Appendix B 1

LADCO Winter Nitrate Study (Draft)

Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) During Jan-Mar 2009

Draft Phase I Report

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Draft Phase I Report

Executive Summary

Analysis of air quality and related measurements obtained during the LADCO Winter Nitrate Study was performed in order to better understand wintertime episodes of elevated fine particle ($PM_{2.5}$) concentrations in the Midwest. This Phase I study was conducted by a team of researchers from the University of Iowa and the University of Illinois. The analysis focused on evaluating and comparing the high time resolution surface observations taken during the three-month period (1 January - 31 March, 2009) at an urban Milwaukee site and a rural site in Mayville, Wisconsin. The Milwaukee site (DNR-SERHQ monitor) is subjected to higher levels of primary pollutants from nearby highways and industry, while the Mayville site, located 65 km northwest of Milwaukee, is largely surrounded by agricultural fields, and is more representative of regional background conditions. The measurements analyzed at these sites included unspeciated hourly $PM_{2.5}$ mass (TEOM, hourly), speciated $PM_{2.5}$ FRM mass (SASS, 24 hour average every 3 days), inorganic gas and aerosol species concentrations (ARA, hourly), precursor gas phase concentrations (denuder ISWS, 24 hour average), and various surface meteorological parameters. All data used in the analysis went through QA checks, and the ARA continuous monitor concentrations were adjusted for consistency with co-located denuder and filter measurements.

Observations during episode periods were contrasted with those during non-episode periods. Wintertime $PM_{2.5}$ episodes were defined as periods where the seven-hour running average concentrations exceeded 27 μg m^{-3} for at least four consecutive hours. Thirteen episodes were identified at the Milwaukee site, and seven were identified at Mayville. There were no rural-only episodes, as all episodes at Mayville were concurrent with Milwaukee episodes. The Milwaukee-only (local) episodes occurred in late February and March. Analysis of the species mass concentrations and their diurnal variations revealed the following:

- The diurnal patterns for $PM_{2.5}$ at both sites were 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 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.

- Episodes (except Milwaukee-only episodes) were characterized by strong enhancements in total nitrate; however, ordering of enhancements differed by site. Episodes had lower ozone concentrations throughout the day.
- During episodes, total nitrate concentrations were about doubled at Milwaukee and tripled at Mayville. About 80% of total nitrate existed in the aerosol phase at these sites, but the partitioning of total nitrate towards the aerosol phase was even stronger (about 90%) during episodes.
- Total ammonia also increased during episodes by a factor of 2-3. This increase can be attributed almost entirely to an increase in ammonium in the aerosol phase, while gas phase ammonia stayed about at the same level during episodes (Milwaukee) or even decreased (Mayville).
- 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).
- NO_y values were much higher at the urban site (26 ppb) than at the rural site (6 ppb). The main difference was in NO, due to local point and area NO_x sources in Milwaukee.
- Milwaukee only-episodes were characterized by the strongest enhancements in sulfate, EC, and OC.
- The OC/EC ratio decreased 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.

To help place the results for the Wisconsin sites in context, the analysis was repeated for an urban-rural pair in Georgia. The SEARCH network urban site in Atlanta (Jefferson Street) and the rural site in Yorkville, were selected to provide data in a winter environment that had warmer temperatures and less nitrate pollution. There were fewer $PM_{2.5}$ episodes in the period studied at the urban site in Atlanta, Georgia (6) than in Milwaukee. The mean and episode conditions at the Georgia sites

displayed a slightly more distinctive diurnal pattern than that at the Wisconsin sites, with a peak at 09:00 and a minimum at 13:00. 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 were on average 2.5 times higher than in Atlanta. These results indicate that nitrate is not much involved in Georgia wintertime episodes. 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 was 2.1 μg m^{-3}, with 61% in the aerosol phase. For Milwaukee, the total ammonia level was 3.3 μg m^{-3}m with 64% in the aerosol phase.

The meteorological conditions for the Midwest winter $PM_{2.5}$ episodes were also analyzed. The number of episodes of $PM_{2.5}$ particle pollution during the 2009 study period was above recent (2002-2008) average levels at both monitoring sites, but was close to average at the regional level. The 2009 winter period was one that featured considerable departures from 1971-2000 climatology, with a colder, drier January and a warm February and March with unusually high precipitation. All the fine particle episodes in the 2009 period studied 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. Milwaukee-only episodes were defined throughout primarily by high relative humidity; low pressure; lower visibility; and lighter, more southerly winds at both sites. 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. The Milwaukee episodes tended to be 5 degrees warmer than climatological mean conditions. Mayville episodes were warmer in the afternoon (relative to climatological mean) than the morning. Despite being warmer, the 2009 episodes had 10% higher relative humidity than average, and moisture from melting and sublimation of snow cover was correlated with stronger episodes. To better quantify the physical conditions during PM events in future studies, co-located photometer and ceilometer observations may be useful.

Back trajectory analysis showed that in most episodes the airmasses had recently passed over Illinois and Indiana. There was no evidence that Mayville episodes were due directly to air pollution transported from Milwaukee; these conditions occurred only eight times out of 1,030 cases for the three months, and never during episodes. Directional source analysis based on analysis of pollution

roses, Bivariate Polar, and Conditional Probability Function found strong directionality for primary pollutant NO_x at the Milwaukee site, with high concentrations measured when winds blew from S – SW at 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. NH_3 showed S-SW directionality at both sites, suggesting that this may not be indicative of local sources. $PM_{2.5}$ showed no directional dependence at either site. At Mayville SO_2 exceeded 2.5 ppb when winds blew from SSW to NW (240 to 320°), suggesting possible contribution from a coal-fired powerplant about 70km west. Episode meteorology may also cause an association with high SO_2 and northwesterly wind dependence. However, the directional feature in the SO2 data does not influence or compromise any of the main objectives of the study on episodic air pollution.

The sensitivity of the inorganic aerosol mass to changes in total ammonia, total nitrate, and total sulfate was evaluated using the ISOROPIA and GFEMN thermodynamic models. These models were validated against previous simulations and experimental data, and against one another. The observed values at Milwaukee and Mayville were used as inputs to the models for the base calculations. The models were run for every hour of the three-month study period for 400 different cases with varying changes in Total ammonia (10), total sulfate (4), and total nitrate (10). Changes in the predicted aerosol mass from these simulations were analyzed for all study hours, all episode hours and all non-episode hours. To evaluate the results of these simulations, two new metrics are proposed: relative sensitivity (fractional) and relative sensitivity (mass). Relative sensitivity (mass), defined as ($\Delta PM_{\text{nitrate reduction}}$ / ΔTNO3) / ($\Delta PM_{\text{ammonia reduction}}$ / ΔTNH3) is used as the main quantitative metric for gauging relative sensitivity to changes in ammonia and nitrate. This metric is found to be 1.0 in Mayville during non-episode conditions, and 0.35 during episodes in Mayville. A value of 1.0 indicates that a 1.0 μg m^{-3} reduction in nitrate will have the same effect on PM2.5 concentrations as a 1.0 μg m^{-3} reduction in ammonia. A value of 0.35 indicates that a 1.0 μg m^{-3} reduction in nitate will only 35% of the effect on PM2.5 concentrations as a 1.0 μg m^{-3} reduction in ammonia. In Milwaukee, this metric is 0.63 during non-episodes, decreasing to 0.54 during episodes. Total mass concentrations of nitrate are typically higher than those of ammonia, so equal mass reductions are usually larger percentage reductions in ammonia.

Analysis using fractional sensitivity shows that the Milwaukee episodes during Jan-Mar 2009 could be cut in half through a reduction in hourly total nitrate levels by ~40%, OR by reduction in hourly total ammonia concentrations by ~40%, OR by reduction in both species by ~26%. The Mayville

episodes during the same period (though already cumulatively less than ½ as severe as those in Milwaukee) could be cut in half through a reduction in hourly total nitrate by ~28%, by reduction in hourly total ammonia levels by ~18%, or by reduction in both ammonia and nitrate by ~15%. Control of other species (e.g., organics, sulfate) should also be considered in episode control scenarios.

Relative sensitivity (mass) was also estimated from the previous Midwest Ammonia Study (Blanchard 2008) as 1.0 for winter months in Mayville (compared to 1.0 from this study). At 4 Midwest Ammonia Study sites closest to Mayville WI, the relative sensitivity (mass) ranged from 0.4 to 2.0 during winter months (DJF). At all 4 sites, the relative sensitivity during an air quality episode (only a single episode was analyzed) decreased substantially to values less than 0.5, possibly corroborating the observed drop in the nitrate sensitivity observed in this study. Preliminary analysis using the gas ratio as a master variable in predicting nitrate sensitivity are encouraging, but further refinements and evaluation against additional data sets are needed.

The findings from this study indicate that a key to understanding winter $PM_{2.5}$ in the Midwest is a better understanding of what controls total nitrate levels. A literature review of daytime and nighttime heterogeneous nitrogen chemistry revealed that nitric acid (HNO_3) is produced primarily by two pathways. In the absence of sunlight, gaseous nitrogen dioxide (NO_2) reacts with ozone to produce the nitrate radical (NO_3). This reaction is followed by the conversion of NO_3 to dinitrogen pentoxide (N_2O_5) and eventually to HNO_3. The last step involves the heterogeneous hydrolysis of N_2O_5 on or in aqueous aerosol particles. Since NO_3 is rapidly photolyzed, the dominant pathway for HNO_3 production during daytime is via reaction of NO_2 with the hydroxyl radical (OH), which produces gaseous nitric acid. The daytime and nighttime production rates at Milwaukee and Mayville during the winter study period were estimated assuming that all NO_3 radicals produced yield HNO_3, and using the observed NO_2 and O_3 measurements and recommended reaction rate constants. When using all data, the production rates during night were of comparable magnitude to the rates during day for both Milwaukee and Mayville. However, the rates were generally higher in Milwaukee, approx. 0.4 ppb/h compared to 0.15 ppb/h at Mayville, due to the higher NO_2 concentrations in the urban environment. During episodes the relative importance of daytime and nighttime contributions changed depending on location. In Milwaukee the upper-limit average nighttime production rate was 0.42 ppb/h compared to 0.70 ppb/h for the average daytime production rate. During episodes in Mayville the upper-limit average nighttime production rate was

0.17 ppb/h compared to only 0.05 ppb/h during daytime, reflecting differences in the timing of the episodes—earlier in the year for Mayville, later in the year for Milwaukee—and the strong differences in OH concentrations with time of year (OH in January is about a factor of 7 lower than in March). These estimates show that the nighttime pathway could contribute up to 50% of the nitrate production in both locations, especially during the earlier (Jan / Feb) episodes. More detailed analysis of the impact of nighttime chemistry on nitric acid and particle nitrate using more comprehensive models are needed to refine these estimates.

Phase II of this study will focus on extending this analysis of the measurements obtained during the LADCO Winter Nitrate Study to include three dimensional regional $PM_{2.5}$ modeling using CMAQ and PMCAMx models. Emphasis will be on better understanding the chemical, atmospheric transport, and thermodynamic processes impacting $PM_{2.5}$ levels and their rural-urban gradients in the winter in the Midwest, evaluation of nitric acid production and its sensitivity to treatments of nighttime chemistry, evaluation of ammonia predictions including spatial patterns, and the sensitivity of modeled PM concentrations and spatial distributions to changes in precursor emissions.

2.0 BACKGROUND

2.1 Introduction

The 2006 United States $PM_{2.5}$ standard under the Clean Air Act has two separate limits for $PM_{2.5}$. A short term limit is applied to peak 24-hour concentrations [35 micrograms per cubic meter of air (μg m^{-3})].[i] There is also a limit on the annual average concentration (15 μg m^{-3}). The change in the 24-hour standard from 65 to 35 μg m^{-3} has made attainment of ambient air quality standards much more difficult in locations that experience short-term episodes of moderately high PM levels (e.g., between 35 and 65 μg m^{-3}). An analysis of 2005-2008 $PM_{2.5}$ levels from over 1000 measurement stations shows that the effect of episodes on attainment is strong in Western states impacted by forest fire PM, and in the upper Midwest states. Within the LADCO area, three of five states (Ohio, Michigan and Wisconsin) have monitors reading in non-attainment solely because of the 35 μg m^{-3} standard. Two other LADCO states (Illinois and Indiana) have monitors in attainment for this period but at levels just below the 35 μg m^{-3} limit. CENRAP states Iowa and Missouri are also affected.

Figure 2-1 gives the value of a PM episode indicator[ii], where a value of 62 or higher (for a period of a year) indicates potential compliance problems with the daily standard (35 PM μg m^{-3}) under the Clean Air Act. While figure 2-1 shows the annual average behavior of the indicator, the seasonal behavior is shown in figure 2-2. The four panels of figure 2-2 sum to the values in figure 2-1. For the states of Wisconsin, Minnesota, Iowa, and Northern Illinois, wintertime is the most active episode season.

A number of studies demonstrate that meteorology and high $PM_{2.5}$ episodes in the Midwestern U.S. are tightly linked. For example, the 2004 NARSTO PM Assessment (Chapter 10, Conceptual Models for PM for North American Regions) stated that the highest $PM_{2.5}$ values usually occur in the upper Midwest during summer and winter months, rather than the spring and fall. Furthermore, the episodes occur under stagnant high-pressure systems when there is shallow turbulent mixing (Chu 2004). At the time of the NARSTO assessment, nitrate and ammonia data were not available to show the extent of the short term winter episodes, so nitrate events were mentioned only in passing, and nitrate is listed as 11% of the annually averaged regional composition (McMurry et al., page 363).

Recently published analysis by Pitchford et al. (2009) on high PM concentrations in the

Midwest, used IMPROVE and STN data to estimate regional distributions of PM nitrate. They found a peak in Iowa (using 2005-2006 IMPROVE data) and a peak around the shore of southern Lake Michigan (using combined IMPROVE and CSN data for 2005-2006).

High $PM_{2.5}$ episodes in urban cities generally occur during the winter, however they can also occur during the summer when solar radiation is not very strong. In the winter, high values occur during stagnant, high-pressure systems usually on the backside of the system (Anderson, Martello et al. 2004). Anderson et al. (2006) found that in the Ohio River Valley, local high $PM_{2.5}$ events frequently occur during frontal passages, where PM transport occurs. Chu (2004) suggested that in urban areas, meteorology and aerosol thermodynamics are as important, if not more important, as the photochemistry in determining high $PM_{2.5}$ concentrations.

Chu (2004) furthermore showed that nitrate events were concentrated in the Nov-Feb period. Chu (2004)'s analysis ends in February 2002. But during winter 2002, Chu (2004) identifies high PM nitrate events on Jan 2 and 5; on Jan 14, 17 and 20; on Jan 26, 29 and Feb 1, 4, and 7; on Feb 13, 16, and 19. The alternation of days is from the fact that the sampling network operates 1 day in 3. Thus Chu (2004) identified nitrate events in five episodes during the Jan/Feb 2002 period with a national scope. Detailed analysis is done by Chu on the Feb 6-8 2002 episode. Within the Midwest and Great Lakes, peak $PM_{2.5}$ occurred in Chicago with 34 $\mu g\ m^{-3}$, and concentrations in Iowa ranged from 18-26 $\mu g\ m^{-3}$. Approximately 40% of the filter mass in Iowa was nitrate, and peak nitrate was in Chicago. Chu (2004) further found that ammonia levels were almost sufficient for full neutralization of nitric acid in the Midwest, and acidic conditions occurred only southeast of the Ohio River.

Blanchard (2008) in collaboration with LADCO published a comprehensive study of PM sensitivity to total ammonia and total nitrate using extensive filter data taken as part of the 2003-2006 Midwest Ammonia Monitoring Project (Blanchard and Tanenbaum 2008). Sites analyzed include Lake Sugema, IA, Bondville, IL, and Mayville, WI. A comparison between the 2008 PM sensitivity report and this work can be found in section 7, thermodynamic sensitivity. Other LADCO reports also address wintertime air quality in the upper Midwest. These include The Effects of Changes in Sulfate, Ammonia, and Nitric Acid on Fine PM Composition at Monitoring Sites in Illinois, Indiana, Michigan, Missouri, Ohio, and Wisconsin (Blanchard and Tanenbaum 2004), $PM_{2.5}$ in the Upper Midwest (LADCO 2003); $PM_{2.5}$ in the Urban Areas in the Upper Midwest (LADCO 2004), and the $PM_{2.5}$ Conceptual Model document (LADCO 2009). Stanier et

al. (Stanier, Carmichael et al. 2009) also published a report on air quality in Iowa, which touches on many of the issues relevant for the LADCO winter nitrate study.

The LADCO (Lake Michigan Air Directors Consortium) Winter Nitrate Study is a measurement campaign designed to understand wintertime episodes of elevated fine particulate ($PM_{2.5}$) concentrations in the upper Midwest. These episodes are often regional and are characterized by low wind speeds, near-freezing temperatures, and elevated levels of ammonium nitrate.

From December 2008 to March 2009, an intensive monitoring campaign was conducted by ARA Inc., the Wisconsin DNR, the Illinois State Water Survey, and LADCO. Continuous measurements of ammonia, ammonium, nitrate, nitric acid, ozone, NOx, NOy, and meteorology were conducted at an urban site (Milwaukee, Wisconsin), and an upwind rural site (Mayville, Wisconsin). Integrated samples of many species were also collected. Analysis of the study data was conducted by researchers from the University of Iowa and the University of Illinois. The analysis also included data from similar instruments at an urban-rural pair in the SouthEastern Aerosol Research and Characterization (SEARCH) network around Atlanta, Georgia.

During the monitoring campaign, 13 episodes were recorded (defined by 7-hour average $PM_{2.5}$ exceeding 27 $\mu g\ m^{-3}$), with seven affecting both sites, and six affecting Milwaukee only. The most severe episode occurred January 21- 23, with average levels of 50 and 38 $\mu g\ m^{-3}$ at the urban and rural sites, respectively.

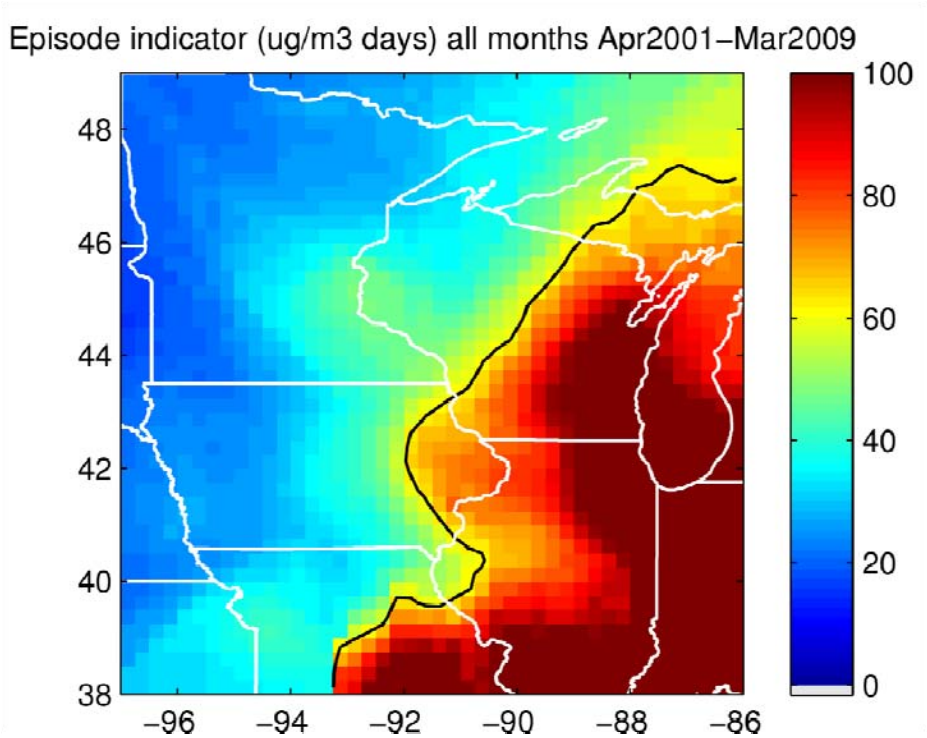

Figure 2-1. Eight year average of PM episode activity as quantified by a PM episode indicator (see note ii). Black line separates areas with an indicator > 62 from areas with an indicator < 62.

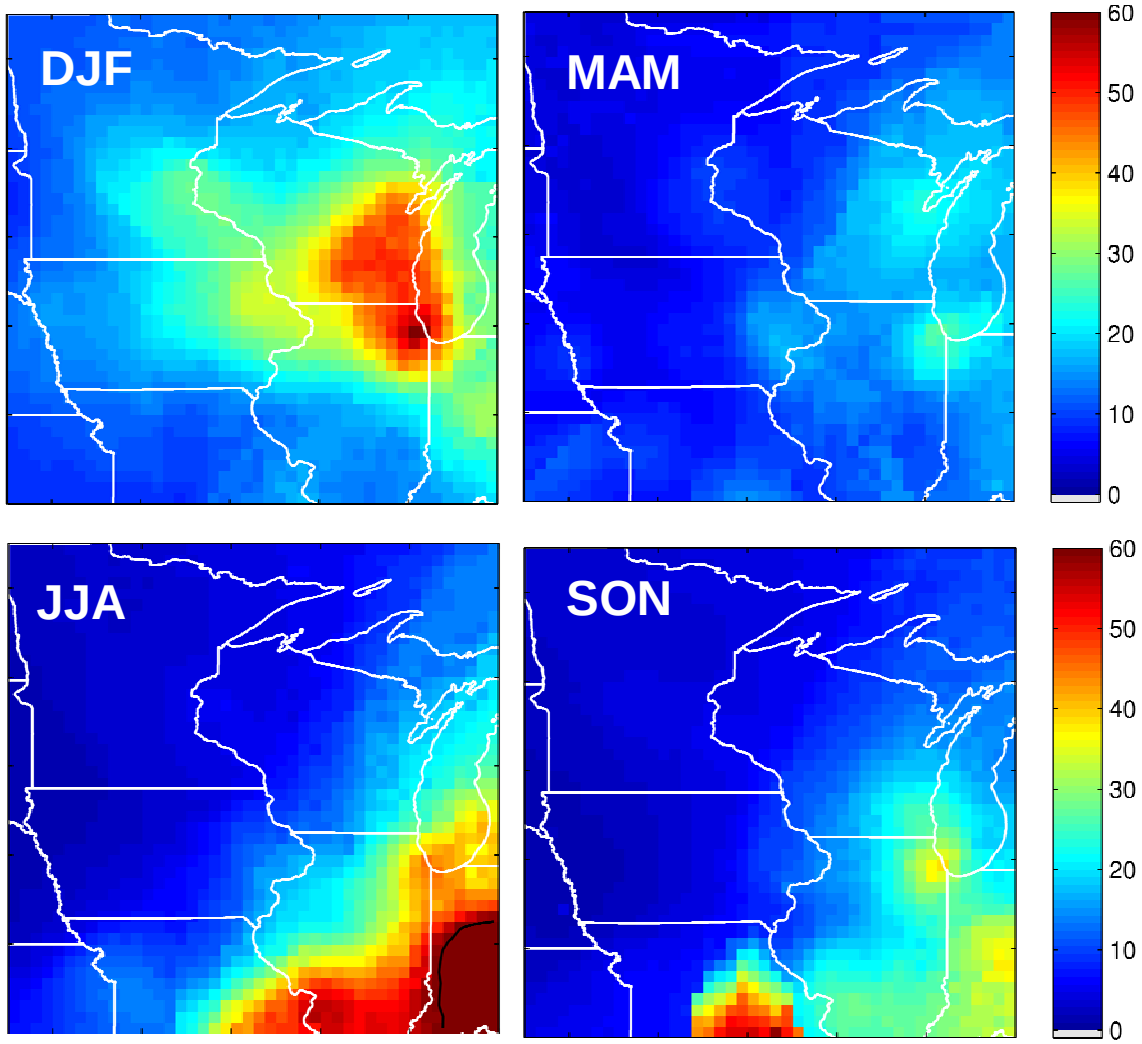

Figure 2-2. Eight year average of PM episode activity divided by season. Quantified by an episode indicator (see note ii).

The objectives of the data analysis portion of the Winter Nitrate Study were as follows.

- What is the typical chemical composition during winter-time episodes (i.e., amount of sulfates, nitrates, etc.) and how does that chemical composition compare to the chemical composition on days when lower concentrations are measured?
- Are there significant differences in $PM_{2.5}$ concentrations (frequency and severity), chemical composition, and source regions (emissions and geographic location) during wintertime episodes between rural and urban sites?
- What are the primary emission sources during winter-time episodes? Are these sources local or regional in nature?

- What meteorological conditions favor winter-time episodes? How can we best use this information to improve wintertime episode forecasting?
- What do the data tell us about particle chemistry?
- Can photochemical modeling accurately predict $PM_{2.5}$ concentrations during the observed winter-time episodes?

2.2 Project Objectives

In response to the LADCO RFP for analysis of the Winter Nitrate Study, the following objectives were proposed. Those that are addressed in this phase I report are listed first. Those that will be addressed in a phase II report are listed second.

Composition During Episodes:

- Divide measurement period into segments according to PM levels and meteorology;
- Assess the role of ammonia in forming particulate nitrate using thermo box model;
- Determine sensitivity of PM levels to reductions in nitric acid and ammonia using thermo box model(s);
- Assess hygroscopic state of aerosol using thermo box model;
- Assess data quality and uncertainty using continuous-filter comparison, charge balance, mass balance, and thermodynamic disequilibrium;
- Compare to previous thermodynamic box model analyses of the Midwest; and
- Compare severity and chemistry of episodes during the study to historical average episodes, and assess spatial extent of episodes sampled during the intensive.

Rural-Urban Gradients:

- Examine urban excess in particulate nitrate; and
- Analyze HYSPLIT back trajectories

Local Primary Sources:

- Perform wind sector analysis / conditional probability analysis / bivariate analysis.

Episode Meteorology:

- Identify meteorological unusual periods (fresh snow, snow melt, high actinic flux due to sun on snow, and fog);

- Conduct a CART multivariate analysis of meteorological variables

Nitrate Formation Chemistry:

- Examine diurnal pattern of nitrate and assess relative importance of daytime (OH) and nighttime (O_3 / N_2O_5) channels;
- Review state-of-science of PM nitrate formation; and
- Compare SEARCH (Atlanta) urban-rural pair data and Wisconsin dat.

Phase II Objectives

3D Modeling

- Conduct 12-km CMAQ model runs for the measurement period on a Midwestern domain. This will support several of the analyses listed below
- PMCAMx modeling of the domain during the time period in

Rural-Urban Gradients

- Model runs with various geographic areas perturbed for NO_x emissions to establish areas where emissions reduction lead to nitric acid reductions

Nitrate Formation Chemistry

- Determine sensitivity of PM nitrate levels to other factors (such as nitrate formation kinetics) using box modeling

Three Dimensional Model Implementation

- Conduct hybrid box model analysis replacing measured variables with modeled (one at a time) to determine areas where model inaccuracies contribute most to model-measurement error for ammonium nitrate
- Compare total modeled ammonia concentrations versus total 3D modeled ammonia as a test of average ammonia emission levels and spatial-temporal patterns (II)
- Assess adequacy of PM nitrate chemistry used in photochemical models and recommend improvements
- Quantify model-measurement agreement during episodes (II), with comparison of CMAQ and PMCAMx

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NOTES

[i] Attainment or nonattainment of the Clean Air Act standards is determined by averaging the 98th percentile concentrations over the past three years (e.g. 2005, 2006 and 2007). For monitors with a full complement of 365 daily samples, the 98th percentile rule means that the 8th highest value in a given year determines attainment.

[ii] The indicator is $\Sigma\max(PM2.5_i\text{-}27.0)$ where $PM2.5_i$ is the daily PM2.5 value estimated from Kriging 24-hr network mass measurements. The value is normalized based on the number of years analyzed.

3.0 STUDY OVERVIEW

In the Great Lake Regions, fine PM ($PM_{2.5}$) have episodically high concentrations in winter. To investigate high PM episodes, speciated $PM_{2.5}$ measurement data from STN measurement sites at the Milwaukee-DNR SERHQ and Mayville sites (Figure 3.1) have been analyzed. An early study of Wisconsin (2003) speciated $PM_{2.5}$ data revealed that the nitrate (NO_3), ammonium (NH_4), sulfate (SO_4) and organic carbon (OC) comprise over 85% of $PM_{2.5}$ mass collected on the quartz filters. In this study, high time resolution measurement data, including gas phase ammonia and nitric acid, were taken during the three months from 1/01/2009 to 3/31/2009. Analysis focused on Milwaukee as an urban site subject to higher levels of primary pollutants, and Mayville as a rural site to characterize the regional background.

The ARA samplers for continuous inorganic gas and aerosol species are part of routine measurements in the SEARCH network (Hansen et al., 2003). Therefore, to provide contrast to another rural-urban pair expected to have warmer temperatures and less nitrate pollution, measurements from the Atlanta (Jefferson St.) and Yorkville locations of the SEARCH network are included in the analysis.

3.1. Site descriptions

The Milwaukee site (DNR-SERHQ monitor) is located in a mixed-use urban area (commercial, retail, residential) just north of the city's downtown area and is exposed to considerable air pollution emanating from nearby highways (vehicular traffic) and industrial sources. The Mayville site, 65 km (40.5 mi) northwest of the Milwaukee site (Figure 3-1), is situated in an open, rural area that is largely surrounded by agricultural fields and has noticeably less exposure to high primary pollutant levels than the Milwaukee site. The bearing from the Milwaukee site to the Mayville site is 310 degrees. Location of Jefferson Street in Atlanta, GA (Urban site) and Yorkville (Rural site) from SEARCH network can be found in figure 3-2. (Hansen et al., 2003). An appendix contains additional site photos for the Mayville and Milwaukee sites.

3.2. List of measurements

Four target chemical species (NO_3, SO_4, NH_4, and OC) in particulate matter were measured in both sites. The critical chemical compounds that affect on gas/particulate surface

chemistry and/or thermodynamics were also measured. These gaseous chemical compounds (NH_3, NH_4^+ etc) were measured by 24hr denuder. Unspeciated hourly $PM_{2.5}$ mass (TEOM, hourly) and speciated FRM, which is called the Speciation Aerosol Sampling System (SASS) instrument, were measured every 3rd calendar day. The SASS monitor collects integrated $PM_{2.5}$ mass samples for each 24 hour measurement period on a quartz filter. The $PM_{2.5}$ speciation filters are collected and sent to RTI Labs (a US EPA contractor), which employs US EPA-approved laboratory methods to quantify $PM_{2.5}$ species' contributions to the total $PM_{2.5}$ mass collected on each filter. RTI's laboratory analysis of each filter's mass yields 24 hr $PM_{2.5}$ concentrations for more than 50 separate compounds, including several ions (e.g., NO_3, SO_4, NH_4, OC) (Wisconsin, ser-report). Milwaukee measured NO_x and Mayville measured SO_2. Measured chemical species and method are summarized in table 3-1. Table 3-2 summarized measured data available from SEARCH network (Hansen et al., 2003).

Table 3-1 Species measured at MILWAUKEE and Mayville site

Measurement	Time average	Units	Source	Method
$PM_{2.5}$	1hr	µg m^{-3}	WDNR	FDMS EPA Param 88101
SO_4	1hr	µg m^{-3}	ARA	See text
NO_3	1hr	µg m^{-3}	ARA	See text
NH_4	1hr	µg m^{-3}	ARA	See text
HNO_3	1hr	ppbv	ARA	See text
NH_3	1hr	ppbv	ARA	See text
NO_x[1]	1hr	ppbv	WDNR	EPA Param 42603
SO_2[2]	1hr	ppb	WDNR	EPA Param 42401
TEMP	1hr	Deg F	WDNR	
Wind Speed	1hr	mph	WDNR	
Wind direction	1hr	Comp Deg	WDNR	
NH_3	24hr	ppbv	ISWS	Denuder
HNO_3	24hr	ppbv	ISWS	Denuder
SO_2	24hr	ppbv	ISWS	Denuder
$PM_{2.5}$	24hr 1 in 3days	µg m^{-3}	WDNR	FRM EPA Param 88101
NH_4	24hr 1 in 3days	µg m^{-3}	WDNR	FRM EPA Param 88101
NO_3	24hr 1 in 3days	µg m^{-3}	WDNR	FRM EPA Param 88301
SO_4	24hr 1 in 3days	µg m^{-3}	WDNR	FRM EPA Param 88401
OC	24hr 1 in 3days	µg m^{-3}	WDNR	FRM EPA Param 88350
NOy	1hr	ppb	ARA	See text
O3	1hr	ppb	WDNR	
Relative Humidity[3]	1hr	%	NWS	
Surface pressure[3]	1hr	mbar	NWS	
Visibility[3]	1hr	km	NWS	
Precipitation[3]	1hr	mm	NWS	

[1.] hourly NOx is only available at MILWAUKEE
[2.] hourly SO_2 is only available at Mayville

[3.] Data were measured at the General Mitchell (MKE airport)

Table 3-2 Species available at SEARCH network. All variables provided by ARA.

Measurement	Time average	Units
$PM_{2.5}$	1hr	$\mu g\ m^{-3}$
SO_4	1hr	$\mu g\ m^{-3}$
NO_3	1hr	$\mu g\ m^{-3}$
NH_4	1hr	$\mu g\ m^{-3}$
HNO_3	1hr	ppb
NH_3	1hr	ppb
O_3	1hr	ppb
CO	1hr	ppb
SO_2	1hr	ppb
$NO/NO_2/NOx$	1hr	ppb
NO_y	1hr	ppb
BC	1hr	ppb
TC	1hr	$\mu g\ m^{-3}$
OC	1hr	$\mu g\ m^{-3}$
Wind Speed	1hr	ms^{-1}
Wind direction	1hr	Compass Deg
TEMP	1hr	deg C
Relative Humidity	1hr	%
Station pressure	1hr	mbar
Precipitation	1hr	mm
Solar radiation	1hr	Wm^{-2}

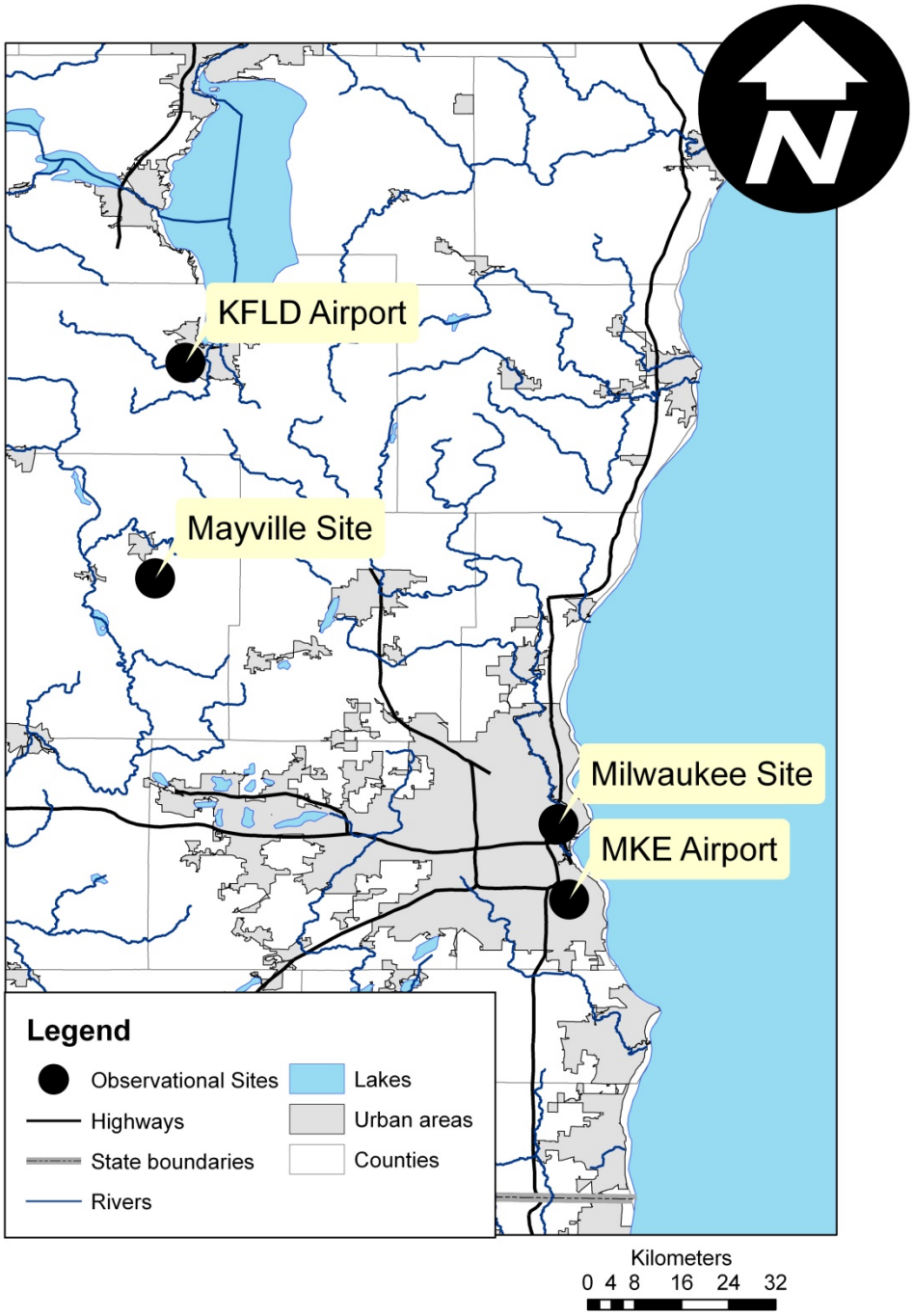

Figure 3-1 Area map showing Mayville site and Milwaukee site

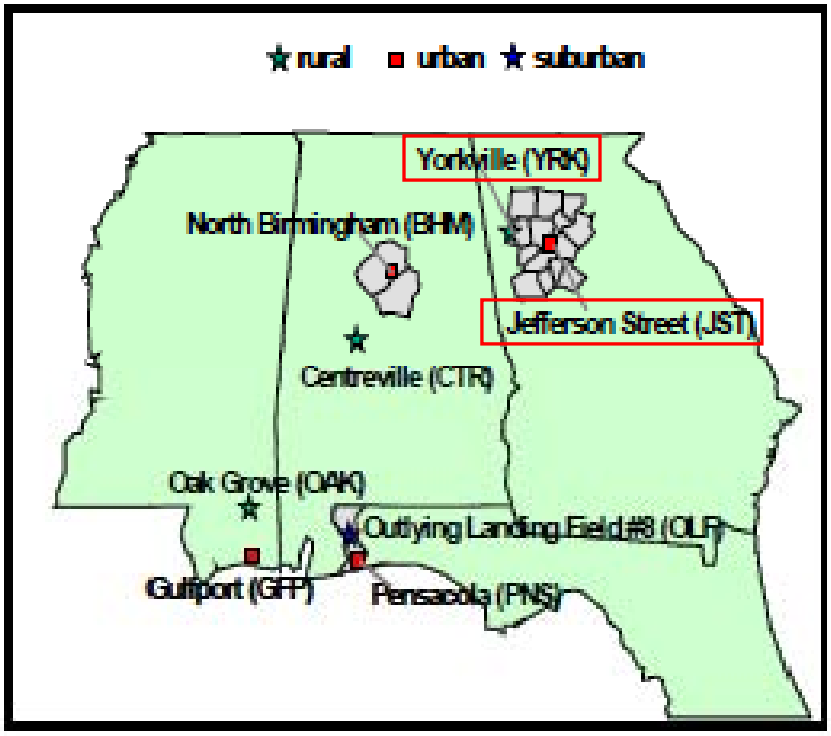

Figure 3-2 Location of Yorkville and Jefferson Street at SEARCH Network

REFERENCES

Wis. Dept of Natural Resources, 2003: **Characterizing Ambient Fine Particulate Matter ($PM_{2.5}$) in Wisconsin 1999-2001**. Bureau of Air Management. Publ AM-329-2003, Feb, 67 pp.

Hansen, D. A., Edgerton, E.S., Hartsell, B. E., Jansen, J. J., Kandasmy, N., Hidy, G.M., and lanchard, C.L. 2003, The southeastern aerosol research and characterization study: part 1-overview, *J. Air & Waste* **53**:1460-1471

4.0 WINTER NITRATE STUDY – SUMMARY OF MEASURED CONCENTRATIONS

4.1 Summary and Examples of Data Adjustments Made to the Wisconsin ARA Data

A full account of QA and adjustments of Wisconsin data can be found in Appendix 2. The primary QA activity was to adjust ARA data so that it agreed better with the integrated measurements (filters by WDNR / EPA STN and denuders by ISWS). To do this, any 24 hour period with 19 or more hours of ARA data was averaged to form a 24-hour mean value, and these values were paired with their corresponding filter or denuder measurements for regression. The goals of the regression were twofold: (1) determine a slope and intercept for adjustment of the data (all corrections were assumed to be linear; there were insufficient comparison data points for nonlinear corrections); and (2) determine a 95% confidence interval on the adjusted (or revised, the terms are used synonymously in the report) ARA dataset.

The slopes, methods, intercepts and confidence intervals can be found in detail in Appendix 2. Figure 4-1 summarizes the overall comparison of the hourly and 24 hour data.

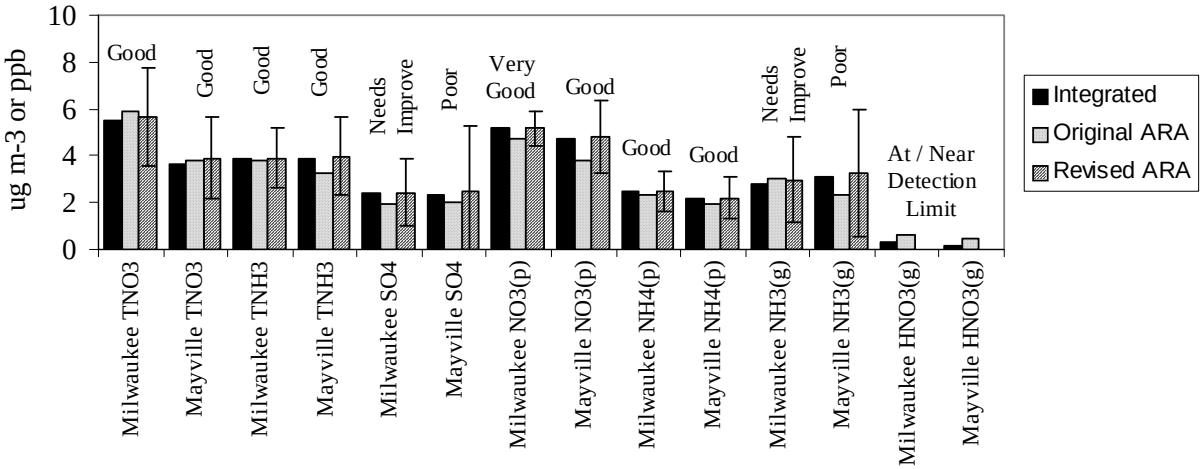

Figure 4-1. Comparison of 24 hour and hourly datasets. Y axis is the mean of the paired samples. Aerosols (labeled as (p) for particulate), total nitrate, and total ammonia as μg m^{-3}, and gases as ppb. Error bars show 95% confidence interval on an individual ARA measurement at the mean concentration. Qualitative rating is based on two factors: bias relative to 24 hour average measurement in the original ARA data, and size of confidence interval in the revised ARA data. See table A2-4.

In summary, weighted least squares regression was performed with weights inversely proportional to the raw measured ARA values [e.g. wi=(ARA_i)-1]. For determining a confidence interval for every hourly ARA data point in the dataset, an error was assumed of the following form: the upper confidence value was $ARA_{corrected} + [f(ARA_{raw}) + \varepsilon]$ and the lower confidence value was $ARA_{corrected} - [f(ARA_{raw}) + \varepsilon]$. The values for f and ε were determined by linear regression of the prediction confidence intervals determined by the regression software.

An example of the best regression result was Milwaukee nitrate, and that is shown in figure 4-2.

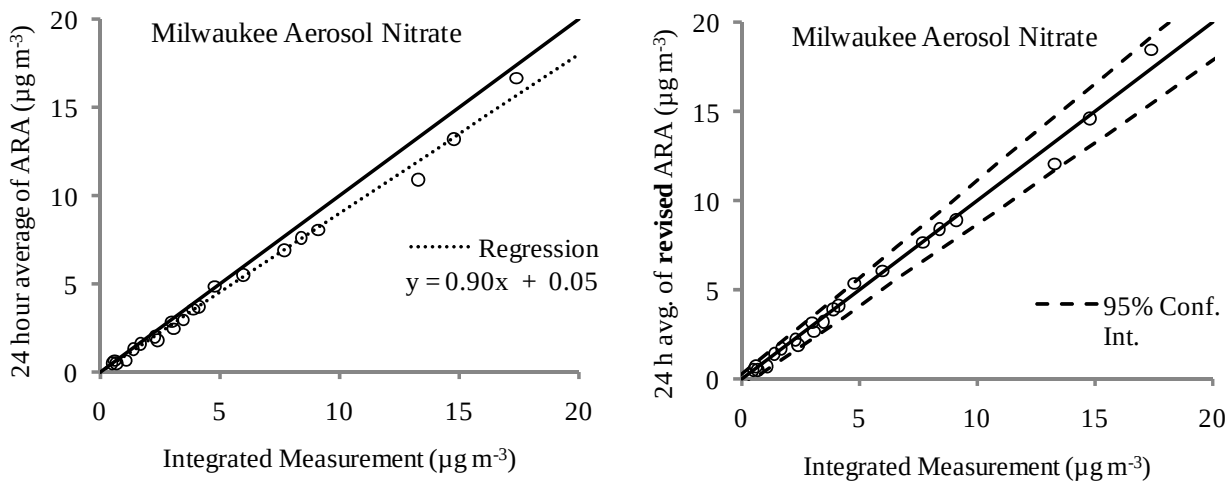

Figure 4-2. Comparison of aerosol nitrate between ARA and filter readings at Milwaukee, with regression result and 95% confidence interval shown. Solid lines are 1:1 lines of agreement.

An example of a poor agreement between hourly and 24 hour samplers was for Mayville NH_3 (g), shown in figure 4-3. As an independent check on the original and revised data, thermodynamic and charge balance was assessed before and after the revision. Figure 4-4 shows the result of the charge balance. It is very good prior to the revision, and improved in most cases after the revision.

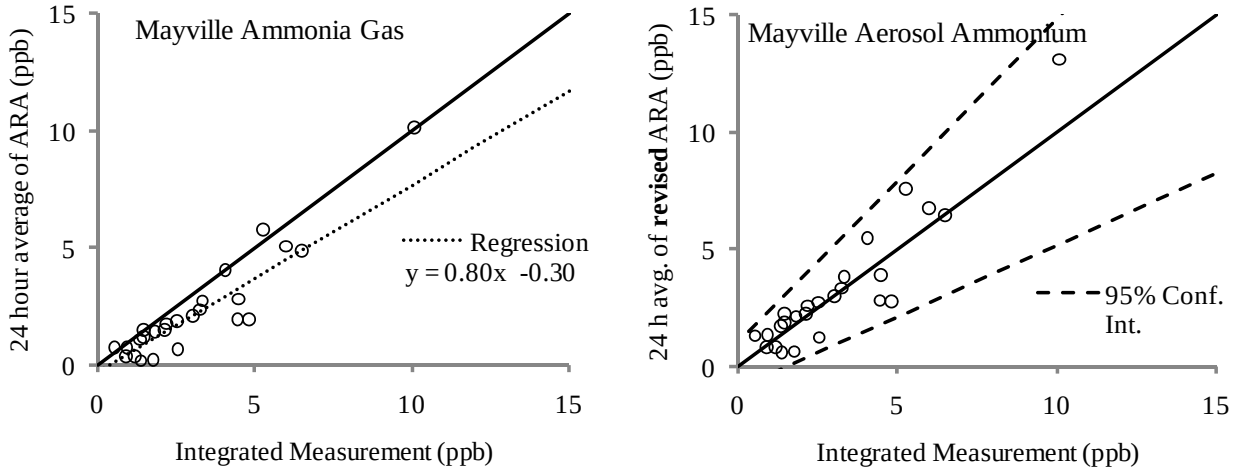

Figure 4-3. Comparison of ammonia gas between ARA and ISWS denuders at Mayville, with regression result and 95% confidence interval shown. Solid lines are 1:1 lines of agreement. .

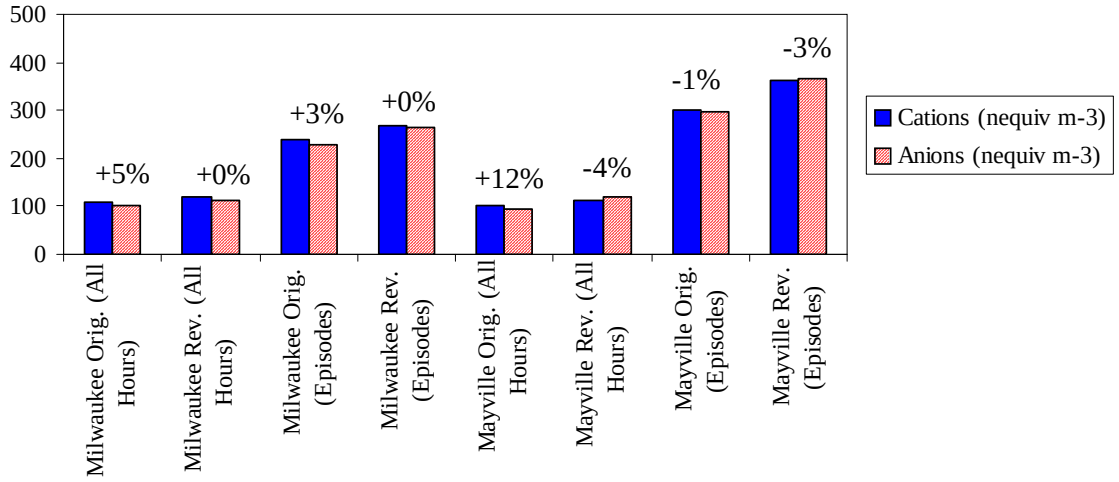

Figure 4-4. Charge balance in the original and revised ARA datasets. Bars indicate the mean values. Text values indicate the median charge balance of all hours with all valid ions. These may be different due to the different statistics of mean and median.

The experimental data was also evaluated using ISORROPIA. The measured total nitrate, total ammonia, and sulfate (both before data revision and after revision) were partitioned and compared to the measured phase partitioning (e.g. aerosol ammonium over total ammonia; aerosol nitrate / total nitrate). Results of this can be found in Appendix 2. Generalizing broadly, at both sites the NH_3 measured partitioning matched the modeled partitioning in both the original and revised dataset, once the measurement error is considered. For HNO_3, the nitrate fraction

was not measured very accurately due to uncertainty in HNO_3. The majority of points have modeled nitrate / total nitrate ratios of > 0.8, but the measured dataset (original) has a large number of points with the measured partitioning in the 0.5-0.8 range. The data revision process alleviates this somewhat, but at the expense of large error bars on HNO_3, on the nitrate aerosol fraction, and some negative HNO_3 values. See figures A2-10 and A2-11.

4.2 Time Averaged Results

The overall results of the monitoring campaigns are summarized in tables 4-1 through 4-4. These give the summary statistics of each measured variable at the two Wisconsin sites, and at the two SEARCH sites.

TABLES NEED ADDITION OF TNO3 AND TNH3 FOR SEARCH SITES