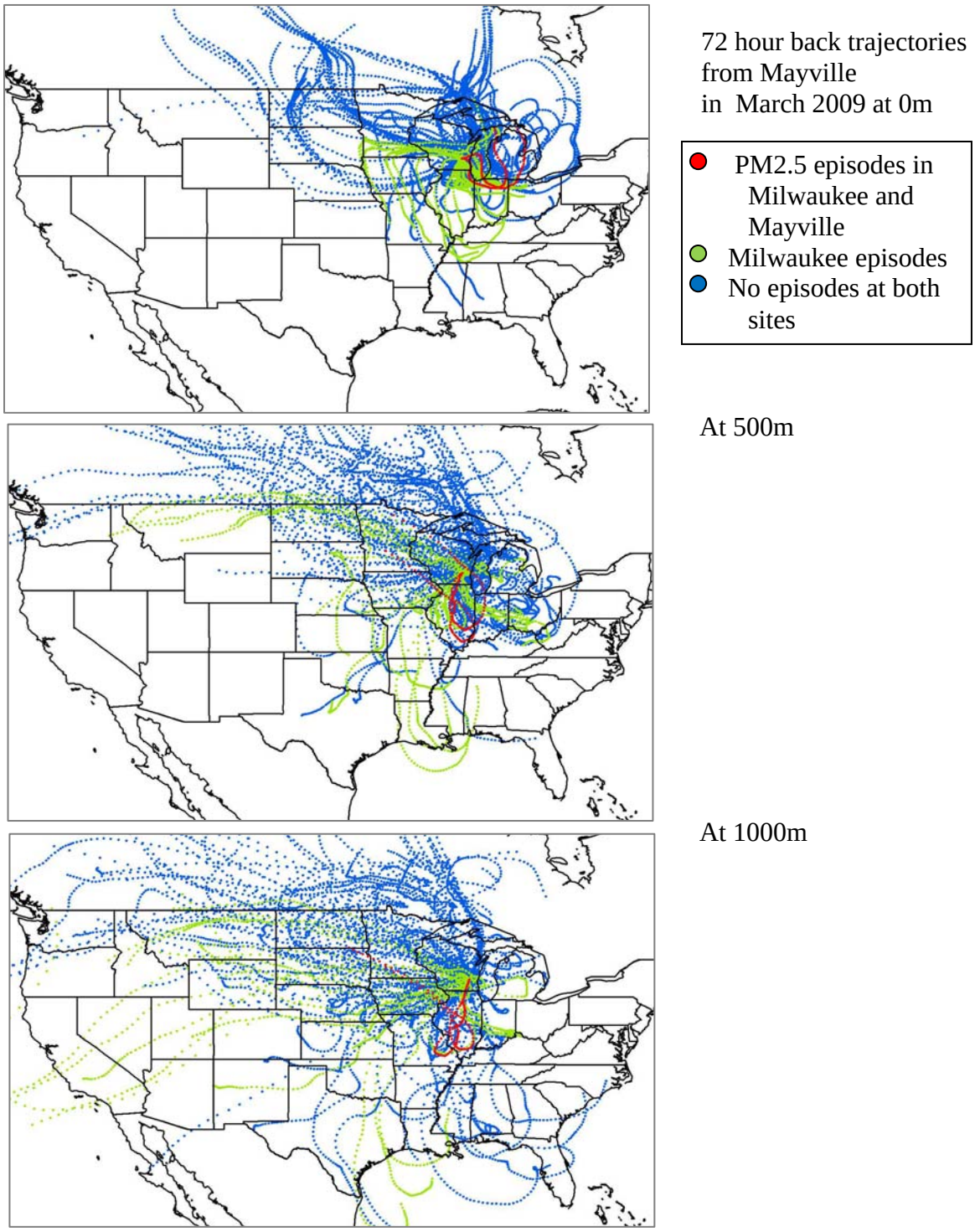
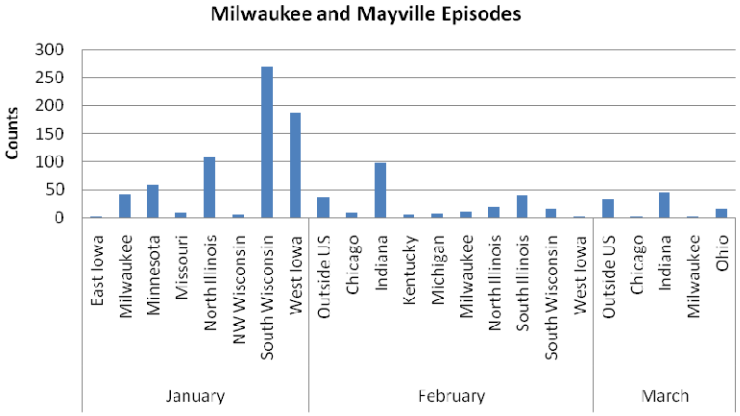
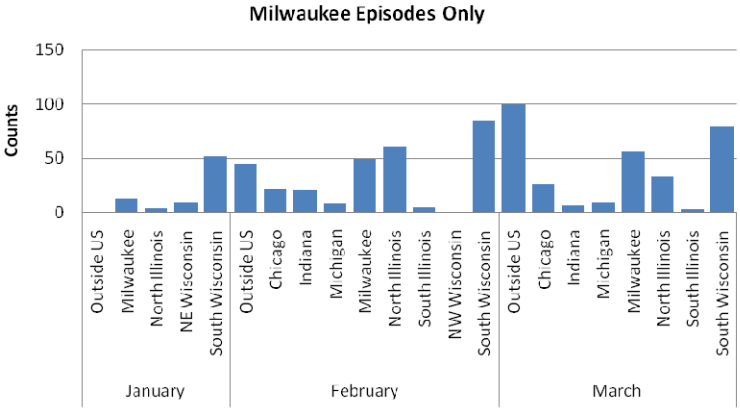


Figure 5-9. 72 hour back trajectories from the Mayville site in March 2009 at 0m, 500m, and 1000m. Back trajectories are analyzed at 6am, noon, 6pm and midnight every day.





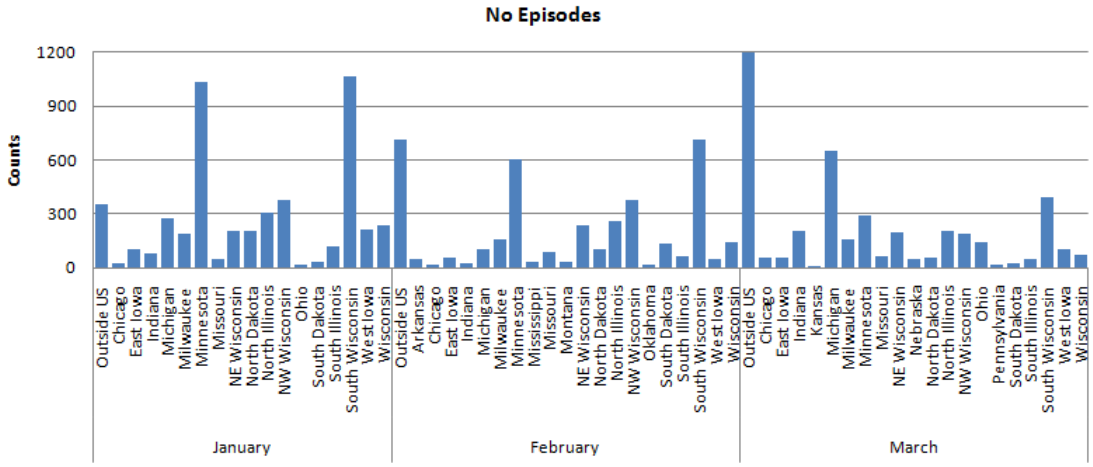


Figure 5-10. Histograms of air mass passages in the 48 hour back trajectories from Milwaukee. Histograms are plotted: 1) when there were PM2.5 episodes both in Milwaukee and Mayville; 2) only in Mayville; 3) only in Milwaukee; and 4) no episodes in both sites.

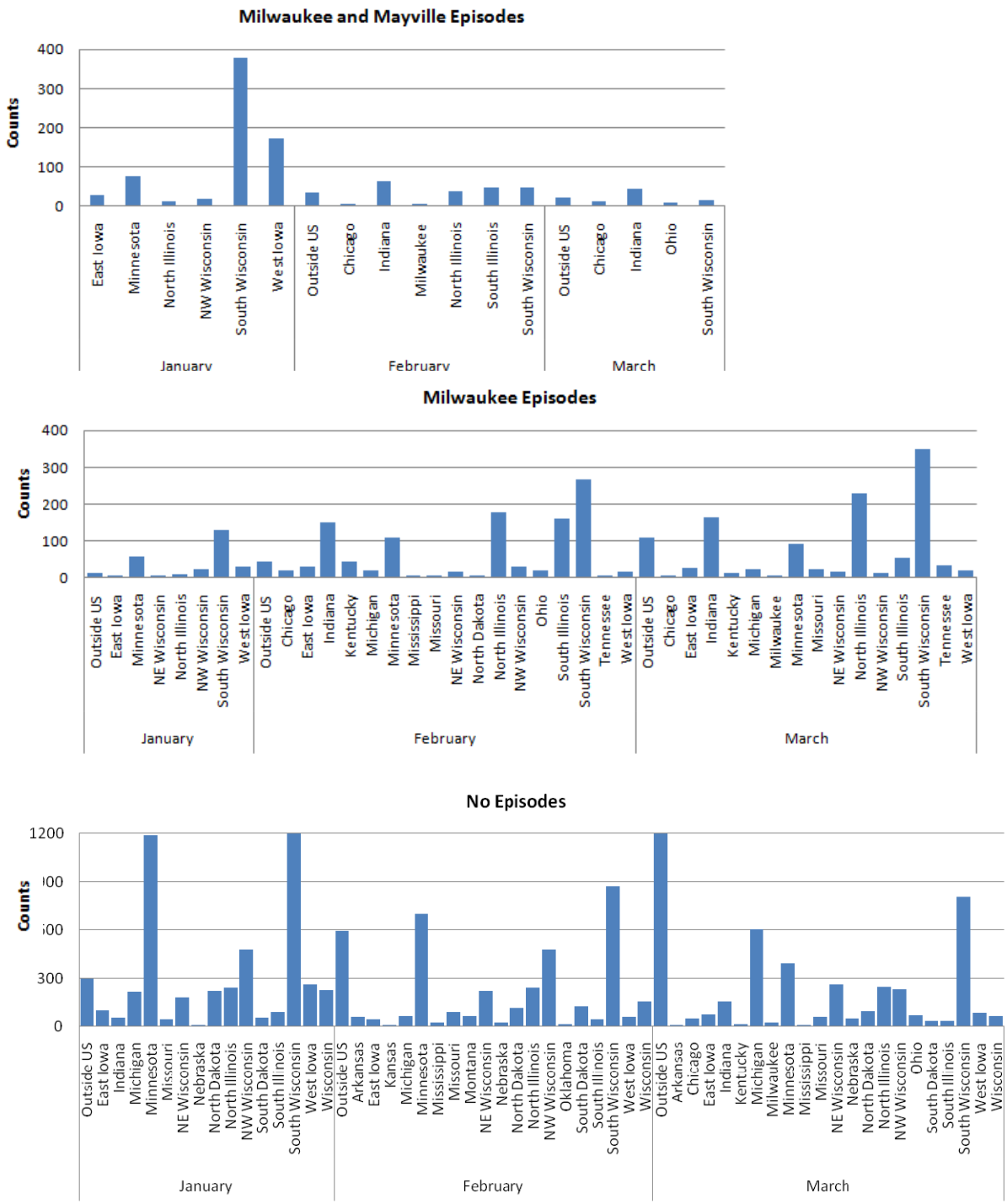


Figure 5-11. Histograms of air mass passages in the 48 hour back trajectories from Mayville. Histograms are plotted: 1) when there were PM2.5 episodes both in Milwaukee and Mayville; 2) only in Mayville; 3) only in Milwaukee; and 4) no episodes in both sites.

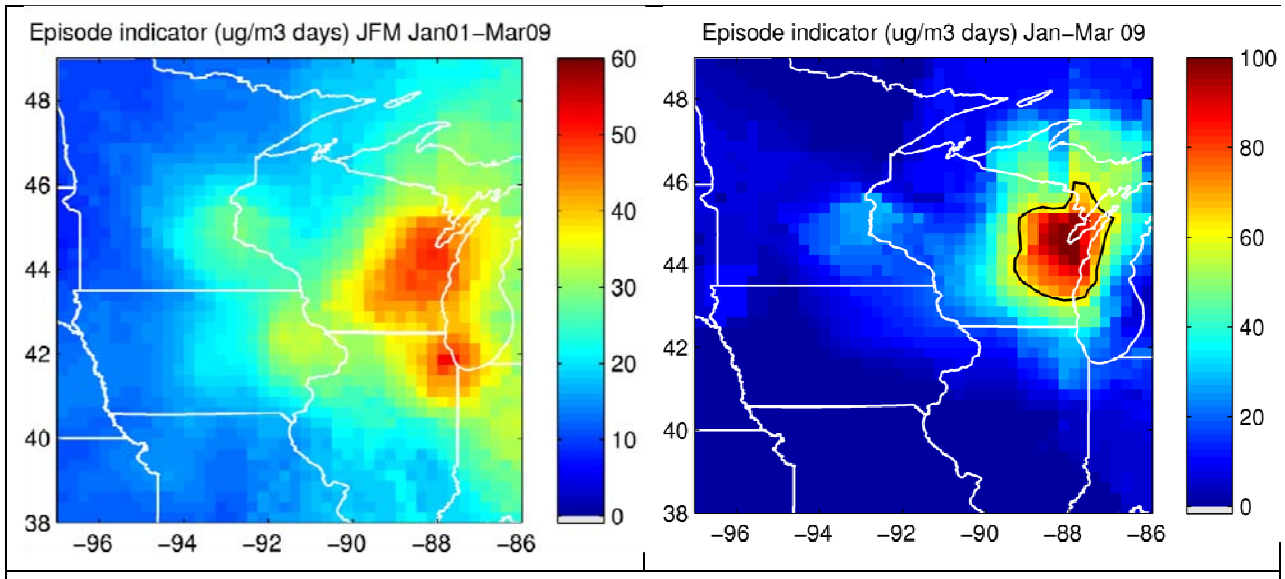


Figure 5-12. Historical average episode activity during January – March and the activity during the WNS period. Left panel shows the average over nine years. Right panel shows the LADCO WNS period. Black line shows a 62 µg m-3 threshold.

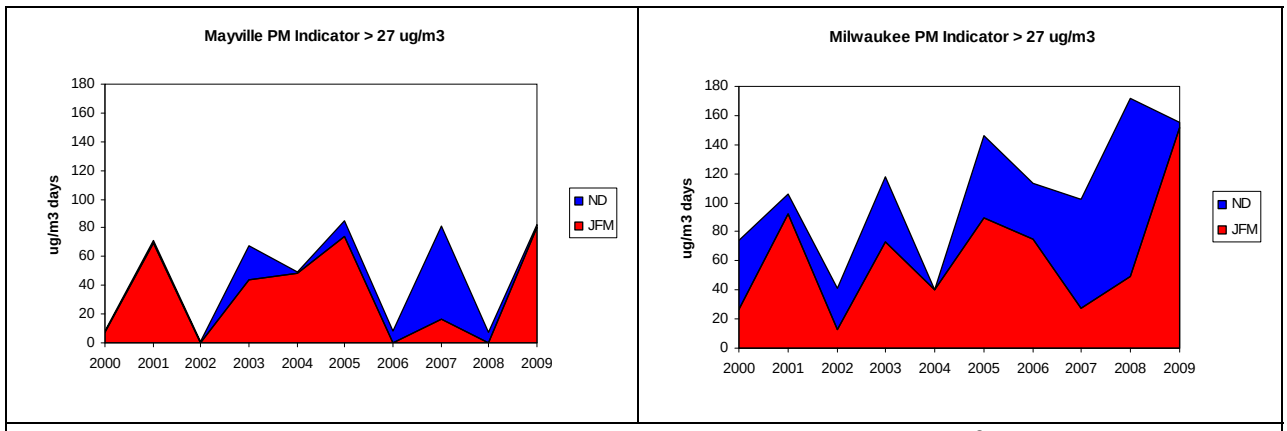
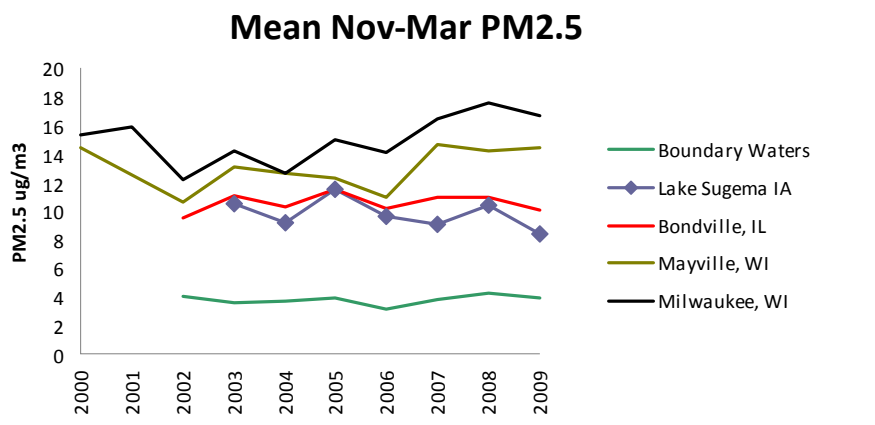
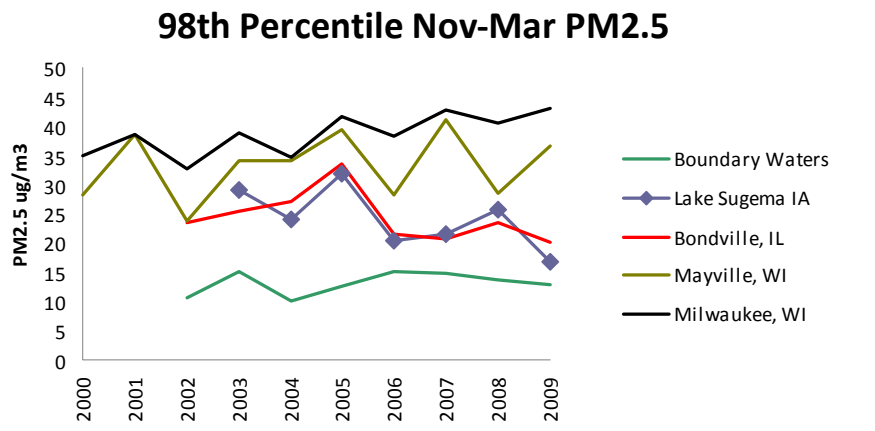


Figure 5-13. The episode indicator graphed on a year-by-year basis for Jan-Mar (red) and Nov&Dec (blue). November and December are offset by a year. For example, Nov08 and Dec08 are graphed at the 2009 tick to indicate the winter of 2008/2009. The LADCO WNS is characterized by the red area during year 2009. At Mayville, the episode indicator was 80 relative to its mean value of 34. At Milwaukee, the indicator was 151 versus an average value of 64. For reference, five episodes each with a single daily $PM_{2.5}$ reading of 37 µg m-3 would give an indicator value of 5x(37-27) or 50.





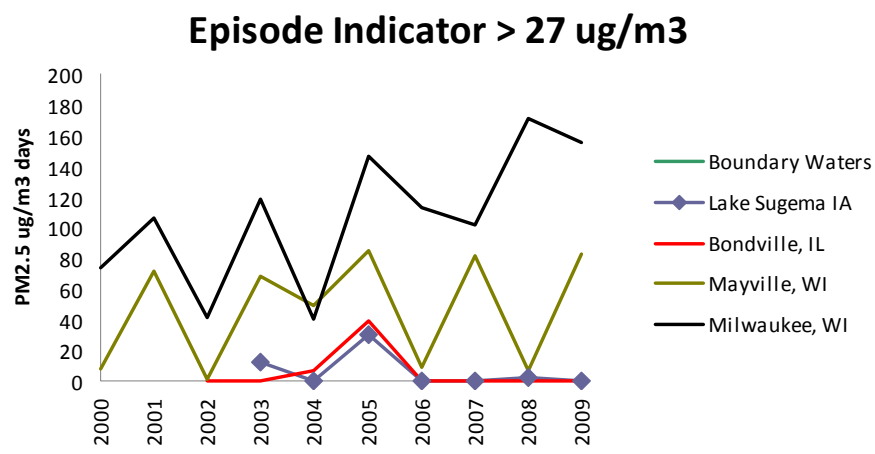


Figure 5-14. Panel A shows mean $PM_{2.5}$ for the cold winter season (Nov-Mar) of each year. Panel B shows the 98th percentile for each of these five month periods, and panel C shows the episode indicator.

6 URBAN AND DIRECTIONAL EXCESS CONCENTRATIONS

6.1 URBAN EXCESS CALCULATIONS

Measured gas and $PM_{2.5}$ species at Milwaukee and Mayville were compared to determine differences in air mass composition during episode and non-episode periods. Specifically, measured gas and $PM_{2.5}$ species were averaged over the study period (from January to March) using all hourly observations, Milwaukee only episode hours, and both Mayville and Milwaukee episode hours. Shown in Figure 6.1 (a-c) are results using the hourly data. Since organic carbon and elemental carbon measurements were available only on a daily basis once every three days, the average of daily $PM_{2.5}$ measurements were analyzed and plotted separately (Figure 6-1 (d-e)). Mayville and Milwaukee showed typical urban-rural contrast; higher NOy, organic carbon and elemental carbon levels in the urban area, due to local sources, and higher ozone concentrations in the rural area. During the $PM_{2.5}$ episodes concentrations of PM nitrate, OC and EC increased significantly, by ~5, 2.5, and 0.4 μgm^{-3} , respectively. The urban excess values during episodes of organic carbon and elemental carbon and total NOy increased significantly (Table 6-1). Figure 6-2 contains similar plots of the SEARCH monitoring sites for all hours, when $PM_{2.5}$ episodes were present and absent at Jefferson Street (Jefferson St. as an urban site and Yorkville a rural site). At the SEARCH monitoring sites, hourly OC and EC measurements are available, so only plots using hourly averages are shown. NOx and NOy levels were higher at Jefferson St., and ozone and ammonia were higher at Yorkville. In contrast to Milwaukee-Mayville measurements, organic carbon was the major constituent that drove the $PM_{2.5}$ episodes, higher than observations in the non-episode periods by 7 μgm^{-3}. Urban excess values were similar for episode and non-episodes periods for OC and EC concentrations, because the enhancements were the same at these sites during the $PM_{2.5}$ episodes.

Table 6-1. Urban excess at Milwaukee in percentages of rural concentrations

Species	All days	Milwaukee-Mayville episodes	Milwaukee only episodes
Sulfate	10	12	10
Ammonium	9	9	10
Nitrate	5	4	8
OC	60	153	64

EC	88	188	53

6.2. DIRECTIONAL SOURCE ANALYSIS

Directional analysis performed is for the period 01/01/2007 to 03/31/2007. Pollution roses, Bivariate polar, and Conditional Probability Function (CPF) analysis was done for all measured species at each site (summarized in Table 3-1). In the followings section, only species showing significant directionality are discussed.

Milwaukee: The Milwaukee site is located on a busy street (N Dr. Martin Luther King Dr.), north of the downtown area, and is exposed to many local sources. As shown in Figure 6-3a, winds from the south southeast were dominant, while winds from the east and north were infrequent. The mean wind speed was 3 ms^{-1}. Primary pollutant NO_x showed strong directionality. Figure 6-4a shows bivariate (wind and measured concentration) polar (angle: wind direction, radius: wind speed) plot of NO_x, where the color represents NOx concentration measured at the site. High concentrations were measured when wind blew from S – SW with wind speeds less than 2 ms^{-1}. This site is located at 700 meter east of interstate 46 and 2.8km north of interstate 794. To ensure the directionality, CPF of NOx is plotted in figure 6-4b. More than 50% of hours with wind from the south to west (180 to 270°) were associated with NOx concentrations exceeding 25 ppb. The CPF of NO_y (Figure 6-4c) also shows the same directionality. CPF of NH_3 (figure 6-4d) shows S-SW directionality however the Mayville CPF for NH_3 shows the same directionality, so this may not be indicative of local sources. The $PM_{2.5}$ bivariate polar plot (Figure 6-5a) does not show directional dependence. Winds associated with high PM are from the south and west and associated with the meteorology of the episodes described in section 5. Generally wind speed was slow (less than 2m/s) and came from SE to SW (135 to 225°) direction when higher concentration were measured. The bivariate polar plot for high PM episodes also shows limited directional and wind speed dependence. This supports that high PM is not from specific local sources. CPF of $PM_{2.5}$ with threshold value of 35 $\mu g\ m^{-3}$ (NAAQS standard) shows about 20% of NW wind exceeded this value.

Mayville: Mayville is a rural area, with wind direction characterized by wind rose (Figure

6-3b) similar to Milwaukee's. Mean wind speed was higher than Milwaukee (4 ms^{-1}) and less wind came from North to East (0 ~ 90°). Figure 6-6a shows CPF of SO_2, NH_3 and NO_y. SO_2 exceeded 2.5 ppb when wind blew from SWW to NW (240 to 320°). This wind direction may be consistent with an impact from the Columbia Energy Center (Coal fired power plant, 2units of 500MW) operated by Alliant Energy Corporation located about 70km away from Mayville site. EPA air emission sources (http://www.epa.gov/air/emissions/index.htm) reported that this power plant emitted about 15% of total amount of SO_2 for 2005 Wisconsin of electricity generation. Episode meteorology may also be causing an association with high SO_2 and the northwesterly dependence, and a more detailed analysis with a longer time series and comparison of $PM_{2.5}$ and SO_2 ratios would be necessary to confirm this. NH_3 was elevated during periods of southwesterly winds and NO_y was elevated during periods of northwesterly winds, but these are likely associated with episode meteorology (i.e. regional transport) or with more localized sources. $PM_{2.5}$ also does not show an overall directional source (Figure 6-7a). However, winds from SE where Milwaukee is located with high wind speed (3 -6 ms^{-1}) were associated with high PM concentrations, possibly indicating urban-to-rural transport. The highest PM2.5 concentrations are associated with PM2.5 episodes, and during these periods, peak PM2.5 at Mayville occurs with wind from the NW at 4-5 ms^{-1} (figure 6-7b).

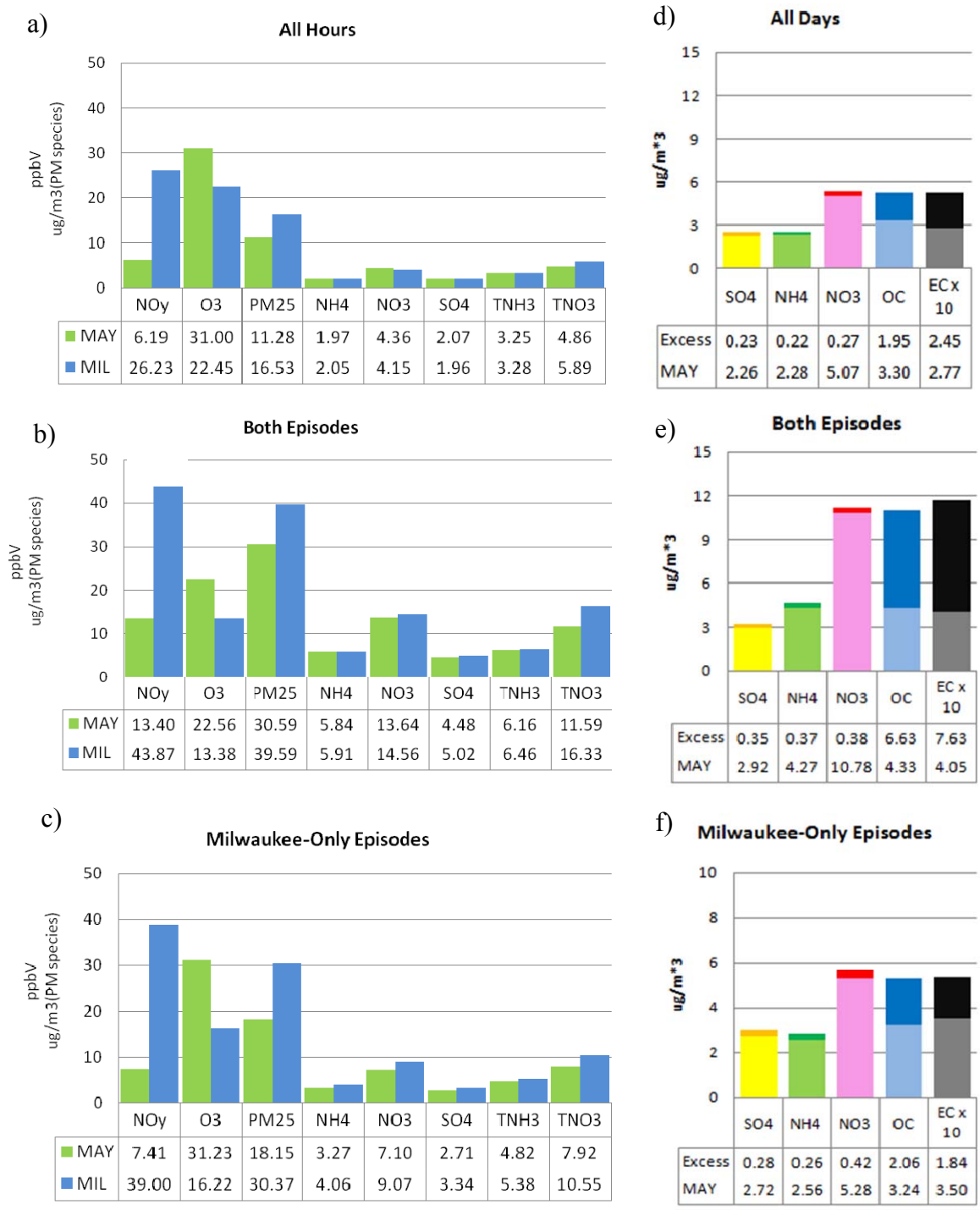
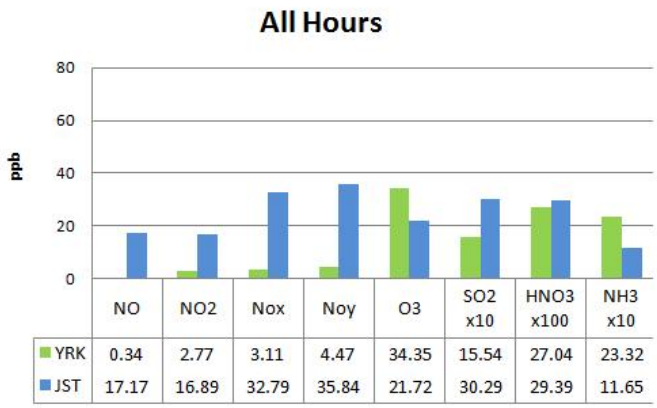
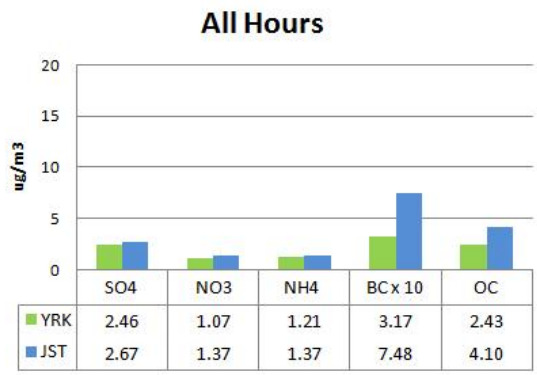
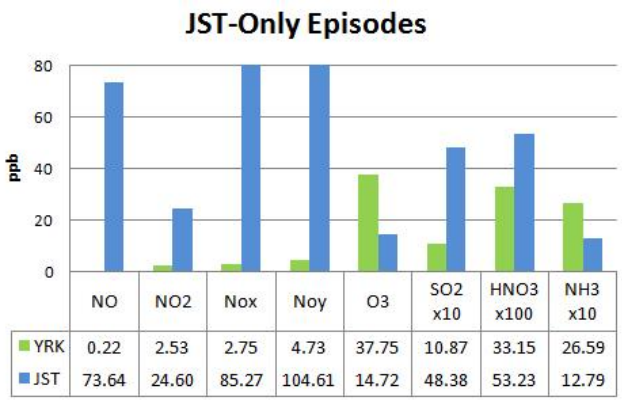
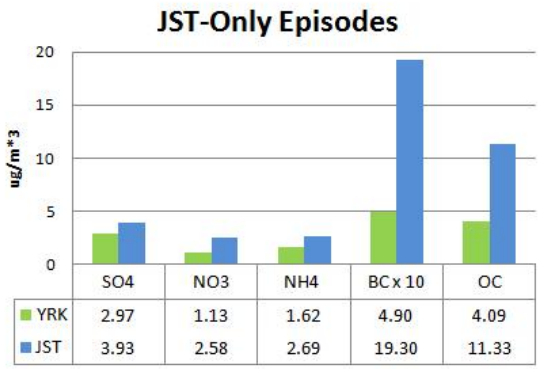


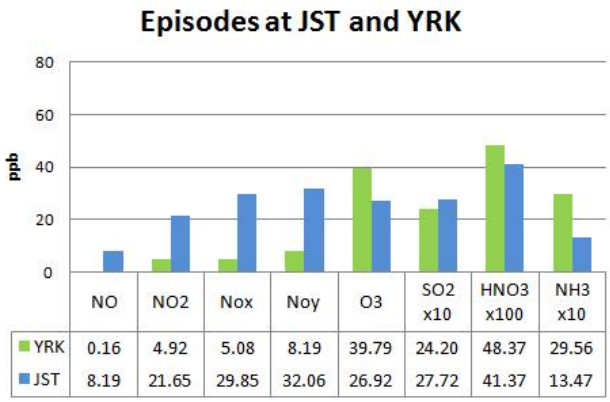
Figure 6-1. Averages of gas and PM2.5 species over the study period. a) - c) are averages of hourly measurements at Mayville (MAY) and Milwaukee (MIL). d)-f) are averages of daily PM species concentrations at Mayville (MAY, bright colors) and urban excess at Milwaukee (Excess, dark colors). Daily PM measurements do not cover the all days in the study period since they are available every three days. EC values are multiplied by 10 for presentation.











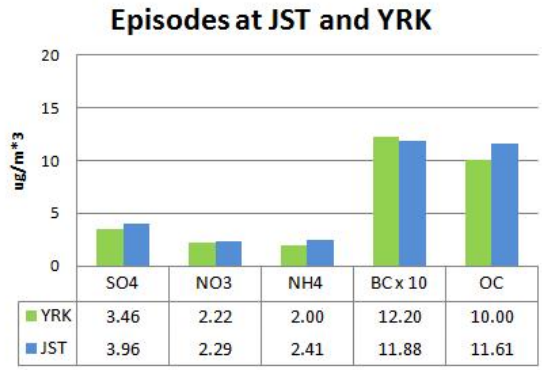


Figure 6-2. Averages of gas and $PM_{2.5}$ species measurements at the Yorkville (YRK, green bars) and Jefferson St. sites (JST. blue bars) from the SEARCH monitoring network (January 2009 to March 2009). All species were measured every hour. Note that BC,SO_2 and NH_3 measurements are multiplied by 10, and HNO_3 by 100 for presentation.

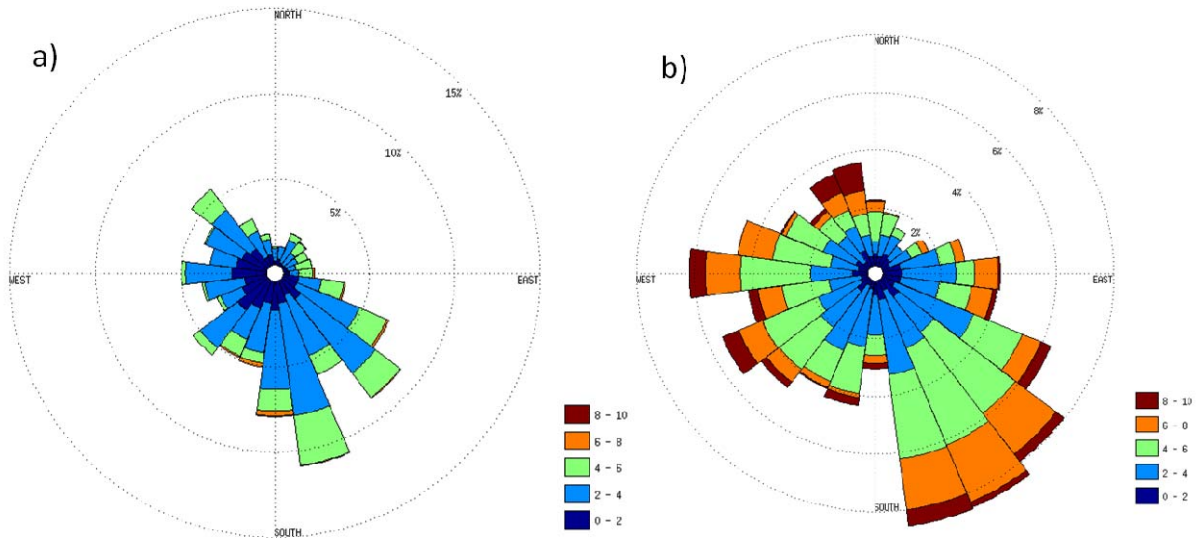


Figure 6-3 Wind rose a) for Milwaukee site b) for Mayville site

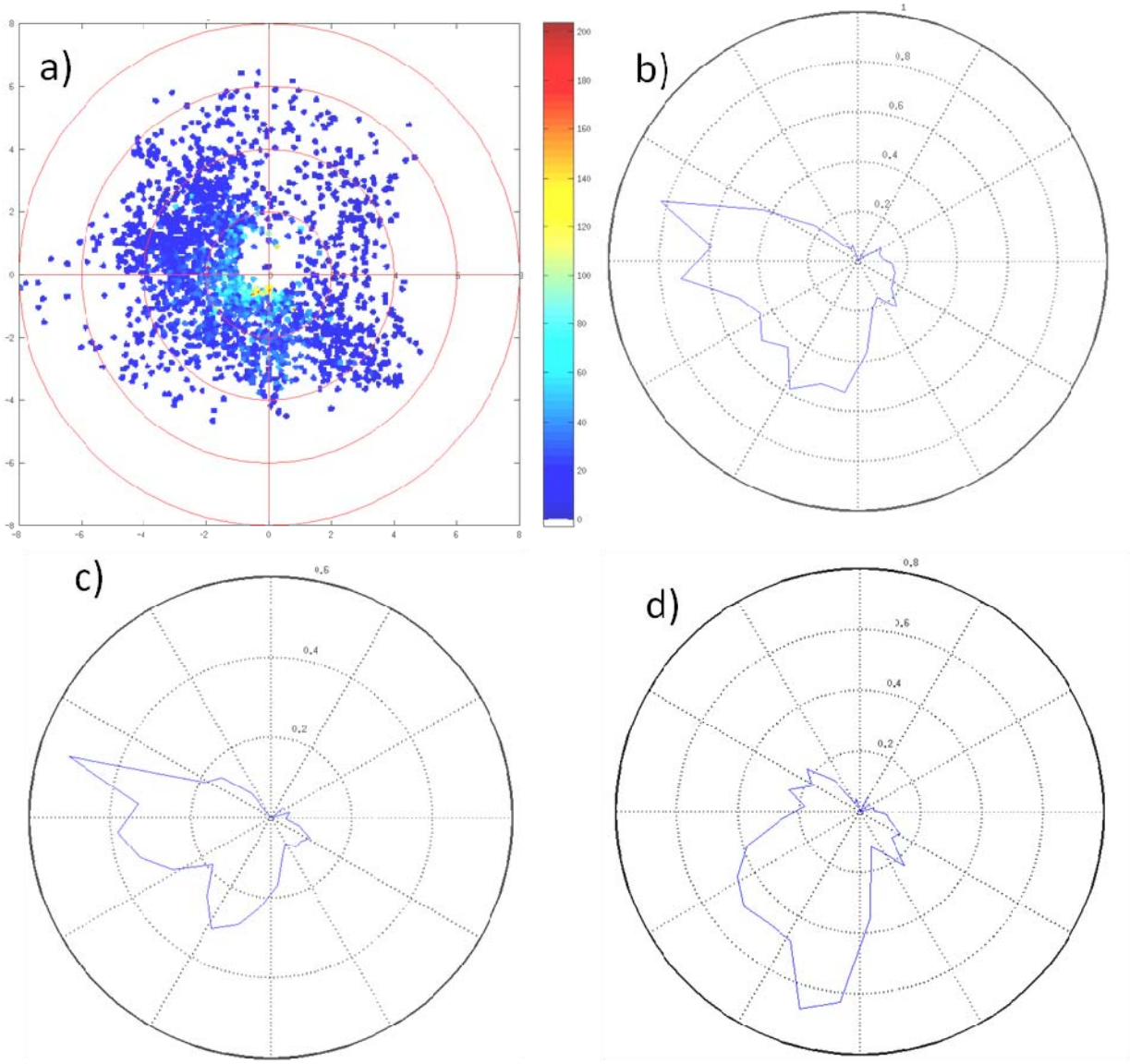


Figure 6-4 a) Bivariate polar plot of NO_x and CPF of b) NO_x (25ppb) c) NO_y(40ppb) and d) NH_3(3ppb) for Milwaukee site. Threshold value of CPF is in parenthesis.

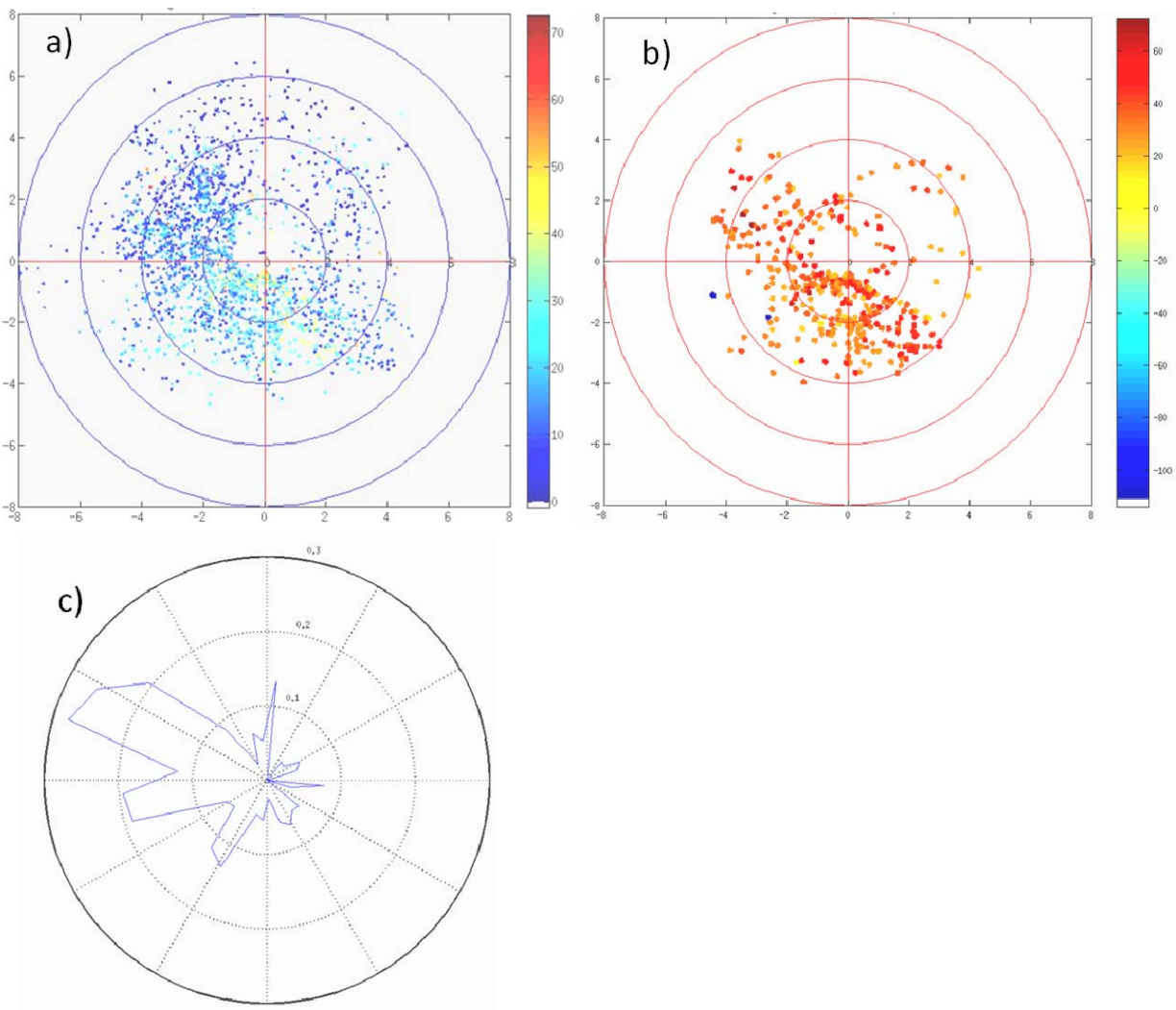


Figure 6-5 Bivariate polar plot of PM2.5 a) for whole period, b) for only high PM episodes and c) CPF of $PM_{2.5}$(35 μgm^{-3}) for Milwaukee site. Threshold value of CPF is in parenthesis.

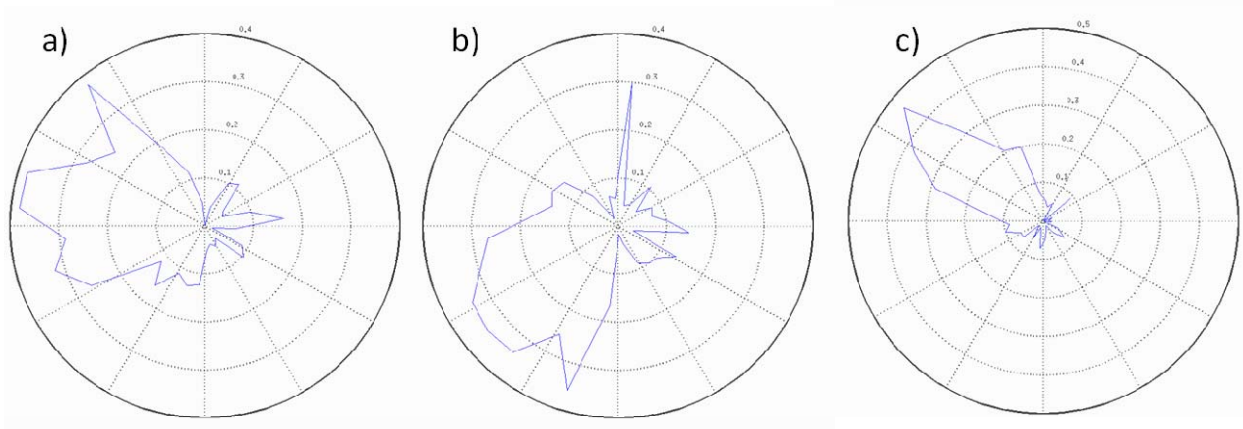


Figure 6-6 CPF of a) SO_2(2.5ppb), b) NH_3(3ppb) and c) NO_y(12ppb) for Mayville site. Threshold value of CPF is in parenthesis.

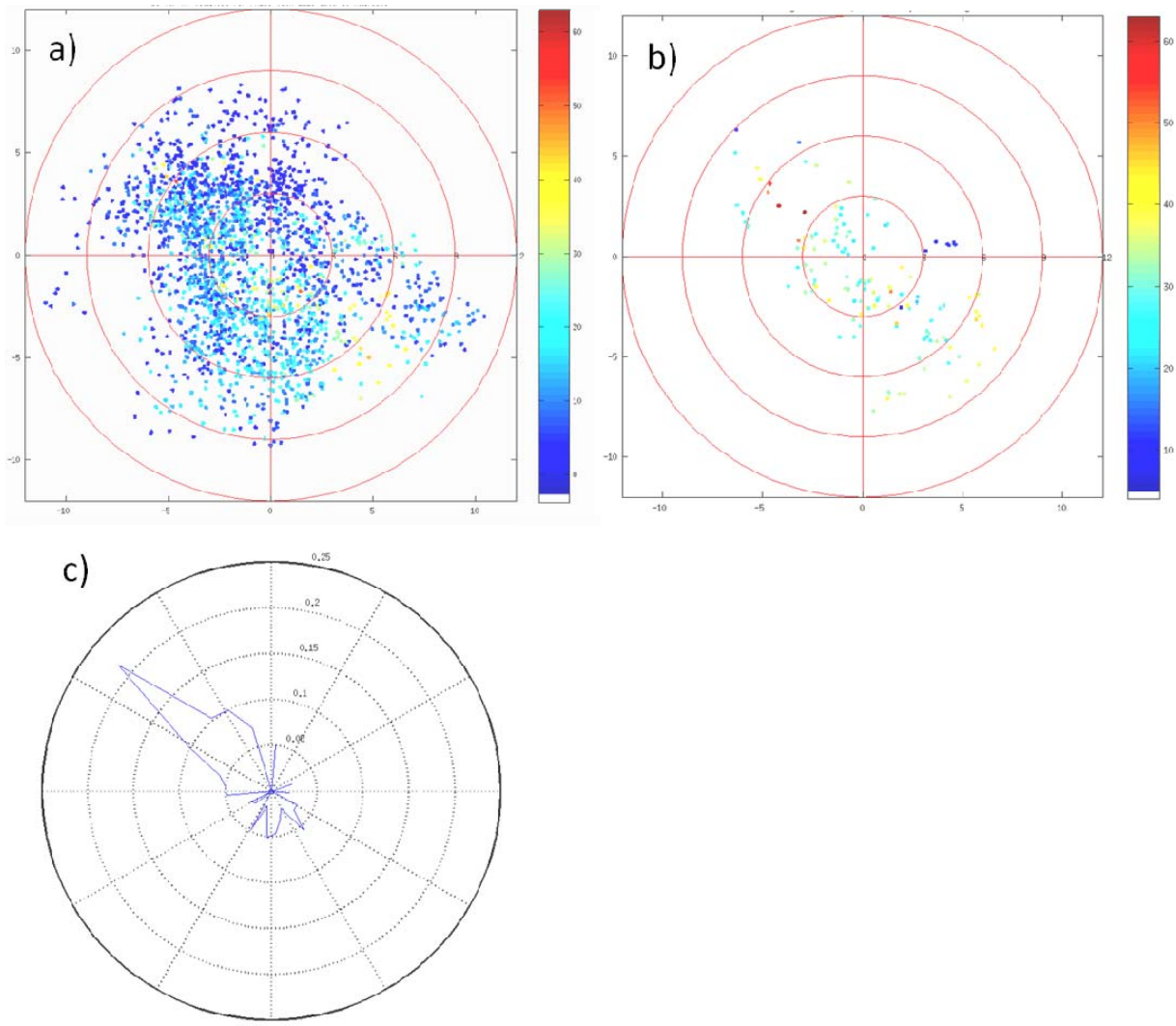


Figure 6-7 Bivariate polar plot of $PM_{2.5}$ a) for whole period, b) for high PM episodes only and c) CPF of $PM_{2.5}$(30 μgm^{-3}). Threshold value of CPF is in parenthesis.

7.0 THERMODYNAMIC SENSITIVITY

7.1 Models used and assumptions regarding aerosol hydration

Two thermodynamic box models were selected for use in this project: ISORROPIA version 1.7 and GFEMN (Gibbs Free Energy Minimization) version 2.2. ISORROPIA (Nenes, Pandis et al. 1998) was employed because of (1) its speed; (2) the fact that it is used within CMAQ; and (3) it was used, in addition to SCAPE, in previous LADCO analyses for the region (Blanchard and Tanenbaum 2008). GFEMN was used because of familiarity with this model at the University of Iowa, and because of its ability to successfully simulate both crystallized and hydrated aerosols during the Pittsburgh Air Quality study (Khlystov, Stanier et al. 2005). Furthermore, GFEMN has been used in other thermodynamic sensitivity studies (Takahama, Wittig et al. 2004; Vayenas, Takahama et al. 2005).

These models were validated against previous simulations and experimental data, and against one another. These are discussed in an appendix. Minor differences were identified between the models, but these were small compared to measurement uncertainty. Data-model agreement was much better under the assumption of hydrated metastable aerosols than under the assumption of aerosols on the deliquescence branch. Therefore, all simulations in section 7 are done with ISORROPIA on the efflorescence branch.

7.2 Methods of sensitivity determination

Thermodynamic sensitivity contour plots were generated by running ISORROPIA for every hour of the study. This was repeated for 400 separate sensitivity cases. 10 levels of total ammonia (30%, 40%, …, 90%, 100%, 110%, 120% of measured levels), 10 levels of total nitrate (30%, 40%, …, 90%, 100%, 110%, 120% of measured levels), and 4 levels of total sulfate (50%, 75%, 100%, and 120% of measured levels) were used. Contour plots were generated for total $PM_{2.5}$ with x axis of fraction of measured nitrate, y axis of fraction of measured ammonia, and z axis of $PM_{2.5}$ concentration. Separate contour plots could be made for each case of sulfate reduction.

Since the model only addressed changes in inorganic constituents, the following formula was used to convert changes in inorganic mass to changes in total $PM_{2.5}$.

$$PM_{2.5,TOT}^{\text{control scenario i}} = PM_{2.5,TOT}\left[1 - f_{inorg}\left(1 - \frac{PMmodel_{2.5,inorg}^{\text{control scenario i}}}{PMmodel_{2.5,inorg}^{\text{no controls}}}\right)\right]$$

While these graphical representations of sensitivity are useful, a visual point of reference for ammonia limited and nitric acid limited regimes is helpful. Therefore, on each contour plot, a ridgeline is drawn, corresponding to points on the graph where equal fractional reductions (relative to the base case, i.e. 1.0x THN_3, 1.0x TNO_3) give equal response for reduction in $PM_{2.5}$. Additional variables used in this section include adjusted gas ratio, gas ratio, and degree of sulfate neutralization.

$$\text{AdjGR} = \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{\text{TA} - \text{DSNxTS}}{\text{TN}} = \frac{[\text{NH}_3](\text{mol}) + [\text{NO}_3^-](\text{mol})}{[\text{HNO}_3](\text{mol}) + [\text{NO}_3^-](\text{mol})}$$

$$\text{DSN} = \frac{[\text{NH}_4^+](\text{mol}) - [\text{NO}_3^-](\text{mol})}{[\text{SO}_4^-](\text{mol})}$$

Two additional measures of ammonia availability are the gas ratio GR and Excess Ammonia (EA) (Blanchard, Roth et al. 2000).

$$\text{GR} = \frac{\text{free ammonia under assumption of full neutralization}}{\text{total nitrate}} = \frac{\text{TA} - 2\text{xTS}}{\text{TN}}$$

$$\text{EA} = \text{free ammonia} = \text{TA} - 2\text{xTS} - \text{TN} - [\text{HCl(g)}] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] - [\text{Cl}^-]$$

7.3 Proposal of relative sensitivity as a key indicator variable and gas ratio as a controlling factor

The following variables are used for quantitative characterization of sensitivity to nitrate and to ammonia reductions, and to the relative sensitivity of nitrate versus ammonia reductions.

Table 7-1. Definitions of sensitivity variables

Symbol in this work	Name	Formula
$S_{NO3\text{-}f}$	Sensitivity to a fractional reduction in total nitrate	$\frac{\Delta PM_{2.5,inorg} / PM_{2.5,inorg}}{\Delta TNO3 / TNO3}$
$S_{NH3\text{-}f}$	Sensitivity to a fractional reduction in total ammonia	$\frac{\Delta PM_{2.5,inorg} / PM_{2.5,inorg}}{\Delta TNH3 / TNH3}$
RS_f	Relative sensitivity (on fractional basis)	$S_{NO3\text{-}f}$ / $S_{NH3\text{-}f}$
$S_{NO3\text{-}M}$	Sensitivity to a mass reduction in total nitrate	$\frac{\Delta PM_{2.5,inorg}}{\Delta TNO3}$
$S_{NH3\text{-}M}$	Sensitivity to a mass reduction in total ammonia	$\frac{\Delta PM_{2.5,inorg}}{\Delta TNH3}$
RS_M	Relative sensitivity (on mass basis)	$S_{NO3\text{-}M}$ / $S_{NH3\text{-}M}$

The conversion between RS_f and RS_M is simply:

$$RS_f = RS_M \frac{TNO3}{TNH3} \quad \text{and} \quad RS_M = RS_f \frac{TNH3}{TNO3}$$

RS_f has the advantage that it is easily calculated from previous work, and from isopleth diagrams with fractional TNO3 and TNH3 as the x and y axes. It has the disadvantage that it varies more for a given gas ratio than RS_M. RS_M has the advantage of tighter correlation with gas ratio than RS_f. The properties of these 6 variables are shown as a function of gas ratio in figure 7-1 and figure 7.2.

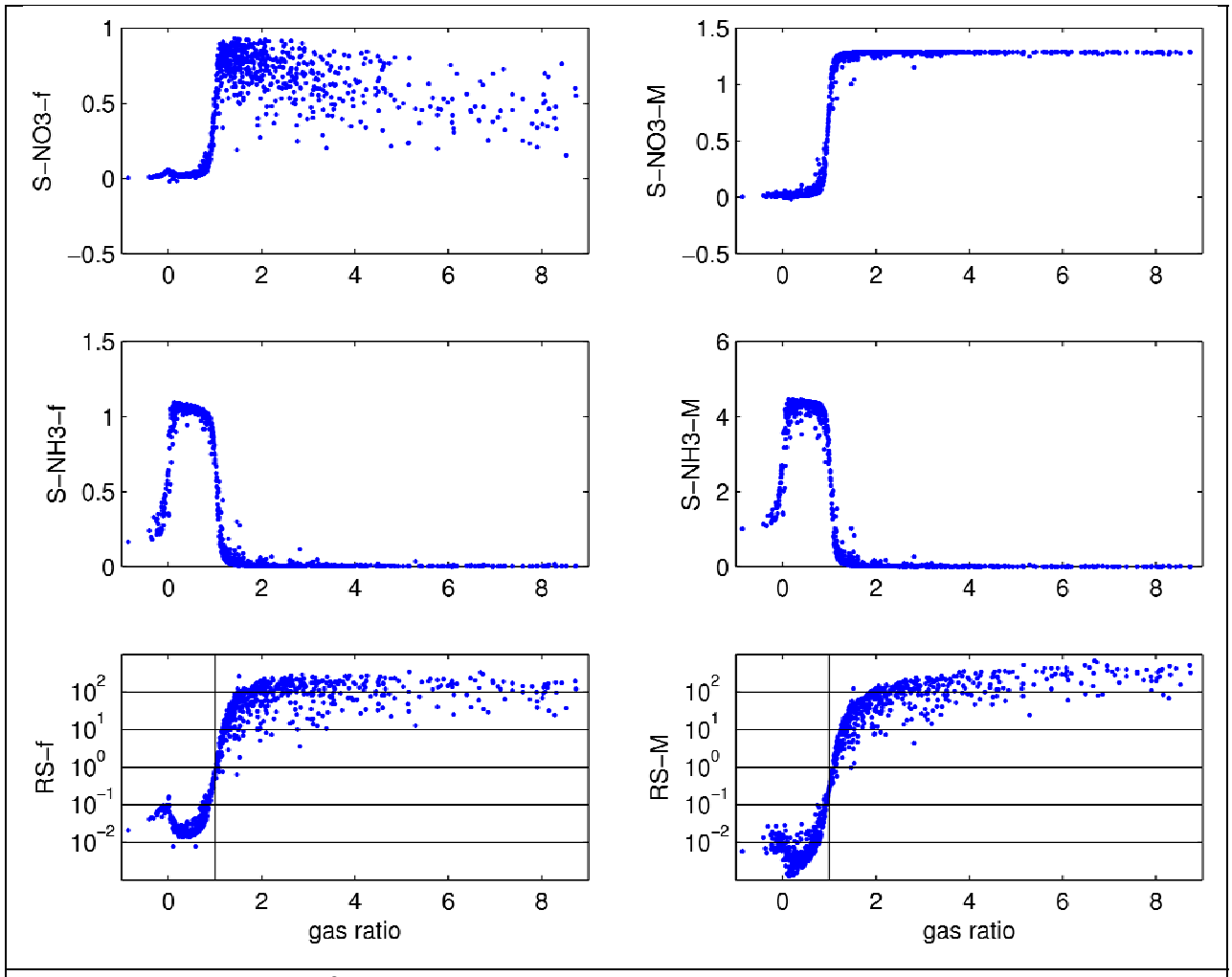


Figure 7-1. Properties of the 6 sensitivity variables in table 7-2 with respect to gas ratio. Blue dots correspond to 1000 test cases modeled in ISORROPIA with random levels of sulfate, nitrate and ammonia (and no chloride or sodium). All cases are fixed at 79% RH, 0°C (the mean conditions for Milwaukee episodes). Fractional sensitivity variables are on the left, mass-based sensitivity variables are on the right. S_{NO3-M} has an upper limit of (62+18)/62 (molecular weight ratios of ammonium nitrate and nitrate) while S_{NH3-M} has an upper limit of (62+18)/18.

We propose operational definitions of sensitivity based on RS_M as follows:

$\infty > RS_M > 8$	Nitrate sensitive / ammonia insensitive
$8 > RS_M > 2$	More sensitive to nitrate than to ammonia
$2 > RS_M > 0.5$	Nitrate and ammonia sensitivity approximately balanced
$0.5 > RS_M > 0.125$	More sensitive to ammonia than to nitrate
$0.125 > RS_M$	Ammonia sensitive / nitrate insensitive

These cut points are illustrated in figure 7-2.

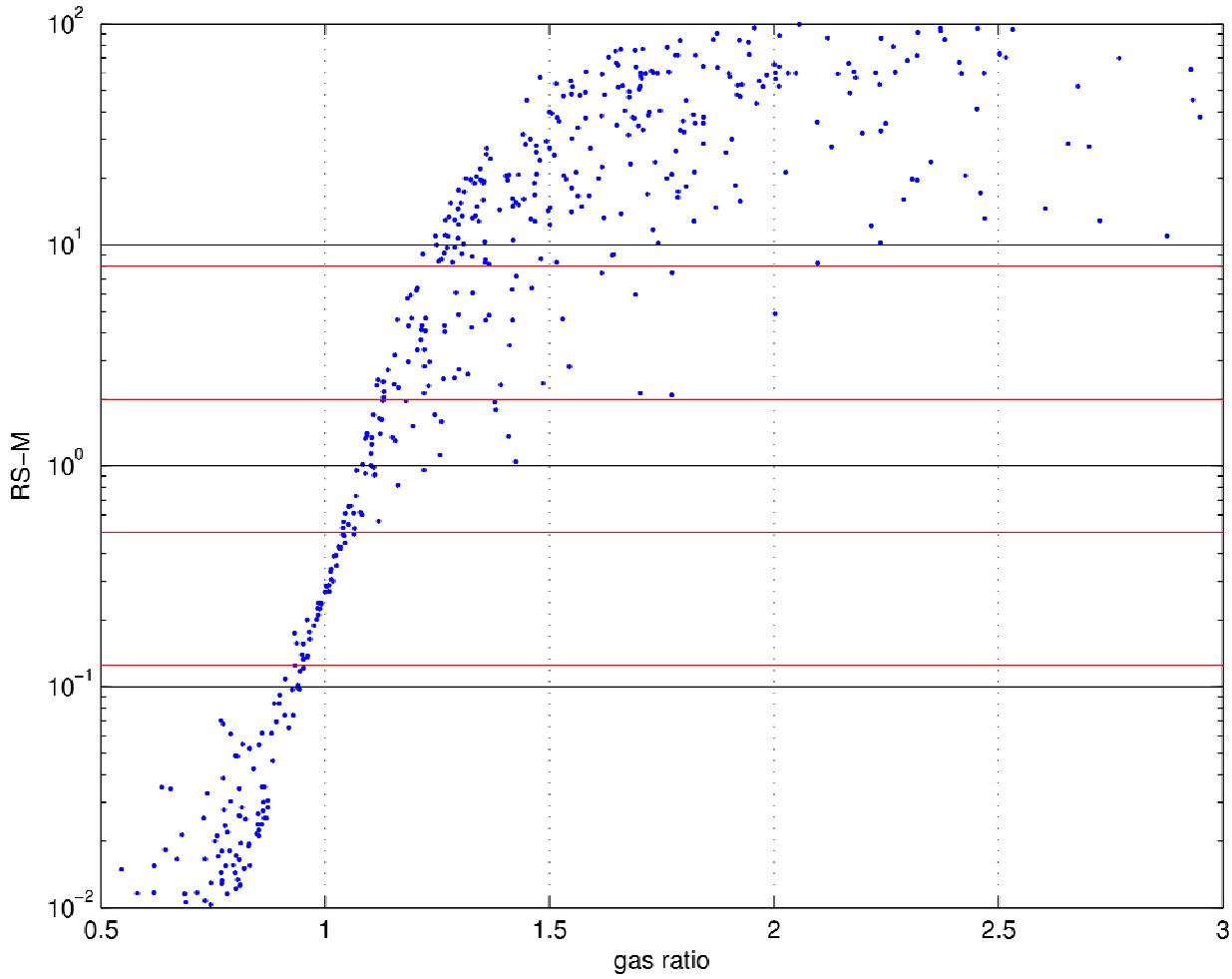


Figure 7-2. RS_M as a function of gas ratio from 0.5 to 3. See figure 7-1 caption for how points were generated. Red lines correspond to the sensitivity regimes defined in text. $RS_M > 8$ is operationally defined as nitrate sensitive / ammonia insensitive, and is when GR > ~2 but can occur for GR as low as 1.25. $8 > RS_M > 2$ is operationally defined as more sensitive to nitrate than to ammonia, and occurs for GR between 1.2 – 1.8. $2 > RS_M > 0.5$ is operationally defined as balanced sensitivity and this occurs from GR of ~1.02 – 1.28. $0.5 > RS_M > 0.125$ is operationally defined as more sensitive to ammonia than to nitrate and occurs for GR ~0.9-1.08. RSM of less than 0.125 is defined as ammonia sensitive / nitrate insensitive and occurs for GR < ~0.9. Scatter (in the y direction) for points with GR < 0.9 is improved when the plot is made versus adjusted gas ratio, but scatter for GR > 1.2 remains whether the plot is versus GR or adjusted GR.

The ratios of total nitrate to total ammonia are necessary for conversion between the RS_f and RS_M variables. These values can be found in table 7-2. The sensitivity regimes from above, the relationship between gas ratio and RS_M from figure 7-2, and the TNO3/TNH3 ratios from the LADCO WNS are combined in table 7-3. This gives the ranges of RS_f and gas ratios associated with various regimes of sensitivity. Please note that the relationship between gas ratio and sensitivity is only applicable for 273 K, 79% RH, and for a single hour.

Table 7-2 – TNO3 and TNH3 values for Mayville and Milwaukee – needed for conversions between mass-based and fractional sensitivities

	Mayville			Milwaukee		
	no episodes	all hours	episode hours	no episodes	all hours	episode hours
TNO3 concentration (mass, µg m^{-3})	4.52	4.79	12.35	4.55	5.62	12.04
TNH3 concentration (mass, µg m^{-3})	3.15	3.24	5.79	2.77	3.30	6.24
TNO3/TNH3	1.44	1.48	2.13	1.64	1.70	1.93

Table 7-3 – Sensitivity Regimes

			Corresponding RS-f values					
			Milwaukee			Mayville		
Regime	RSM Cutoff	Associated Gas Ratio	No episode	All hours	Episodes	No episode	All hours	Episodes
Nitrate sensitive / ammonia insensitive		GR > ~2 but can occur with GR as low as ~1.25						
	8		13.1	13.6	15.4	11.5	11.8	17.1
More sensitive to nitrate than to ammonia		1.2 > GR > ~1.8						
	2		3.2	3.4	3.8	2.9	3.0	4.3
Nitrate and ammonia sensitivity approximately balanced		~1.02 > GR > ~1.28						
	0.5		0.82	0.85	0.96	0.71	0.74	1.06
More sensitive to ammonia than to nitrate		~0.9 > GR > ~1.08						
	0.125		0.21	0.21	0.24	0.18	0.18	0.27
Ammonia sensitive / nitrate insensitive		GR < ~0.9						

7.4 Results and discussion

Now with operational definitions for what constitutes ammonia or nitric acid sensitivity, we can proceed with the analysis of the LADCO WNS data.

7.4.1 Concentration isopleths based on fractional sensitivity

A more complete set of contour diagrams can be found in an appendix. The following figures are the "all study hours" contour plot for Milaukee (figure 7-3), the "all study hours" plot for Mayville (figure 7-4), the "episode only" plot of Milwaukee (figure 7-5), and the "episode only" plot for Mayville (figure 7-6).

Using figure 7-3 as an example, it can be seen that the base case $PM_{2.5}$ concentration (at x=1, y=1) is 16.8 μg m^{-3}. A 30% reduction in nitrate with no ammonia reduction results in a modeled mean concentration of 15.4 μg m^{-3}. A 30% reduction in ammonia with no nitric acid reduction results in a modeled mean concentration of 15.5 μg m^{-3}. The ridgeline is just below the x=1, y=1 point. The ratio of $\Delta PM_{2.5}$ for a 30% nitrate only reduction to the $\Delta PM_{2.5}$ for a 30% ammonia only reduction is RS_f and is equal to 1.04. Table 7-3 has the sensitivity regimes for Milwaukee "all hours" and RS_f between 0.85 and 3.4 would be classified as balanced sensitivity. To convert the RS_f to RS_M, the ratio of total ammonia to total nitrate is needed from table 7-2 (TNO3 = 5.62; TNH3 = 3.30). RS_M is then 1.04 x 3.30 / 5.62 or 0.61. This is between 0.5 and 2 and is therefore classified as balanced sensitivity.

Figure 7-4 (all hours, Mayville) is qualitatively similar to figure 7-3. The PM2.5 concentrations are lower reflecting the urban excess of PM2.5. Figure 7-5 (episode hours, Milwaukee) is also qualitatively similar. Figure 7-6 (episode hours, Mayville) is qualitatively different. In that case, the ridgeline is above the 1:1 point, an indication that episode hours at Mayville are more sensitive to ammonia reductions that the other 3 cases.

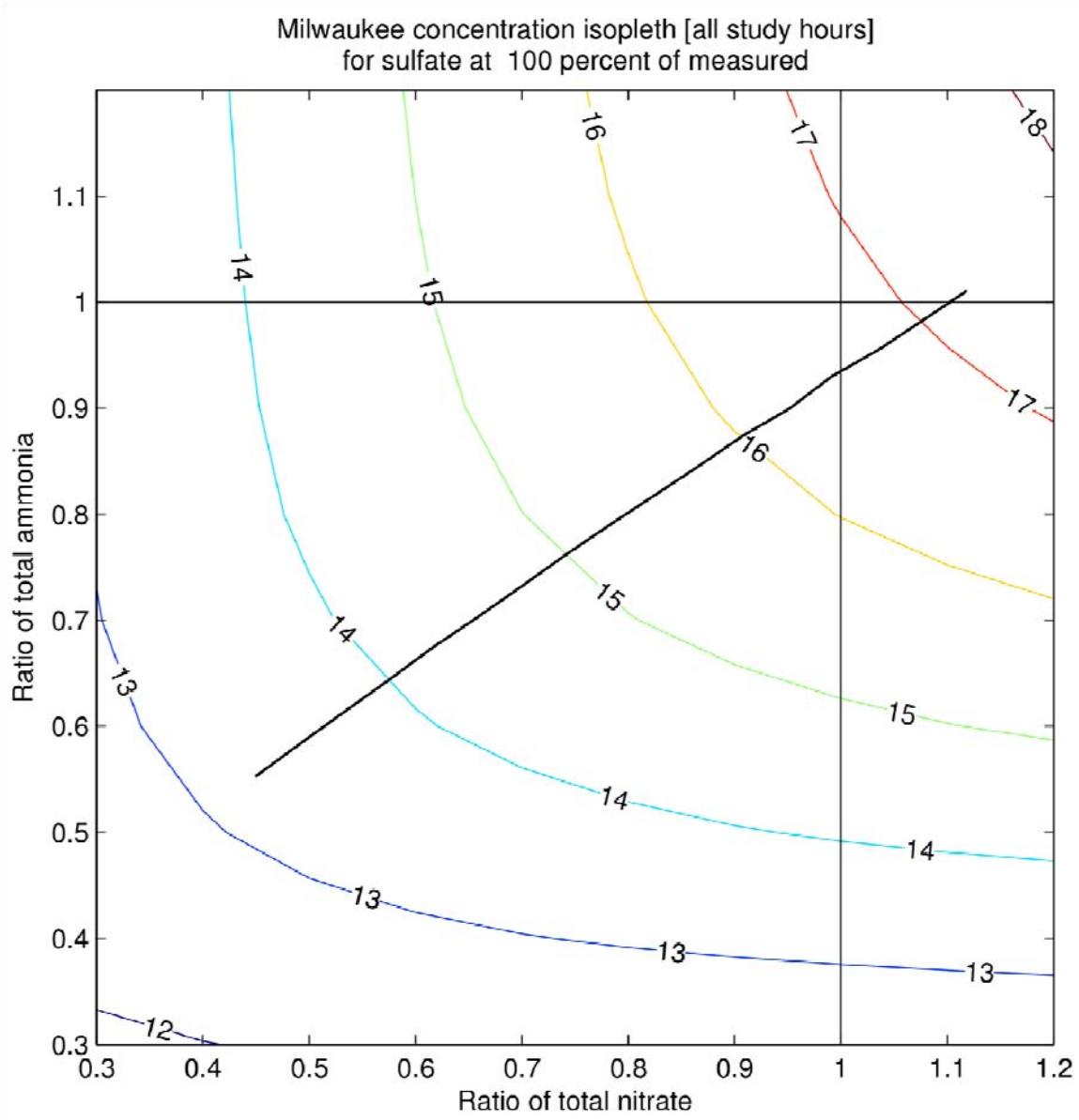


Figure 7-3. Sensitivity of $PM_{2.5}$ to reductions in total nitrate and total ammonia.

SITE: MILWAUKEE

PERIOD: ALL STUDY HOURS

SULFATE LEVEL: 100% OF MEASURED VALUE

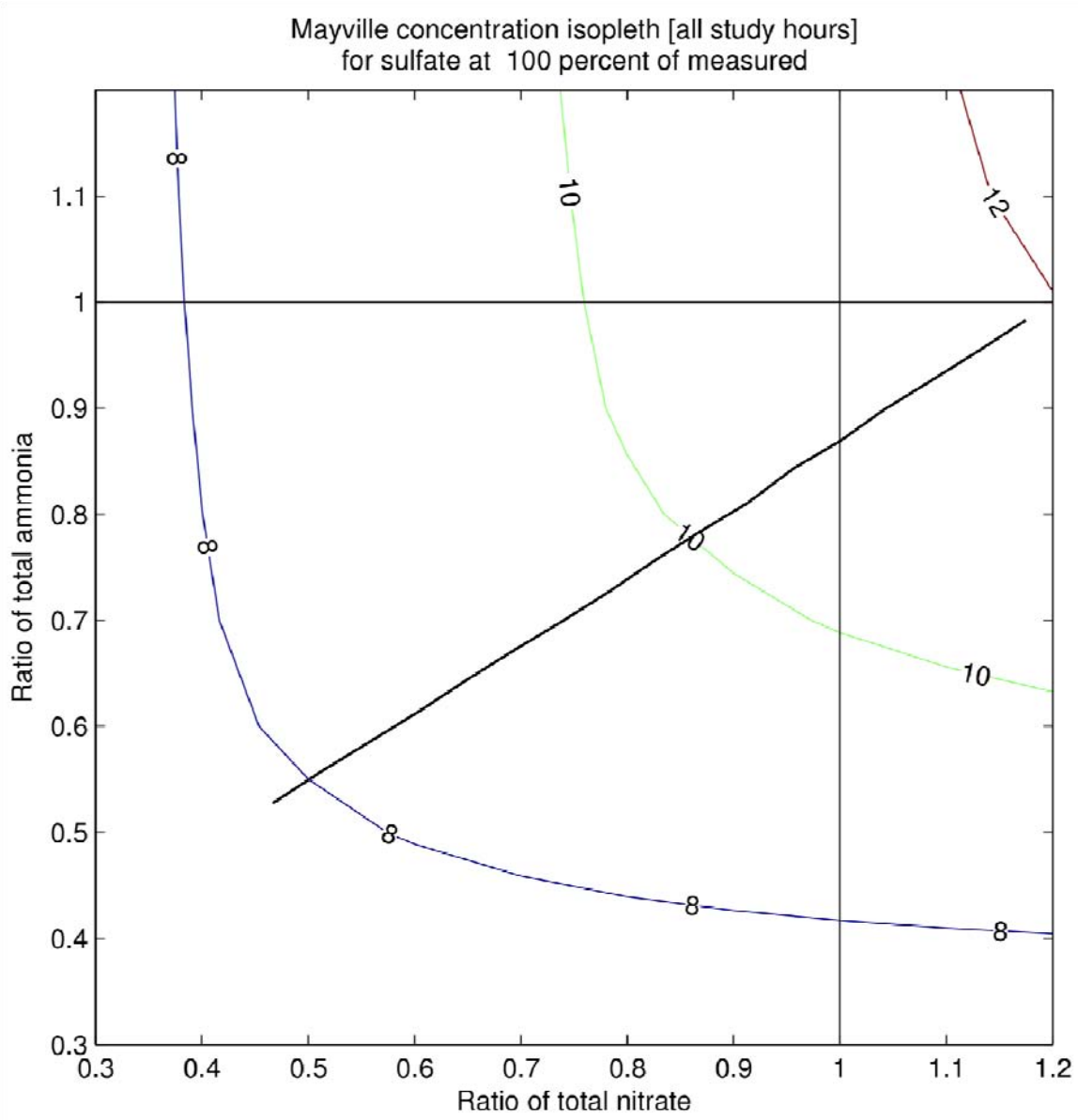


Figure 7-4. Sensitivity of $PM_{2.5}$ to reductions in total nitrate and total ammonia.

SITE: MAYVILLE

PERIOD: ALL STUDY HOURS

SULFATE LEVEL: 100% OF MEASURED VALUE

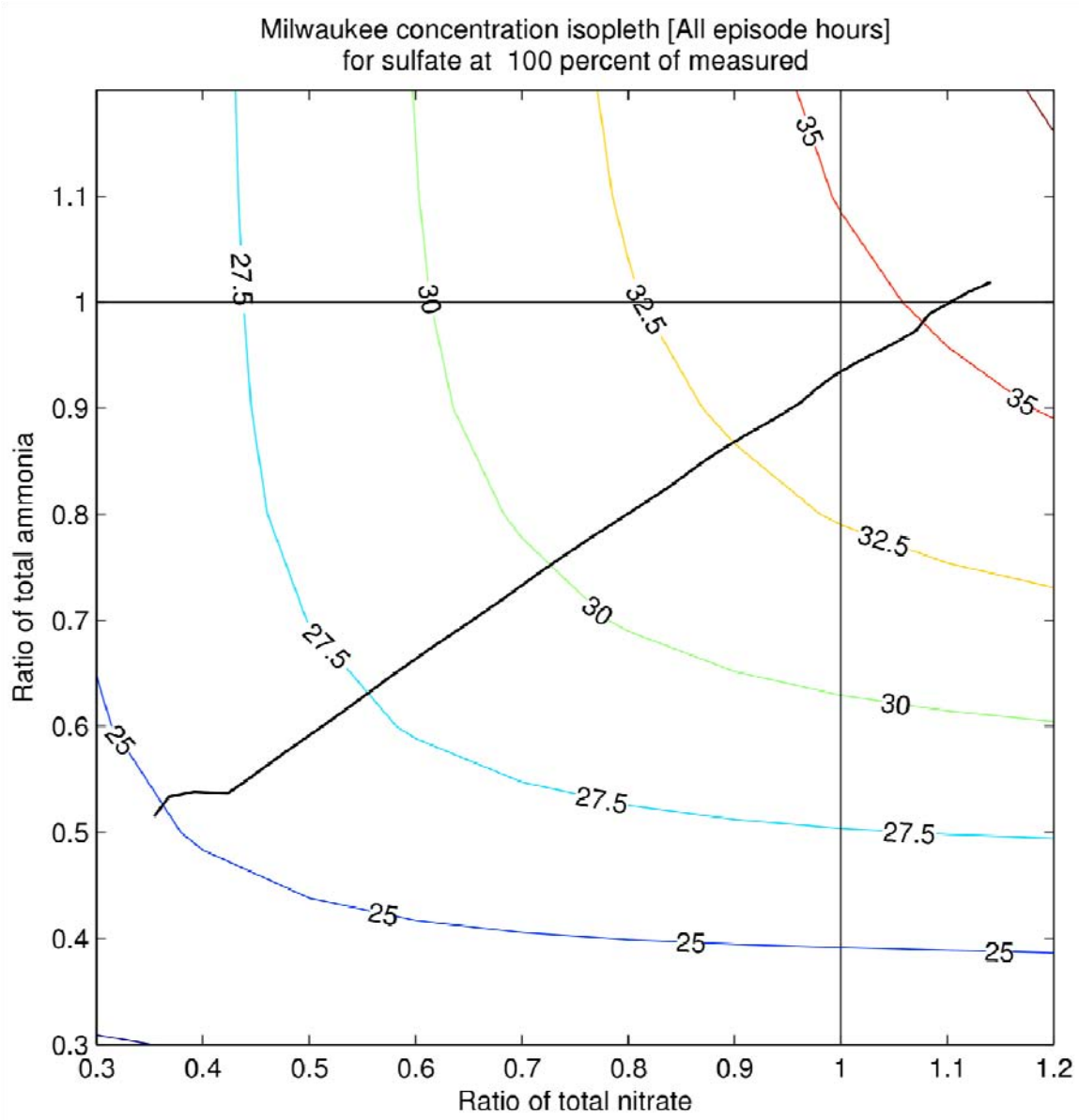


Figure 7-5. Sensitivity of $PM_{2.5}$ to reductions in total nitrate and total ammonia.

SITE: MILWAUKEE

PERIOD: ALL EPISODE HOURS ONLY

SULFATE LEVEL: 100% OF MEASURED VALUE