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Overview of the LADCO winter nitrate study: hourly ammonia, nitric acid and $PM_{2.5}$ composition at an urban and rural site pair during $PM_{2.5}$ episodes in the US Great Lakes region

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Abstract. An overview of the LADCO (Lake Michigan Air Directors Consortium) Winter Nitrate Study (WNS) is presented. Sampling was conducted at ground level at an urban-rural pair of sites during January–March 2009 in eastern Wisconsin, toward the western edge of the US Great Lakes region. Areas surrounding these sites experience multiday episodes of wintertime $PM_{2.5}$ pollution characterized by high fractions of ammonium nitrate in PM, low wind speeds, and air mass stagnation. Hourly surface monitoring of inorganic gases and aerosols supplemented long-term 24-h aerosol chemistry monitoring at these locations. The urban site (Milwaukee, WI) experienced 13 $PM_{2.5}$ episodes, defined as periods where the seven-hour moving average $PM_{2.5}$ concentration exceeded 27 $\mu g\,m^{-3}$ for at least four consecutive hours. The rural site experienced seven episodes by the same metric, and all rural episodes coincided with urban episodes. Episodes were characterized by low pressure systems, shallow/stable boundary layer, light winds, and increased temperature and relative humidity relative to climatological mean conditions. They often occurred in the presence of regional snow cover at temperatures near freezing, when snow melt and sublimation could generate fog and strengthen the boundary layer inversion. Substantial contribution to nitrate production from nighttime chemistry of ozone and NO_2 to N_2O_5 and nitric acid is likely and requires further investigation. Pollutant-specific urban excess during episode and non-episode conditions is presented. The largest remaining uncertainties in the conceptual model of the wintertime episodes are the variability from episode-to-episode in ammonia emissions, the balance of daytime and nighttime nitrate production, the relationship between ammonia controls, NO_x controls and ammonium nitrate reductions, and the extent to which snow and fog are causal (either through meteorological or chemical processes) rather than just correlated with episodes because of similar synoptic meteorology.

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1 Introduction

$PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 µm) in the ambient environment is a significant public health risk factor (Schwartz and Dockery, 1992; Dockery and Pope, 1994; Laden et al., 2000; Smith et al., 2009; Pope et al., 2009). In the Upper Midwest, defined in this paper as Minnesota, Iowa, Wisconsin, Illinois, Indiana and Michigan, there are numerous locations at or near public health limits for $PM_{2.5}$ set under the US Clean Air Act (USEPA, 2011). US regulations have defined both annual and short-term limits on fine particulate matter. Both the 1997 $PM_{2.5}$ standard (referred to herein as the annual or 15 $\mu g\,m^{-3}$ standard) and the 2006 $PM_{2.5}$ standard which limits the 98th percentile of the 24-h concentration (referred to herein as the daily 35 $\mu g\,m^{-3}$ standard) are relevant to the Upper Midwest region. While the majority of the nonattainment areas are solely in nonattainment of the annual 15 $\mu g\,m^{-3}$ standard, a substantial fraction exceed the daily 35 $\mu g\,m^{-3}$ standard. Governmental agencies and other entities in locations just below regulatory air quality limits (e.g. many locations in the Upper Midwest) consider current and possible future $PM_{2.5}$ concentrations when planning for economic development and environmental permitting and regulation.

Recurrent cold weather $PM_{2.5}$ episodes greatly influence air quality in this region, similar to episodic air pollution in California's Central Valley (Pun and Seigneur, 1999; McMurry et al., 2004), Northwestern and Central Europe (Schaap et al., 2002), and the Po Valley of Italy (Putaud et al., 2010; Schaap et al., 2004; Carbone et al., 2010). A number of recent studies demonstrate key points from these recurrent episodes: episodes are tightly coupled with meteorological conditions, and ammonium nitrate comprises a large fraction of the $PM_{2.5}$ during episodes (LADCO, 2009; Chu, 2004; McMurry et al., 2004; Blanchard and Tanenbaum, 2008; Pitchford et al., 2009; Katzman et al., 2010; Bender et al., 2009; Baek et al., 2010). However, a large number of questions about these episodes remain unanswered. Geographical extent, urban-rural variation, sensitivity to local and regional emissions changes, nitrate production rates and pathways, the role of organic nitrogen species, and relationship to snow cover and fog extent are important knowledge gaps. Answers to these questions may hold insight for other regions with high ammonium nitrate concentrations and/or aerosol fractions.

Because of these factors, there is a need for (a) an accurate conceptual understanding of $PM_{2.5}$ episodes in the region; (b) tested field methods for characterizing episodic air quality at appropriate spatial and temporal scales; (c) air quality models with demonstrated skill during episodes; (d) assessment of potential public policy measures that might lower $PM_{2.5}$ concentrations by changing episode frequency or severity; and (e) forecast models that might predict episode conditions in advance, allowing proactive measures and precautionary air quality alerts.

We present the results from an intensive field campaign designed to understand inorganic gas and aerosol $PM_{2.5}$ constituents during wintertime episodes. The monitoring was conducted during January–March 2009 in the Upper Midwest, toward the western edge of the US Great Lakes, and is called the Lake Michigan Air Directors Consortium Winter Nitrate Study (LADCO WNS). The study was conducted with the overall motivation of addressing or enabling all five of the elements listed above. This paper provides an overview of the field study and its key results.

In the LADCO report on the WNS, Baek et al. (2010) include intercomparison of measurements by an identical sampling systems from an urban-rural pair of Southeastern Aerosol Research and Characterization (SEARCH) sites in Georgia. This provides a contrasting air pollution environment sampled by the same techniques (Hansen et al., 2003) with similar NO_x, NO_y, and O_3 levels in winter but with warmer temperatures and higher levels of organic carbon. Results from the SEARCH sites and Georgia-to-Wisconsin comparisons are not included in this paper, but interested readers are referred to the report. In summary, episodes at the SEARCH sites were less frequent, shorter in duration and intensity, and had organic carbon as the major contributing species rather than ammonium nitrate.

Background

Nitrate pollution during cold seasons has been recognized for some time in California, and in parts of Europe. The awareness of wintertime PM episodes in the Upper Midwest region of the US is comparatively recent. For example, the 2004 review and assessment (McMurry et al., 2004) listed nitrate as 11 % of the annually averaged regional $PM_{2.5}$ (Chapter 10, Conceptual Models for PM for North American Regions) and makes no special mention of episodic contributions to impaired air quality. Chu (2004) examined Speciation Trends Network (STN) data nationwide from March 2001–February 2002 and showed that episodes were wintertime (November–February) occurrences coincident with stagnant high-pressure systems, weak mixing, and high nitrate fractions ($\sim$ 40 %). Episodes were heavily influenced by meteorology and aerosol thermodynamics. Pitchford et al. (2009) and Katzman et al. (2010) came to similar conclusions using larger datasets of atmospheric PM measurements. Pitchford et al. (2009) mapped wintertime nitrate concentrations using Interagency Monitoring of Protected Visual Environments (IMPROVE) and STN data and found a peak in wintertime nitrate in a region extending from Iowa to the shore of southern Lake Michigan. Regarding the processes likely important to episodic nitrate elevation, Katzman et al. (2010) highlighted emissions of the nitrate precursor NO_x from combustion sources into stagnant air masses and increases in relative humidity sufficient to cause deliquescence

and subsequent enhancement of ammonium nitrate aerosol concentrations through gas-to-particle partitioning.

The first comprehensive study of inorganic thermodynamic sensitivity in the Upper Midwest examined reductions in mean $PM_{2.5}$ concentrations from reduction of sulfate and nitrate (Blanchard and Tanenbaum, 2004). Within this same timeframe, field campaigns began to more routinely incorporate time resolved measurement of gas and aerosol inorganics, and/or thermodynamic sensitivity modeling of inorganic PM (Wittig et al., 2004a; Takahama et al., 2004; Vayenas et al., 2005; Blanchard and Hidy, 2003; Chow et al., 2008; Fisseha et al., 2006). Data analysis of measurements taken in 2003–2006 through the Midwest Ammonia Monitoring Project extended earlier thermodynamic sensitivity work, and began to ask new questions, such as sensitivity of aerosol concentrations to ammonia reductions, as well as thermodynamic sensitivity during episodes as a distinct issue from seasonally averaged sensitivities (Blanchard and Tanenbaum, 2008).

Bender et al. (2009) and Baek et al. (2010) analyzed nitrate and $PM_{2.5}$ data from the EPA AQS database and IMPROVE to quantify inter-annual variability of episodes, regional versus local contributions to episodes, and map episode occurrence across the region. Bender et al. (2009) also reported a preliminary assessment of the skill of the Community Multiscale Air Quality (CMAQ) modeling system at reproducing cold season episodes.

Several studies have addressed other issues relevant to wintertime $PM_{2.5}$ episodes, including relative contribution of regional and local sources to aerosol concentrations (e.g. LADCO, 2004), nitrate versus non-nitrate aerosol nitrogen species (Lee et al., 2008), and statistical associations between air quality variables (Ghosh et al., 2010).

A number of studies have attempted to quantify air quality model skill in the study region and to explore sensitivity to emissions reductions of SO_2, NO_x, and NH_3 (Spak and Holloway, 2009; Makar et al., 2009; Pinder et al., 2008; Appel et al., 2008; Baker and Scheff, 2008, 2007; Tesche et al., 2006; Mathur et al., 2008).

Many of the aforementioned field studies, thermodynamic analysis, and modeling studies focus on air quality at long time scales (e.g. seasonally averaged). This is in part due to limitations in the underlying datasets which often are limited to daily or 1-in-3 day integrated samples. A distinguishing feature of the current work is an explicit and quantitative focus on air quality episodes at hourly time resolution with simultaneous measurement of inorganic aerosols and gases.

To establish a useful conceptual model of episodes, the relative importance and spatial variation of nitrate production and loss pathways must be better understood. During the daytime OH and NO_2 react to form HNO_3, which then partitions between gas phase and the aerosol nitrate phase. In the absence of sunlight and NO, the reaction $NO_2+O_3 \rightarrow NO_3+O_2$ is followed by the conversion of NO_3 to N_2O_5, which in turn can form HNO_3 via hydrolysis on aqueous aerosols (e.g. Chang et al., 2011). Modeling studies show that the nighttime pathway of nitrate formation can have a large impact, especially in colder climates or during wintertime (e.g. Alexander et al., 2009). However, regional studies for winter-time and fog conditions are still lacking. Parameterization of the efficiency of the nighttime pathway is a difficult problem that introduces uncertainty in model simulations (Evans and Jacob, 2005; Mathur et al., 2008; Riemer et al., 2003, 2009; Roustan et al., 2010).

2 Objectives

Against this background – a documented history of nitrate-dominated wintertime episodes in the Upper Midwest – but with many unanswered questions about the detailed gas- and aerosol-chemistry of episodes, the meteorology of episodes, and the efficacy of potential control strategies, the LADCO WNS was conceived and carried out from December 2008–March 2009. Continuous measurement of gas and aerosol-phase nitrate and ammonia at rural urban pairs was the key aspect of the study design.

The objectives of the LADCO WNS are shown in Table 1. Objectives one through seven are addressed in this paper. Objective eight (thermodynamic sensitivity) work is presented in Baek et al. (2010). Further investigation of nitrate chemistry, policy implications of control strategies, and 3-D chemical transport model skill evaluation for episodes is ongoing with initial results reported in Spak et al. (2012).

3 Experimental

The urban (Milwaukee, WI) and rural (Mayville, WI) sites (referred to collectively as the Wisconsin sites) are shown in Fig. 1. Details for these monitoring sites and associated sites for supporting meteorology are included in Table 2.

The Milwaukee site is located in a mixed-use urban area (commercial, retail, residential) just north of downtown Milwaukee and is influenced by nearby roadways and industrial sources. The distance of this site to Lake Michigan is 3 km, and the site is therefore influenced by lake-induced meteorology (Sills et al., 2011). The Mayville site, 65 km northwest of the Milwaukee site (Fig. 1), is situated in a rural area with low population density, and is largely surrounded by tilled agricultural fields. Livestock operations (predominantly dairy cattle) are also prevalent in Wisconsin.

The monitoring campaign was conducted between December 2008 and March 2009. Participating organizations included Atmospheric Research & Analysis Inc. (ARA), the Wisconsin Department of Natural Resources (WDNR), the Illinois State Water Survey (ISWS), and LADCO. Table 3 summarized measured species, sampling intervals, data sources and specific methods of analysis.

Hourly concentrations of sulfate, nitrate, ammonium, NO_y, nitric acid, and ammonia were measured at Mayville

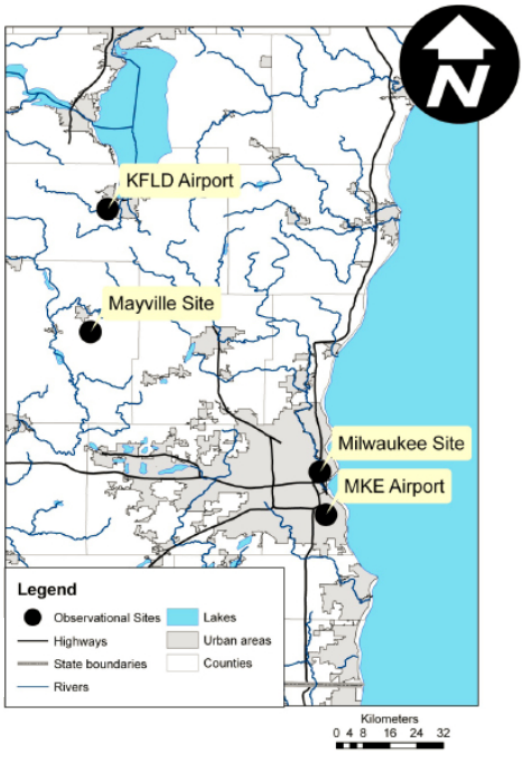

Fig. 1. Area map of WNS sites and meteorological stations KFLD and MKE Airport.

and Milwaukee with the iCAMS (Inorganic Continuous Aerosol Measurement System) from 1 January–31 March 2009. The iCAMS uses combinations of oxidation and reduction catalysts and denuders to measure NO_y, NO_3^-(a), HNO_3(g), NH_4^+(a), SO_4^{2-}(a), and NH_3(g) at 60-min time intervals (Edgerton et al., 2006). This system utilized four instruments which are described briefly below and in more detail by Edgerton et al. (2006).

The first instrument measured NO_y and NO_y^* (NO_y^* is NO_y denuded to remove HNO_3). HNO_3 was then calculated as NO_y-NO_y^*. The second instrument measured total nitrogen plus ammonia in one channel (TN), and total nitrogen without ammonia in the other channel (TN*). NH_3(g) was calculated as TN-TN*. The third instrument employed three channels to measure $PM_{2.5}$ NO_3^- and NH_4^+. The first channel was denuded and filtered to provide a baseline signal. The second and third channels measured baseline plus NO_3^- and baseline plus NO_3^- and NH_4^+, respectively. NO_3^- was calculated as the difference between channel 2 and channel 1, while NH_4^+ was calculated as the difference between channel 3 and channel 2. Fine particulate SO_4^{2-} was measured using a variation of the Harvard School of Public Health approach in which $PM_{2.5}$ SO_4^{2-} is reduced to SO_2 in a 1000C Inconel tube. Potentially interfering gases (SO_2, HNO_3, and NH_3) for particulate measurements were removed by denuders prior to the converters. For the nitrogen-containing species, target analytes were converted to NO and then quantified via NO-ozone chemiluminescence (Thermo-Environmental Model 42c trace-level). SO_2 from the SO_4^{2-} converter was analyzed via pulsed UV fluorescence (Thermo-Environmental Model 43c trace-level). Analyzers were zeroed for ten minutes at least once a day and challenged with NO and *n*-propyl nitrate three times per week.

Data from all analyzers were acquired with 1-min time resolution, then zero-corrected, calibration-corrected and aggregated to 5-min, 60-min and 24-h averages. Zero and calibration corrections were performed automatically on raw 1-min data by interpolating between successive zeros (calibrations) and applying the interpolated correction to each 1-min concentration. 5-min averages were reviewed and flagged for outliers, instrument malfunctions and down time and residual effects from zeros and calibrations. Flagged data were re-aggregated to 60-min averages for use in this work.

The iCAMS measurements conducted by ARA are operationally defined. Analyzers are calibrated with NIST-traceable NO and SO_2, but there is limited verification that NO and SO_2 detected by the analyzers originates solely from target compounds (e.g., NO_3^-, NH_4^+ and SO_4^{2-}). For example, organo-nitrates and organo-sulfates have been observed in summer (Gao et al., 2006; Surratt et al., 2007). To the extent they are converted to NO and SO_2 in the iCAMS, these compounds would contribute positive biases to reported NO_3^- and SO_4^{2-}. Atmospheric amines could also cause positive biases in reported NH_4^+ concentrations, while incomplete conversion could result in negative biases for all compounds. The presumptions (not universally true) for iCAMS are: (1) the NO_y converter quantitatively reduces all reactive odd nitrogen and rejects all reduced nitrogen; (2) the KCl denuder used to measure NO_y^* removes only HNO_3; (3) particulate NO_3^-, NH_4^+ and SO_4^{2-} vastly outweigh their organic counterparts.

Several studies have attempted to test the above presumptions. Williams et al. (1998) conducted a field intercomparison of NO_y measurements outside Nashville, TN in anticipation of one of the Southern Oxidants Study field campaigns. Results of this study showed that NO_y could be measured with extant techniques (including iCAMS) with an uncertainty of approximately $\pm 22\,\%$. Williams et al. (1998) also reported that HNO_3 could be measured with an uncertainty of approximately $\pm 16\,\%$ and that NH_3 did not interfere significantly (i.e. $< 3\,\%$ conversion) with NO_y measurements so long as the Mo converter temperature did not exceed 350 °C. Edgerton et al. (2006) compared continuous and filter based measurements of NO_3^-, NH_4^+ and SO_4^{2-} obtained from the SEARCH network during 2002 and showed strong, but variable, correlations between continuous and filter based data sets. This observation lead Edgerton et al. (2006) to conclude that adjustment of the continuous observations based on filter data was required, at least for the iCAMS prototype then under development. After adjustment, mean absolute

Table 1. Objectives of the LADCO WNS.

Objectives	Comments
Data validation and instrument-to-instrument intercomparison	Data quality and uncertainty assessed using comparison of continuous data and integrated filter/denuder measurements.
Identify and characterize the intensity and frequency of short term episodic air pollution at the monitoring sites	Used hourly mass measurements to identify episodes.
Characterize aerosol and gas phase composition on average and during short-term episode pollution events	Used SO_4^{2-}, NO_3^-, NH_4^+, OC, EC, NO_y, CO, HNO_3, NH_3, SO_2, and O_3 to answer (1) how does that chemical composition on episode and non-episode days, and (2) how does chemical composition vary during episodes between rural and urban sites?
Examine the rural-urban gradient	Concentration differences, enhancement ratios, and diurnal patterns quantified during episodes and non-episodes for rural and urban sites.
Identify the influence of local primary sources	Wind sector analysis and conditional probability analysis performed to identify potential localized sources. Back trajectory analysis performed to quantify regional transport.
Episode meteorology	Meteorological conditions favorable for episodes analyzed, including CART analysis, and examination of fog and snow.
Nitrate formation chemistry	Diurnal patterns of nitrate, O_3 and other species analyzed to assess relative importance of daytime (OH) and nighttime (O_3/N_2O_5) channels.
Thermodynamic sensitivity	Thermodynamic box models used as tools to investigate thermodynamic and hygroscopic state.

Table 2. Details of monitoring sites.

Site	Latitude	Longitude	AQS Site ID	Surrounding Land Use	2000–2009[2] Jan–Mar $PM_{2.5}$ ($\mu g\,m^{-3}$)
Milwaukee[1] (DNR SER HQRS)	43.0611° N	87.9125° W	55-079-0026	Mixed-use urban	15.2 (2.0) 39.6 (6.4)
Mayville[1]	43.4350° N	88.5278° W	55-027-0007	Rural	13.5 (1.8) 33.3 (7.8)
KFLD Airport[1]	43.7709° N	88.4884° W	–	Rural and suburban mix	NA
MKE Airport[1]	42.9420° N	87.8973° W	–	Mixed-use urban	NA

Source: [1] http://www.epa.gov/airdata/, [2] Top value is the mean of the 10 annual January–March means. Bottom value is the mean of the 10 annual January–March 98th percentiles. Values in parenthesis are one standard deviation of the statistic based on the 10 annual values contributing to the mean.

Table 3. List of monitored parameters.

Species	Averaging time (h)	Units	Organization Providing Data	Method
$PM_{2.5}$	1 h	$\mu g\,m^{-3}$	WDNR	FDMS EPA Param 88101 Method Code 181 (Thermo Scientific TEOM 1400 FDMS or 1405 8500C FDMS w/VSCC)
SO_4^{2-}	1 h	$\mu g\,m^{-3}$	ARA	iCAMS (reduction in 1000 °C stainless steel/UV-fluorescence)[1]
NO_3^-	1 h	$\mu g\,m^{-3}$	ARA	iCAMS (Mo converter/detection as NO)[2]
NH_4^+	1 h	$\mu g\,m^{-3}$	ARA	iCAMS (filter diff./Pt/Mo converters/detection as NO)[3]
HNO_3	1 h	ppbv	ARA	iCAMS (denuder diff./Mo converter/detection as NO)[4]
NH_3	1 h	ppbv	ARA	iCAMS (denuder diff./Pt/Mo converters/detection as NO)[5]
NO_y	1 h	ppb	ARA	iCAMS (Mo converter, detection as NO)[5]
NO_x[6]	1 h	ppbv	WDNR	EPA Param 42603
SO_2[7]	1 h	ppb	WDNR	EPA Param 42401
Temperature	1 h	Deg F	WDNR	
Wind Speed	1 h	mph	WDNR	
Wind direction	1 h	Deg	WDNR	
NH_3	24 h	ppbv	ISWS	Denuder, EPA Param 42604
HNO_3	24 h	ppbv	ISWS	Denuder, EPA Param 42305
H_2SO_3, H_2SO_4	24 h	ppbv	ISWS	Denuder, EPA Param 42401
$PM_{2.5}$	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88101, MetOne Teflon filters, method code 118
NH_4^+	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88301
NO_3^-	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88306
SO_4^{2-}	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88403
OC	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88305[8]
EC	24 h 1 in 3 days	$\mu g\,m^{-3}$	WDNR	FRM EPA Param 88307[8]
O_3	1 h	ppb	WDNR	FRM EPA Param 44201
Relative Humidity	1 h	%	NWS	See [9]
Surface pressure	1 h	mbar	NWS	See [9]
Visibility	1 h	km	NWS	See [9]
Precipitation	1 h	mm	NWS	See [9]

[1] Estimated limit of detection 0.1–0.2 $\mu g\,m^{-3}$, [2] estimated limit of detection 0.1 $\mu g\,m^{-3}$, [3] estimated limit of detection 0.07 $\mu g\,m^{-3}$, [4] estimated limit of detection 0.1 ppb, [5] estimated limit of detection 0.1–0.2 ppb, [6] hourly NO_x is only available at Milwaukee, [7] hourly SO_2 is only available at Mayville, [8] OC and EC samples were analyzed by RTI using quartz filters on a SASS sampler, [9] from General Mitchell Airport (MKE).

errors for continuous data were reduced to 14 %, 11 % and 9 % for NO_3^-, NH_4^+ and SO_4^{2-}, respectively. Schwab et al. (2006) performed laboratory and field tests of a commercial version of the SO_4^{2-} analyzer used in SEARCH. Results showed near-quantitative (95 %) recovery for laboratory generated ammonium sulfate aerosol. Comparison with filter-based measurements, on the other hand, showed the continuous measurements to be biased low by about 20 %. Saylor et al. (2010) analyzed continuous and denuder-based NH_3 measurements at several SEARCH sites. Results showed that continuous measurements were typically biased low (5–45 %) with an overall uncertainty of 20–25 %.

Gas phase species (NH_3 and HNO_3) were also measured at 24-h time resolution on every third day using URG tandem annular denuders prepared and analyzed by the Illinois State Water Survey (ISWS) with previously used protocols (Sweet et al., 2004). The air sample stream first passed through a Teflon-coated cyclone (URG-2000-30EN; nominal 2.5 µm cut at 10 lpm) to minimize potential interferences from particulate matter. An upstream denuder (Denuder "A"; URG-2000-30B; 242 mm) captured ammonia from the sample stream by reaction with the phosphorous acid (H_3PO_3) coating on the interior surfaces. A 2nd denuder (Denuder "B"; URG-2000-30B; 150 mm) captured nitric acid with the sodium carbonate (Na_2CO_3) coating. The denuders were mounted in a non-thermostatted enclosure. Exposed samples and unexposed travel blanks (shipped capped along with field samples but never mounted or opened outside the laboratory) were extracted under clean laboratory conditions with 30 ml of ultrapure (Barnstead E-pure©) water in two rinses. Denuders "A" and "B" were extracted simultaneously yielding a single extract, from which precise aliquots are analyzed by the NADP Central Analytical Laboratory for ammonium by flow-injection colorimetry, and for nitrate and sulfate by ion chromatography with suppressed conductivity detection. With very few exceptions, laboratory blank concentrations were negligible.

Both WNS sites were established STN sites and therefore had filter-based 24-h $PM_{2.5}$ measurements on a 1-in-3 day schedule. The OC and EC measurements were on quartz filters in the SASS sampler, prior to the adoption of the URG300N sampler after 7 October 2009 at these sites. Hourly $PM_{2.5}$ mass was by FDMS TEOM.

Meteorological data included the collocated hourly data from measurement sites (temperature, wind speed and direction, and relative humidity). These were supplemented with data from the national weather stations at KFLD airport in Fond du Lac, WI and MKE airport in Milwaukee (http://www.ncdc.noaa.gov/cdo-web/). Visibility, dry and wet bulb temperature, dew point temperature, and pressure were used from the two airport stations. Snow data were taken from the SNODAS product (a modeling and data assimilation system developed by National Operational Hydrologic Remote Sensing Center (NOHRSC, 2009) of NOAA and accessed from the National Snow and Ice Data Centre (NSIDC) website at http://nsidc.org/data/g02158.html). Radiation measurement from the SURFRAD network station at the Bondville Atmospheric Environmental Research Station (BEARS) site just outside of Champaign-Urbana, Illinois were used. One minute time-resolution records of downwelling and upwelling solar radiation were used from an Eppley Precision Spectral Pyranometer (PSP) (broadband spectral range from 280 to 3000 nm).

4 Data analysis

The multiple sources of speciation data (iCAMS, ISWS, and WDNR routine monitoring) were combined into a single database, averaged to common time intervals where necessary, and graphed for visual inspection. As recommended in Edgerton et al. (2006), as practiced in similar studies (e.g. Wittig et al., 2004b), and to facilitate intercomparison with previous studies that assessed thermodynamic sensitivity using integrated filter and denuder measurement, the hourly iCAMS data were adjusted by linear adjustments (slope and offset) to maximize agreement between 24 h averages of iCAMS and paired integrated measurement.

Weighted least squares regression was performed with weights inversely proportional to the raw measured 24-h averaged iCAMS values. For determining a confidence interval for every hourly iCAMS data point in the dataset, an error was assumed of the following form: the upper confidence value was $\mathrm{iCAMS}_{\mathrm{corrected}} + [f\,(\mathrm{iCAMS}_{\mathrm{raw}}) + \varepsilon]$ and the lower confidence value was $\mathrm{iCAMS}_{\mathrm{corrected}} - [f\,(\mathrm{iCAMS}_{\mathrm{raw}}) + \varepsilon]$. The values for f and ε were determined by linear regression and the estimates were then used to construct confidence and prediction intervals. Analyses were carried out in SAS v9.2.

For determination of episode start and end times, the hourly $PM_{2.5}$ mass time series was used. Episodes were defined as periods where the moving average $PM_{2.5}$ hourly concentration (7 h window for moving average) exceeded $27\,\mu g\,m^{-3}$ for 4 or more consecutive hours. This is a relatively low threshold which yields more periods classified as episodes than alternative threshold definitions such as $35\,\mu g\,m^{-3}$. Setting the threshold at 75 % of the $35\,\mu g\,m^{-3}$ standard has a rationale that the periods in excess of $27\,\mu g\,m^{-3}$ likely share chemical and meteorological similarities with the periods in excess of $35\,\mu g\,m^{-3}$, that the regulatory standard may someday be decreased, and that the size of the episode dataset is increased to allow better consideration of variability between episodes.

Gas ratio, an indicator of available ammonia (Ansari and Pandis, 1998) was analyzed for episode and non-episode periods. High gas ratios indicate higher ammonia availability; a value of one is often used to separate ammonia-rich and ammonia-limited conditions.

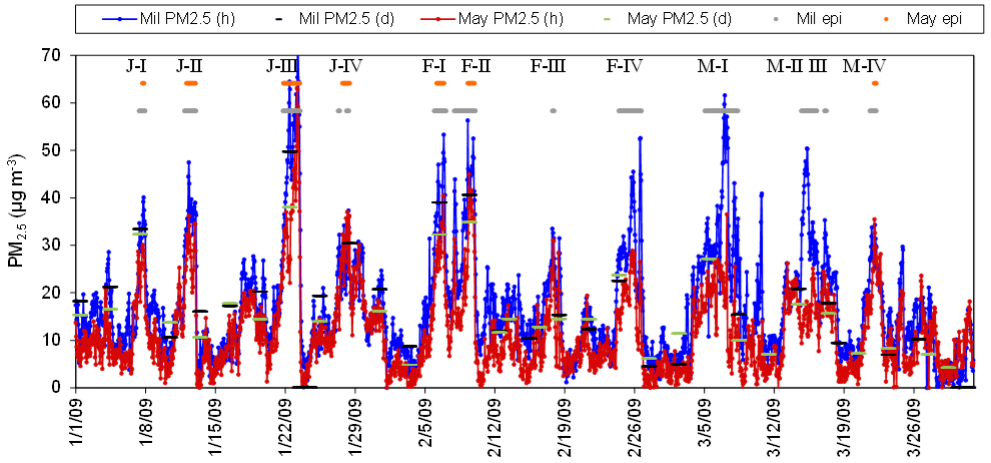

Fig. 2. Hourly and daily $PM_{2.5}$. Blue (hourly) and black (24 h) $PM_{2.5}$ concentrations are shown for Milwaukee. Red (hourly) and green (daily) $PM_{2.5}$ concentrations are for Mayville. Grey and orange bands indicate hours that have been designated as episode hours. Grey is for Milwaukee while 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.

Table 4. Key mean measured values during the period 1 January–31 March 2009.

Parameter	Milwaukee	Mayville
$PM_{2.5}$ ($\mu g\,m^{-3}$)	17.1	11.7
Total nitrate ($\mu g\,m^{-3}$)	5.6	4.8
Total ammonia ($\mu g\,m^{-3}$)	3.3	3.3
Gas ammonia (ppb)	2.3	2.4
Nitrate aerosol/total nitrate	78 %	69 %
NO_y (ppb)	27	6.3
Temperature (°C)	−3	−5
Ozone (ppb)	22	31
OC ($\mu g\,m^{-3}$)	3.6	3.2
EC ($\mu g\,m^{-3}$)	0.52	0.3
Gas Ratio (d'less)	1.5	1.7

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

Where TA is total ammonia, TS is total sulfate, and TN is total nitrate (all in molar concentrations). The iCAMS SO_4^{2-} was used for total sulfate, the iCAMS TN* for total nitrate, and the iCAMS NO_3^- + NH_3(g) for total ammonia.

5 Results and discussion

Some key mean measured values during the 3 month study period are shown in Table 4. More detailed tables with information on the descriptive statistics of the complete list of variables can be found in the Supplement, Tables S1–S2.

5.1 Summary of site-specific $PM_{2.5}$ mass

Time series of $PM_{2.5}$ mass concentrations (Fig. 2) show the hourly values and (where available) 24 h integrated filter values. Episode periods (discussed below) are also indicated as horizontal bars labeled with Roman numerals. From Fig. 2, the high degree of correlation between the urban and rural pair is evident. The urban (blue) is usually higher, and the difference between blue and red traces (i.e. the urban excess in overall $PM_{2.5}$) is also evident. The episodes have a characteristic saw tooth shape with a linear build up, and followed by a rapid clearing of the air. Time series of additional species (e.g. NH_3(g), NO_3 aerosol, etc.) can be found in the Supplement.

5.2 Intercomparison of 24-h integrated and continuous concentrations

The continuous and integrated measurements were intercompared, and the intercomparison result was used as the basis for data adjustment as described above. Two example comparisons are shown in Fig. 3. Milwaukee aerosol nitrate was close to 1 : 1 agreement, exhibited high correlation, and required only minor adjustment. Mayville NH_3(g) had a lower correlation and required a larger adjustment. Slopes, intercepts and confidence interval parameters can be found in the Supplement (Table S3) and more information is in appendix 2 of Baek et al. (2010).

Agreement between integrated and continuous techniques can be summarized through classification according to fractional bias and correlation. Type I (better agreement) was defined as meeting either of the following two conditions: (1) absolute fractional bias < 0.2 and $R^2 > 0.9$ between integrated and continuous techniques; (2) absolute fractional bias

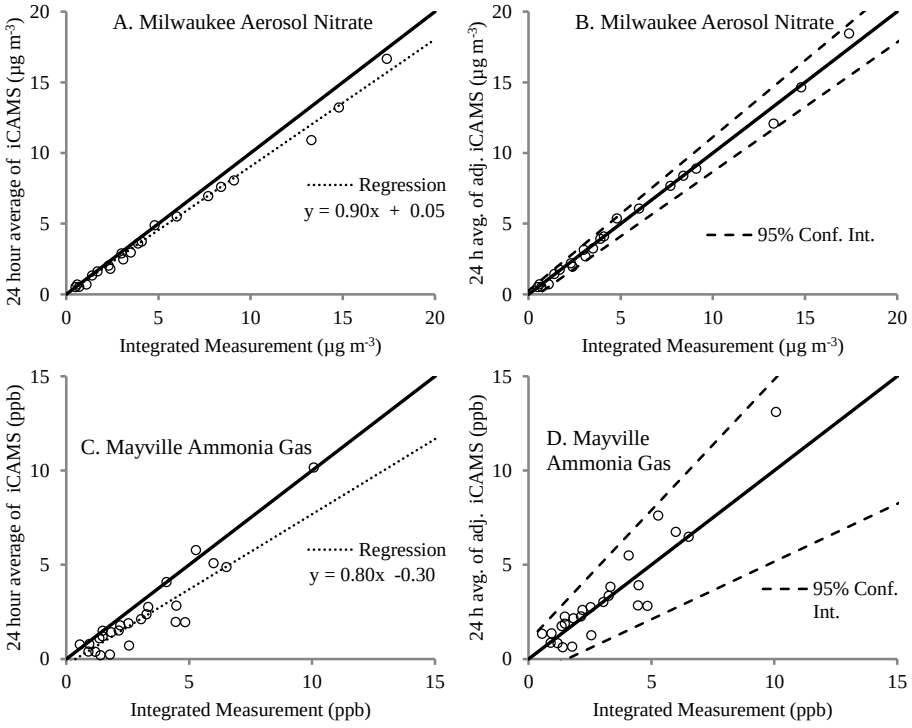

Fig. 3. Examples of iCAMS data before and after adjustment by linear regression against 24 h integrated filter values. As an example of a sample with good agreement between continuous and integrated methods, total nitrate from Milwaukee (panel **A**) is shown. The revised values (panel **B**) are shown together with a 1 : 1 line and confidence intervals. As an example of a case with more bias and scatter, Mayville gas phase ammonia comparison between averages of iCAMS data and denuders is shown before (panel **C**) and after (panel **D**) adjustment.

< 0.1 and $R^2 > 0.75$ between integrated and continuous techniques. Type II (lesser agreement) was defined as not meeting the type I criterion. Type I included particulate NO_3^- (Milwaukee and Mayville), total NO_3 (Milwaukee and Mayville), particulate NH_4^+ (Milwaukee and Mayville), SO_4^{2-} (Milwaukee), and particulate NO_3^- (Milwaukee). All other measurements were type II. In cases where the filter measurements are generally accepted as having low bias and high precision (such as 24 h filter-based sulfate measurements), agreement between the iCAMS and integrated measurements is probably a good test of the iCAMS data quality. For other integrated measurements that are subject to potential measurement artifacts (e.g. aerosol nitrate) or that are performed less frequently (e.g. nitric acid and ammonia by denuder), a lack of agreement between the two techniques is more difficult to interpret.

For HNO_3(g) at the Wisconsin sites, the continuous measurement was higher than integrated measurements (0.59 vs. 0.28 ppb, and 0.49 vs. 0.18 ppb, at Milwaukee and Mayville, respectively) and fairly close to the limit of detection of about 0.1 ppb. Thermodynamically modeled HNO_3(g) (0.37 and 0.15 ppb, respectively at Milwaukee and Mayville) agreed more closely with the integrated denuder measurements. Therefore, the reported HNO_3(g) in this work is the iCAMS total nitrate minus iCAMS aerosol nitrate.

The experimental data was also evaluated for internal consistency using the ISORROPIA thermodynamic model (Nenes et al., 1999) and a calculation of hourly charge balance. 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). The linear data adjustment improved or left unchanged model-measurement agreement for all species at both sites. Average cation concentrations (109 nequiv m^{-3} at Milwaukee versus 100 nequiv m^{-3} of anions; 100 and 93 nequiv m^{-3}, respectively, at Mayville) agreed to within 9 % at both sites and agreement was unchanged or improved with the data adjustment.

5.3 Episode identification

As shown in Table 5, Milwaukee had the highest number of episodes (13), while the Mayville site had seven episodes. All episodes that occurred at Mayville also had a concurrent Milwaukee episode. Therefore episodes could be described as “Shared episodes” or “Milwaukee only”. The exact start and end times of shared episodes at the urban and rural sites were not identical.

Table 5. Summary table for episodes.

			Milwaukee		Mayville	
Episode Name	Start Date	End Date	Peak 7 h $PM_{2.5}$	Avg. $PM_{2.5}$ during period	Peak 7 h $PM_{2.5}$	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

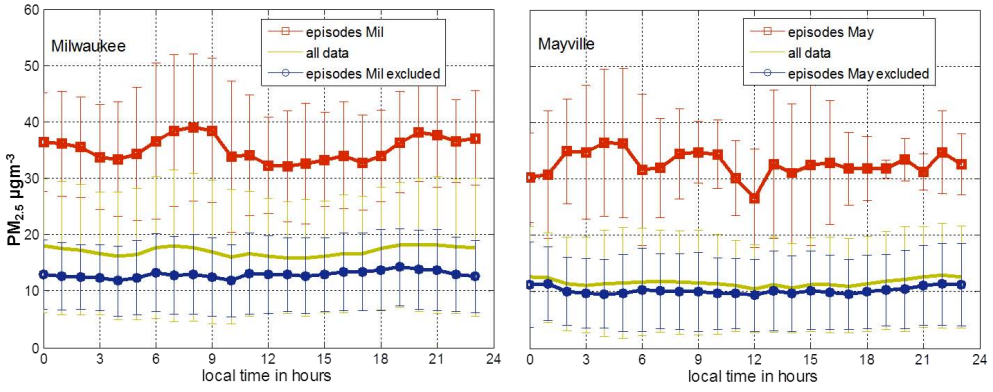

Fig. 4. Diurnal pattern for $PM_{2.5}$ at Milwaukee (left) and Mayville (right).

5.4 Diurnal pattern

The diurnal patterns for $PM_{2.5}$ were very flat during episodes and non-episodes, with a slight (a few $\mu g\,m^{-3}$) increase at Milwaukee during episodes at 08:00 a.m. and a small increase at the beginning of the night (Fig. 4). The trends in $PM_{2.5}$ indicate that the conventional model of nighttime accumulation followed by daytime ventilation of pollutants did not apply (on average or during episodes) during the study periods. Future field studies focused on cold season nitrate should include measurement of mixed layer height to further investigate this.

The diurnal patterns for total nitrate and total ammonia (not shown) were flat, except for a morning peak in TNO_3 and midday minimum at the Milwaukee site which is $\sim 20\,\%$ over the mean value. This diurnal pattern in TNO_3 at Milwaukee may be due to interference of NO_x since mean NO_x levels in Milwaukee are $\sim 15\times$ those of total nitrate.

Ozone levels (Fig. 5) were higher at the rural site, peaked in the afternoon, and (at the urban site) had an early morning O_3 decrease coincident with NO increase. Episodes were associated with decreases in O_3 levels, particularly later in the day.

5.5 Particulate matter composition

A key objective of the field study was to determine the chemical composition on average and during episodes. Several different summaries of chemical composition were required due to variation in sampling frequency (hourly, daily, and 1-in-3 day) and due to missing data. The first analysis was performed using hourly inorganic aerosol composition and hourly $PM_{2.5}$ mass, and required the smallest number of simultaneous measurements (SO_4^{2-}, NO_3^-, NH_4^+, and $PM_{2.5}$). A second analysis added 24-h OC and EC values to the analysis, assuming the 24-h average concentration was valid for all hours in the hourly comparison. A third composition analysis

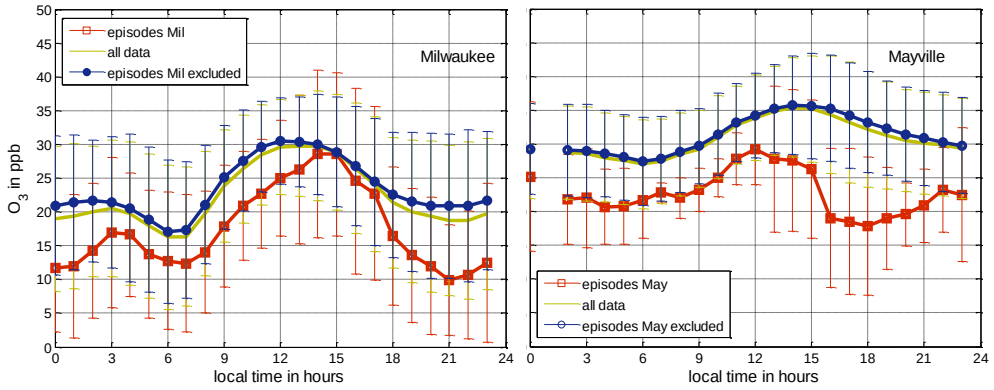

Fig. 5. Diurnal pattern for ozone at Milwaukee (left), and Mayville (right). Error bars represent one standard deviation.

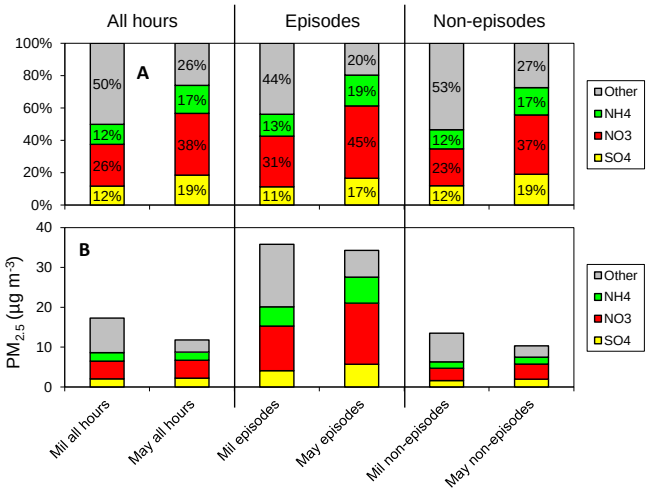

Fig. 6. Inorganic composition on a fractional **(A)** and absolute **(B)** basis.

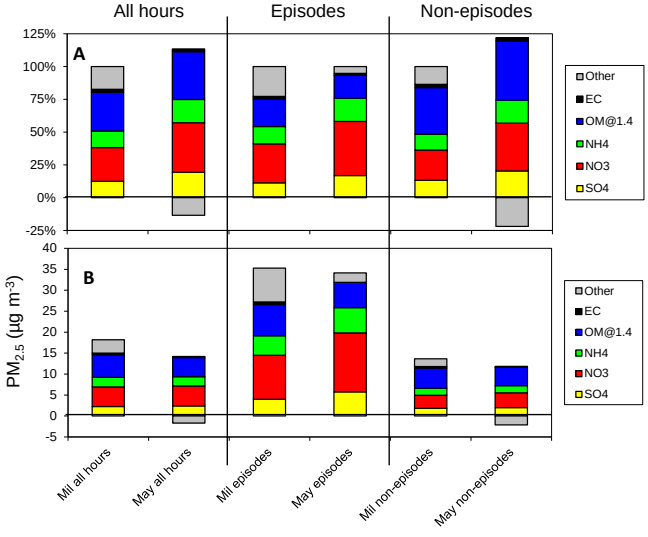

Fig. 7. Inorganic and carbonaceous composition on a fractional **(A)** and absolute **(B)** basis. Negative concentrations (seen at Mayville) are from cases where the sum of species is greater than the measured $PM_{2.5}$ mass measurement.

used hourly inorganic gases and aerosols to evaluate partitioning of nitrate and ammonia.

Inorganic aerosol composition (Fig. 6) shows the large contribution of ammonium nitrate during episodes in Milwaukee and Mayville. A similar calculation including carbonaceous aerosol (Fig. 7) shows the "other" contributing to episodes in Fig. 6 is mainly organic carbon. Negative concentrations in Fig. 7 are the result of the sum of species being greater than the $PM_{2.5}$ measurement. A value of 1.4 for the OM/OC was assumed for OC to OM conversion.

Particle composition showed a large contribution of nitrate and/or organic constituents (together summing to at least 60 % of aerosol mass) irrespective of episodes or non-episodes. Also, the change in particle mass during episodes was largely due to nitrate. Non-episodic nitrate concentrations were 3.1 and 4.8 $\mu g\,m^{-3}$ in Milwaukee and Mayville, respectively. During episodes, these rose to 10.5 and 14.1 $\mu g\,m^{-3}$. Non-episodic ammonium concentrations were 1.6 and 1.7 $\mu g\,m^{-3}$ in Milwaukee and Mayville, respectively. During episodes, these rose to 4.7 and 6.0 $\mu g\,m^{-3}$. The carbonaceous mass fraction of the particulate was greater than 35 % at both sites and all periods (and often much larger) except for Mayville episodes, where it was only 21 %.

Figure 8 below shows a time series of several relevant species for the strongest episode. Figure 8a and b show the aerosol time series for 7 days, including the Jan III episode. A long build up period of about 2 days (interrupted by some decreases in the sampled concentration during midday on 22nd) was followed by a cold front that drastically lowered $PM_{2.5}$ in about 12 h on 23rd. Horizontal lines of length 24 h show concentrations from filters. Figure 8c and d show ozone concentrations, NO_y, and the breakdown of NO_y into its main constituents as sampled by the iCAMS: HNO_3, nitrate aerosol, NO, and NO_2. There is no purple shading in Fig. 8d because no chemiluminescant NO_x measurements were taken at Mayville. The agreement between the

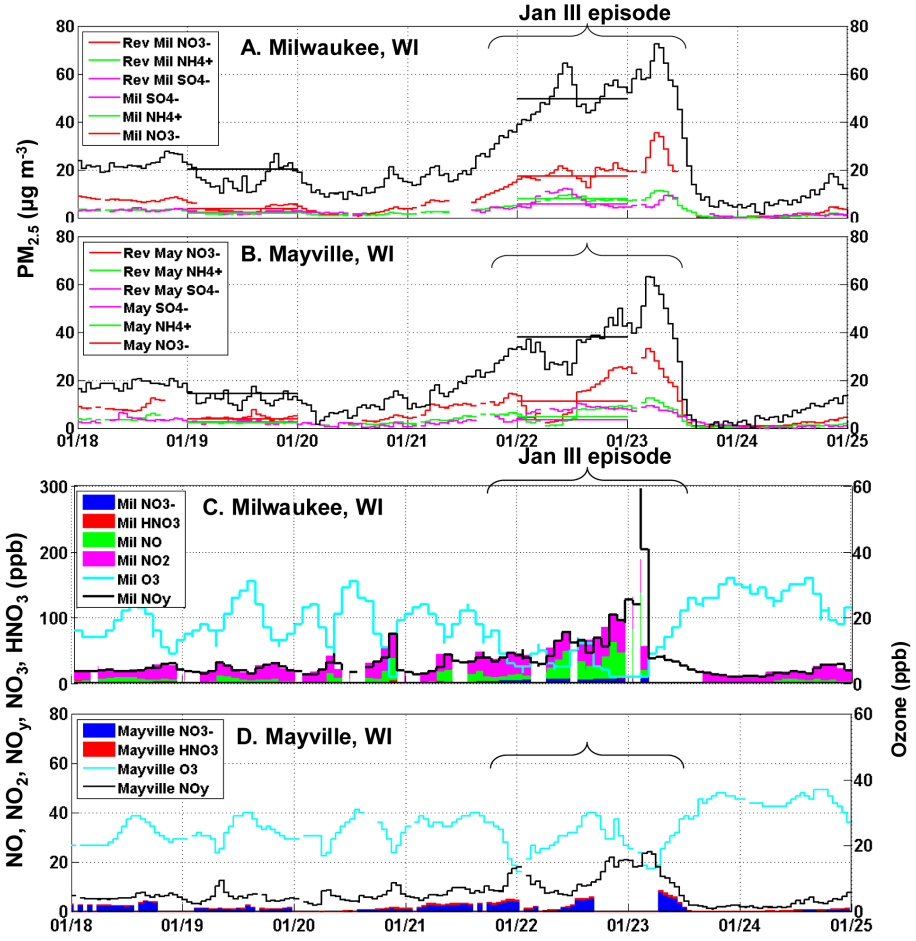

Fig. 8. Seven day time series from the Wisconsin sites that includes the strongest air pollution episode (Jan III episode beginning during the afternoon of 21 January and ending midday on 23 January). Total and inorganic aerosol species (panels **A** and **B**) show the agreement between the continuous and integrated (flat lines 1 day in 3) samplers, and the large contribution of nitrate to the episode, particularly at the Mayville site. Black lines are for total $PM_{2.5}$. Gas species and NO_y breakdown (panels **C** and **D**) show several important system features (discussed in the text). Note the left hand axis scale change between Milwaukee (panel **C**) and Mayville (panel **D**).

independent samplers (NO_y, HNO_3, and NO_3^- from iCAMS, NO and NO_2 from WDNR) shows that the iCAMS system was operating well during this episode. The HNO_3 gas concentration (red in Fig. 8c and d) is insignificant in the figure since HNO_3 concentrations were less than 1 ppb. Ozone was lower during the episode in Milwaukee. Complete hourly time series for gases and aerosols are found in the Supplement file.

The OC/EC ratio was examined for episode and non-episode periods to assess the contribution of secondary organic aerosol to episodes (Cabada et al., 2002). The ratio decreased during episodes, indicating increase in the primary fraction of organic aerosol. To further investigate the hypothesis of secondary organic aerosol contributing to Wisconsin episodes (perhaps in aqueous chemical pathways in clouds or fog), OC, EC, and $PM_{2.5}$ data from 1-in-3 samples from January 2001 to October 2009 were used to calculate OC/EC and $OC/PM_{2.5}$ ratios. The larger analysis came to the same conclusion (appendix 12 of Baek et al., 2010). OC/EC ratios depended on season (highest ratio in summer, lowest in winter, at both sites). At Milwaukee, the OC/EC ratio decreased with increasing $PM_{2.5}$ in both warm and cold seasons, suggesting strong influence of primary emissions during both summer and winter $PM_{2.5}$ episodes. As expected due to warm season SOA production, the decrease is slightly more pronounced in winter. In Mayville, OC/EC ratios decreased with increasing $PM_{2.5}$ in winter, but increased slightly with $PM_{2.5}$ in summer.

Enhancement ratios ($C_{i,\text{episode}}/C_{i,\text{non-episode}}$) and enhancement ratios relative to that of $PM_{2.5}$[$(C_{i,\text{episode}}$ $PM_{2.5\text{-nonepisode}})/(C_{i,\text{non-episode}}PM_{2.5,\text{episode}})$] quantify changes in relative particle concentration during episodes. Figure 9 shows that both WNS sites during episodes had similar profiles of enhancement ratios relative to $PM_{2.5}$. Enhancement ratios relative to $PM_{2.5}$ were largest for ammonium and nitrate. The figure shows a lower enhancement

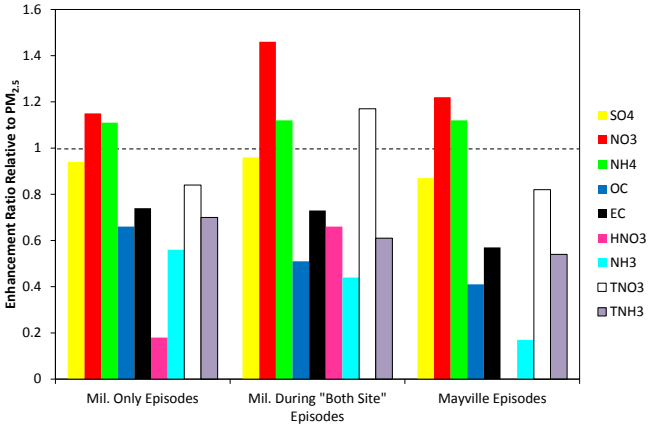

Fig. 9. Enhancement ratios relative to that of $PM_{2.5}$ during episodes of various species.

ratio relative to $PM_{2.5}$ for TNH_3 than for TNO_3 for episodes that encompassed both sites. Other important enhancement ratios were those for NO_x and NO_y. The NO_x enhancement ratio was ∼1.9–2.0 for Milwaukee and ∼1.7 for Mayville. The NO_y enhancement ratios were 2.1 and 2.5 for Milwaukee and Mayville, respectively.

The progression in PM chemistry towards lower gas ratios at high $PM_{2.5}$ concentrations can be seen in Fig. 10. The widening ratio (enhancement) of total nitrate relative to total ammonia at the Milwaukee site and the slight decrease in gas ratio are apparent. The ratio TNO_3/TNH_3 versus hourly $PM_{2.5}$ was investigated through linear regression. For Mayville, the drop in the gas ratio with $PM_{2.5}$ was clear, and the TNO_3/TNH_3 ratio increased with $PM_{2.5}$ and the slope was statistically significant in linear regression. For Milwaukee, the TNO_3/TNH_3 ratio versus $PM_{2.5}$ had a positive but not statistically significant slope, with influence by a single episode (Mar I) with a high gas ratio (and thus high TNH_3).

5.6 Gaseous measurements and ammonia availability

Inorganic gas concentrations were (on average) much more constant than their aerosol counterparts. In other words, during Wisconsin episodes, the total nitrate and total ammonia increased but the increase was mainly in the particulate phase. Figure 10 graphs gas ratios (averaged over individual episodes and non-episodes) and other variables as a function of $PM_{2.5}$. Most of the gas ratios are above one, the typical threshold for ammonia sensitive conditions. Milwaukee gas ratios were, on average, higher than the rural Mayville site. The gas ratio decreased slightly during episodes on average. One episode is left off the graph in Fig. 10a, the Mar-I episode had a gas ratio of 5.6 and a $PM_{2.5}$ concentration of 29 $\mu g\,m^{-3}$.

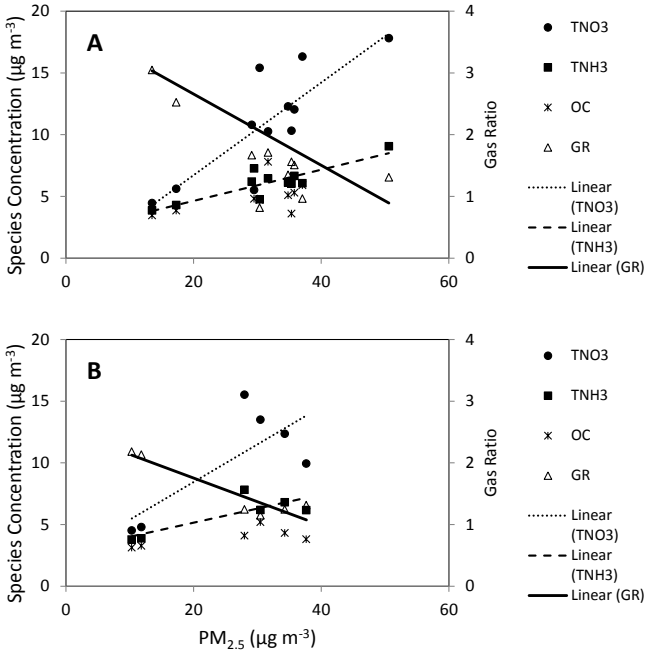

Fig. 10. Total nitrate, total ammonia, OC, and gas ratio as a function of $PM_{2.5}$ for various periods in the Milwaukee **(A)** and Mayville **(B)** datasets. Lines represent linear regression of datapoints. For Milwaukee, the linear regression equation for TNO_3 is $-0.8 + PM_{2.5} \times 0.37$ and for TNH_3 it is $2.1 + PM_{2.5} \times 0.13$. For Mayville, the linear regression equation for TNO_3 is $2.4 + PM_{2.5} \times 0.30$ and for TNH_3 it is $2.9 + PM_{2.5} \times 0.11$. One Milwaukee datapoint for gas ratio is not plotted but does influence the regression (the Mar I episode with a gas ratio of 5.6).

5.7 Meteorology and WNS episode

The 2009 WNS took place during a winter that featured considerable departures from 1971–2000 climatology of Southeastern Wisconsin. Snowfall in December across the region was a record high. January was colder than normal (by 2.7 °C on average) and dryer than normal, with only 48 % of the climatological precipitation average. February and March were slightly warmer than normal (+0.94 °C and +0.67 °C, respectively) with unusually high precipitation (39 % and 42 % above normal). The period between 18 January to 8 February had only a trace of precipitation and two days of measurable snowfall at Milwaukee. This period included 4 pollution episodes.

The onset of episodes was typically characterized by an approaching surface low pressure system, resulting in the arrival of warm, moist and stagnant air. These were the primary local signals for the initiation of a wintertime episode. The occurrence of episodes conform to the existing LADCO conceptual model of $PM_{2.5}$ episodes throughout the year (LADCO, 2009) and the empirical Classification and Regression Tree (CART) for Midwestern daily average $PM_{2.5}$ concentrations. CART analysis performed for Milwaukee

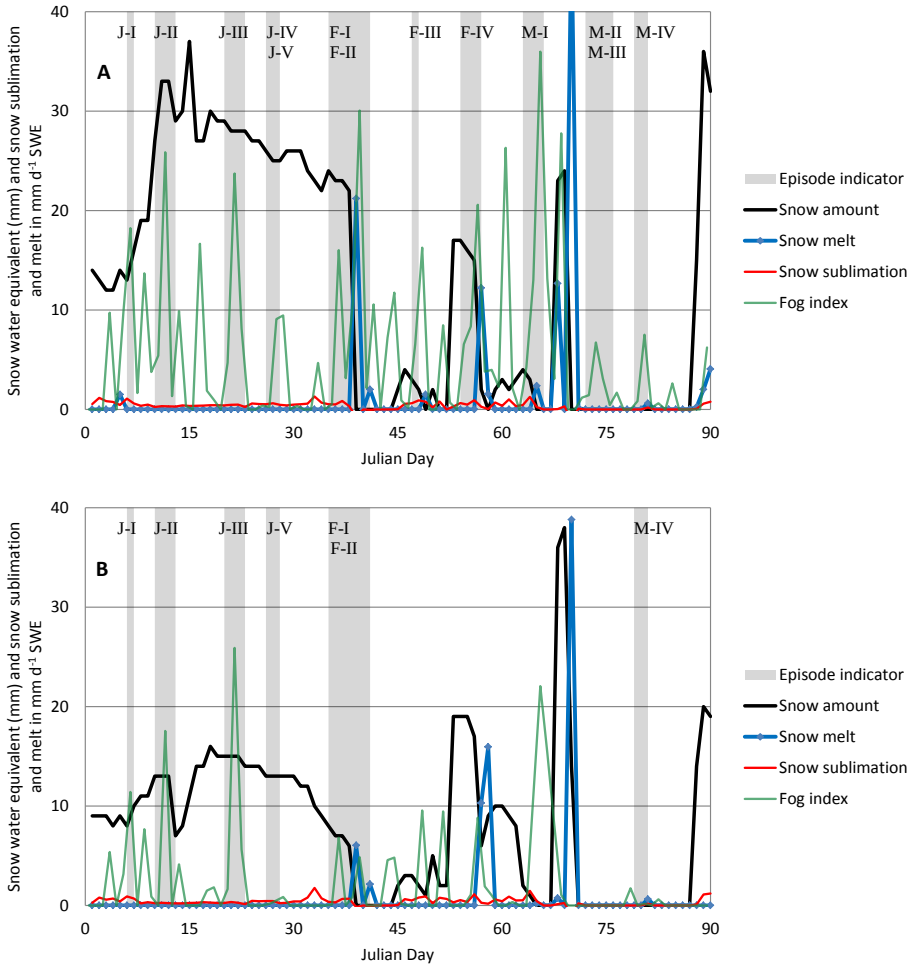

Fig. 11. Time series showing snow cover, snowmelt, snow sublimation, fog, and episodes as a time series for Milwaukee **(A)** and Mayville **(B)**. Rain also occurs in this time period but is not shown. All variables are at daily time resolution to match the daily resolution of the SNODAS data. The fog index is calculated from hourly visibility data, and a value at 100 % of the y-axis scale would result from 24 h of the maximum visibility deficit in the data (16.3 km). Only hours with the temperature within 2.5 °C of dew point and wind speed less than 4 m s^{-1} are considered to have fog in the index calculation.

and Mayville using upper air soundings from Green Bay, WI identified temperature aloft (850 mbar) and the boundary layer lapse rate (quantified as surface temperature minus temperature aloft) as the two most important meteorological variables associated with $PM_{2.5}$ events (Baek et al., 2010). These variables are indicators of inversion conditions, and their change is strongly correlated with synoptic systems.

Episodes were commonly accompanied with snow cover. Snow cover (as the snow water equivalent in mm) is shown in Fig. 11. January episodes occurred during continuous snow cover, since the first major thaw was not until the Feb-II episode. Although February and March did not have consistent snow cover, all four episodes in February and the first in March began on days with at least 1.2 cm of snow cover at both sites, and all of them ended with the snow completely melted in Milwaukee. We hypothesize that snow cover was an important source of ambient moisture, enhancing particle growth and increasing aerosol water mass during many of the events. Snow melt and sublimation may also have contributed to weak boundary layer mixing and low mixed layer depths. We further speculate that snow, sublimating snow, and evaporating melt water may release deposited aerosol precursors during episodes, including nitric acid and ammonia. NO_x release from snow has been documented, both from photolysis of deposited N (Bock and Jacobi, 2010) and from soil microbial action beneath snow (Helmig et al., 2009). Assuming a constant mixed layer height, deposition lifetime for nitrate of 5 days, a total nitrate average concentration of 5.57 µg m^{-3}, and 4 weeks of deposition prior to melting, the release of all deposited nitrate into the boundary layer at once would be lead to 31 µg m^{-3} of total nitrate. Of course, most of the nitrate during thaw periods remains in the runoff, but this nevertheless represents a potentially large pool of nitrate that may be relevant to the progression

of episodes. Detailed analysis of correlation snowmelt and TNO_3 and snowmelt has not been conducted, but may be a promising area for future work; it is complicated by the fact that chemical production, phase partitioning, deposition, and release from the snowpack all occur simultaneously.

Fog events were also consistent with the episodes in the WNS site. Figure 11 shows fog intensity based on visibility reduction at the nearby airports, dew point, and wind speed. Many of the episodes have significant increases in the occurrence of fog. That said, there are also many foggy periods with no corresponding air pollution episode. Much of this correlation is due to the fact that fog and particle events are caused by the same low, stable boundary layer conditions, and the foggy days were directly attributable to snowpack melting and sublimation. While aqueous chemistry in fog is known to enhance the generation of secondary fine particles and to maintain stable inversions, the study did not find any statistically significant quantitative residual relationship between fog and fine particle concentration observations.

The dispersing role of wind at Milwaukee is evident for two particular days (17 January and 21 February) which did not show substantial $PM_{2.5}$ increases despite meeting many meteorological criteria for an episode (low pressure, increasing temperature, high humidity). Averaged over the study, wind speed at Milwaukee during the WNS averaged 2.97 m s^{-1}, dropping to 2.30 m s^{-1} during episodes. During 17 January winds ranged from 4.1–4.2 m s^{-1}. Wind speed reached 6.0 m s^{-1} on 21 February (accompanied by a strong drop in pressure, rising temperatures, and high RH). $PM_{2.5}$ concentrations remained below 27 and 20 µg m^{-3} during these days, respectively. The absence of snow cover prior to (and occurrence of precipitation during) the 21 February period may have further limited $PM_{2.5}$ accumulation.

The impacts of actinic flux on rates of photochemical reactions have been hypothesized as a potential factor in wintertime particle events. Inspection of the time series of upwelling plus downwelling radiation (serving as a proxy for actinic flux) shows periods of high values relative to monthly climatological means before the strongest episodes. For example, average upwelling and downwelling radiation summed to 195 W m^{-2} from 14 to 22 January, and 250 W m^{-2} from 28 January to 6 February. This can be compared to 121 W m^{-2} for the remaining days in January and February. These periods of relatively high actinic flux (with snow cover and upwelling radiation greater than 40 % of the total) preceded the Jan III episode on 21 January, and the Feb II and III episodes which began on 5 February. The solar radiation values quoted are averages over all 24 h of the day. They are from Bondville, IL, which is the closest SURFRAD station but is 326 km from southern Wisconsin. The sunny periods occurred during large high pressure systems that affected multiple states.

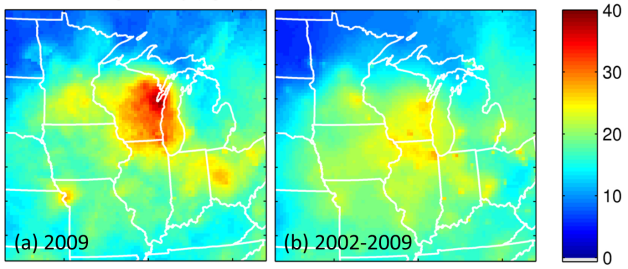

Fig. 12. 5th highest daily $PM_{2.5}$ concentration during January–March period, using 18 km $PM_{2.5}$ maps kriged from IMPROVE and AQS surface observations. LADCO WNS study period **(a)** shows higher than normal episodic concentrations in Wisconsin while **(b)** shows the average of 8 yr of 5th high values, and hotspots are most prominent in cities Wisconsin and northern Illinois.

5.8 Air mass trajectories

Air mass trajectories were analyzed using the NOAA HYSPLIT model from 1 January to 3 April 2009 (Baek et al., 2010). Winds blew mostly from the west and northwest in January, and episodes typically occurred in air masses originating to the west and west-southwest at low wind speeds. Higher $PM_{2.5}$ concentration periods were associated with transport from regions located to the south, including southern Wisconsin, western Iowa, Illinois, and Indiana. Lower $PM_{2.5}$ concentration periods were associated with transport from regions to the west and north, including Minnesota and Canada. Based on trajectory analysis, there was no evidence that Mayville episodes were ever due directly to air polluted during passage over Milwaukee. Episode trajectories from the NW (and thus from the general direction of Mayville and the surrounding rural areas of central Wisconsin) did occur, but were slightly less common that trajectories from the west, southwest, and south.

5.9 Interannual variability

Figure 12 maps intensity of short term $PM_{2.5}$ using the 5th highest $PM_{2.5}$ concentration during the January–March period. The gridded values are calculated by kriging of all available $PM_{2.5}$ measurements (IMPROVE, STN, and AQS) on a daily basis for period in question. Kriging was performed with GSLIB using month-specific Guassian semivarigrams (Deutsch and Journel, 1998). Sill, nugget, and range parameters were optimized on a monthly basis (by nonlinear least squares) to match the experimental semivariogram.

Figure 12a maps the 2009 season during which LADCO WNS measurements were taken, while Fig. 12b graphs the average of the 5th highest concentration for the 8 yr period from 2002–2009. In eastern Wisconsin, the 2009 period had much higher peak $PM_{2.5}$ concentrations relative to the 8 yr average. The same conclusion is reached by analysis of individual monitoring data (which does not rely on the kriging

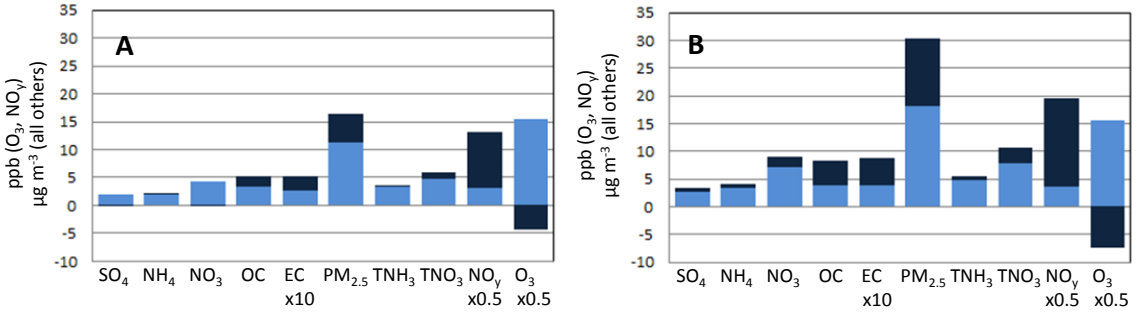

Fig. 13. Urban excess. Gas and inorganic aerosol species measured from continuous monitors and organic aerosol from integrated measurements are graphed. Light bars correspond to the rural site of the pair, and the dark increment is the urban excess. Ozone has an urban deficit rather than urban excess. Panel **(A)** is for all study hours, panel **(B)** is for periods when episodes occurred at both Milwaukee and Mayville. Note the change of scale for EC, NO_y and O_3.

estimation). The long term episode activity (as quantified by the 5th highest daily concentration during January–March) is broadly spread over southeastern Wisconsin, northern Illinois, and eastern Iowa, with slightly elevated levels in Green Bay, Madison, Milwaukee, and Chicago.

Geographic extent of the "both site" and "single site" episodes were compared by examining maps of EPA and state $PM_{2.5}$ monitor values found in Baek et al. (2010). Most single site episodes occurred during periods of elevated regional $PM_{2.5}$ (with the region of elevated areas typically including areas with higher concentration locations in Fig. 12). However, the urban excess (which can be seen as a time series in Fig. 2 and on average in Fig. 13) is important to creating "Milwaukee only" episodes. The M-II and M-III episodes may be exceptions, and the area of elevated $PM_{2.5}$ may be more confined to Milwaukee or perhaps to the shore of Lake Michigan from Green Bay to Chicago.

5.10 Urban and directional excess concentrations

The measurement database taken for the study was well suited for calculating the so-called "urban excess" of pollutants at the urban sites on average and during episodes. Figure 13 shows urban excess for NO_x, NO_y, OC, EC, and $PM_{2.5}$. The urban excess of total nitrate was very small, suggesting that nitrate was largely a regional pollutant except when there were urban-only episodes.

In order to identify potential local sources with impact on the measurements, and characterize the regional representativeness of sampling sites, wind direction versus concentration was examined using conditional probability function plots (Kim and Hopke, 2004), pollution roses, and bivariate polar plots (Carslaw et al., 2006). Summarizing the results of Baek et al. (2010), at the Milwaukee site, NO_x and NH_3 came preferentially from the directions 150 to 240° (e.g. from the south and southwest). The explanation of this feature in NO_x was the presence of the Milwaukee downtown to the south and interstate freeways to the south and west. The explanation of this feature in NH_3 is likely a combination of regional transport (the same directionality was seen at the Mayville site) and local emissions. While important to monitored concentrations, these directionally specific patterns were likely not large enough to influence the generalizability of the study results to the surrounding airsheds.

5.11 Nitrate chemistry discussion

Total nitrate concentrations increased (relative to non-episode hours) by factors of 2.7 at both Milwaukee and Mayville. The increases relative to the average of all hours were by factors of 2.1 and 2.6, respectively. Considering only shared episode hours (which typically were for the strongest episodes) the factor in Milwaukee was 3.7 times non-episode conditions. Most of the nitrate existed in the aerosol phase – 80 % for Milwaukee and even higher about 90 % in Mayville. Total ammonia was increased during episodes relative to non-episodes by a factors of 2.3 (Milwaukee) and 1.8 (Mayville). 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).

The nighttime pathway could contribute up to 50 % of the nitrate production at the WNS locations, especially during the earlier (January and February) episodes, consistent with the results by Alexander et al. (2009). Further work is required to investigate the sensitivity of the diurnal patterns in NO_y to the nighttime (Reaction R1) versus daytime (Reaction R2) pathway.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R1)}$$

$$NO_2 + OH \rightarrow HNO_3 \quad \text{(R2)}$$

Reaction (R1) is followed by the conversion of NO_3 to N_2O_5 and eventually to HNO_3. Assuming that all NO_3 radicals produced by Reaction (R1) yield HNO_3, nighttime production of HNO_3 can be calculated from observed NO_2 and O_3 and the corresponding rate constant (Sander et al., 2003). Competing

reactions of NO_3 with NO and VOC result in a lower production rate, hence the rate of Reaction (R1) represents an upper limit. As a lower limit we estimate an efficiency of this conversion of 30 % (Vayenas et al., 2005).

Since the OH radical was not measured during the LADCO study, modeled mixing ratios from CMAQ were used as an estimate. Hourly modeled OH concentrations were taken from local surface-level gridcell values in a regional simulation with CMAQ 4.6 for January–March 2002, as described and evaluated by Grabow et al. (2012). The monthly diurnal average values were used to calculate HNO_3 production. Uncertainties in the modeled OH concentrations introduce uncertainties in the estimate of the reaction rate for Reaction (R2). The HNO_3 production rates during night were of comparable magnitude to the rates during day for both Milwaukee and Mayville. Rates estimated in this way (from measured NO_2, O_3, and modeled CMAQ OH concentrations) were generally greater at Milwaukee than at Mayville (e.g. 0.4 compared to 0.15 ppb h^{-1}) due to the higher NO_2 concentrations. In January, with OH concentrations the lowest, the nighttime pathway is of the greatest importance relative to the competing pathway through OH. This preliminary analysis reflects surface concentrations only, and vertical gradients are anticipated, especially for N_2O_5, aerosols, and O_3. These gradients necessitate the use of models or vertically resolved measurements to more fully probe nitrate formation chemistry.

6 Conclusions

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 Upper Midwest portion of the Great Lakes region. 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. Many $PM_{2.5}$ episodes were measured during the period (in fact the study period was far above mean $PM_{2.5}$ episode activity), and the study design of an urban rural site pair added much insight about the episodes. Conclusions from the study presented below are likely applicable to the future study, modeling, and understanding of cold-weather ammonium nitrate episodes in other regions of the US and elsewhere.

The measurements analyzed at these sites were extensively inter-compared, and continuous measurements were adjusted using slope and offset adjustments to maximize agreement (in a least squares sense) with integrated measurements. Agreement between integrated and continuous techniques was classified as good or very good for particulate NO_3^- (Milwaukee and Mayville), for total nitrate (Milwaukee and Mayville), for total NH_3, and for particulate NH_4^+. For SO_4^{2-} and NH_3(g), agreement between integrated and continuous techniques was less favorable.

A simple episode classification scheme involving the moving average of the hourly $PM_{2.5}$ concentration was used to divide episode and non-episode periods. 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. The diurnal patterns for $PM_{2.5}$ at both sites were flat during episodes and non-episodes, with a slight (a few microgram per m^3) increase at Milwaukee during episodes at 08:00 a.m. Assuming that emissions are generally similar on a daily basis during this time of year, this suggests that large variations in $PM_{2.5}$ in Wisconsin are caused by synoptic disturbance rather than cyclical diurnal changes in boundary layer height and wind speed.

Mean concentrations during episodes, non-episodes, and during all hours were determined and compared. During episodes, total nitrate concentrations were increased by a factors of 2.1 and 2.6, respectively, at Milwaukee and Mayville compared to the all-study averages of nitrate. The study mean concentrations of nitrate were 6 and 5 µg m^{-3}, respectively, at Milwaukee and Mayville. Peak 1 h concentrations of $PM_{2.5}$ and nitrate reached 73 and 35 µg m^{-3}, respectively, at Milwaukee. The corresponding concentrations at Mayville were 63 and 27 µg m^{-3}, respectively. About 80 % of total nitrate existed in the aerosol phase at these sites, and 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 1.8–2.3. 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). The gas ratios in Milwaukee were higher than in Mayville (e.g. 3.1 vs. 2.2) during non-episodes. During episodes, the ordering remained the same, with the gas ratios at 1.5 (Milwaukee) and 1.2 (Mayville). The observation that total nitrate concentrations increased more than total ammonia during most episodes may be important to the understanding and control of the episodes.

Urban-rural contrasts in episode frequency and in concentrations were investigated. Episode frequency and severity were higher at the urban site. Episodes affecting both sites (as opposed to more local urban episodes) were associated with increases in the fraction of $PM_{2.5}$ from ammonium nitrate, while urban (Milwaukee) only episodes were characterized by the strongest enhancements in sulfate, EC, and OC. Urban excess was most prominent for NO_x, NO_y, OC, EC, and $PM_{2.5}$, while ozone was higher at the rural site.

The analysis of meteorological condition reveals that the initiation of all the episodes were characterized by

approaching high level ridge/surface low pressure system moving into the region. Compared to 1971–2000 climatology, the winter study period of 2009 featured considerable departures that include high snow fall in December with a colder, drier January and a warm February and March with unusually high precipitation. 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. Fog and snow cover were both correlated with episode intensity. Fog was typically due to melting and sublimation of snow cover. Fog accompanied events at Mayville more often than at Milwaukee. Regional snow cover was present over southeastern Wisconsin and northern Illinois at the onset of late winter episodes and usually melted by the end of the episode, contributing moisture to the shallow boundary layer. To better quantify the physical conditions during PM events in future studies, co-located photometer and ceilometer observations may be useful.

A key to understanding winter $PM_{2.5}$ in the Upper Midwest is a better understanding of the emission sources, chemical processes, and loss pathways responsible for total nitrate concentrations. The daytime and nighttime production rates of nitrate at Milwaukee and Mayville during the winter study period were estimated using known rate constants, observed O_3, and NO_2, and modeled OH concentrations. Estimates of nighttime and daytime nitrate production were of comparable magnitude for both Milwaukee and Mayville. However, the rates were generally higher in Milwaukee. These estimates, while uncertain, show that the nighttime pathway could contribute up to 50 % of the nitrate production in both locations, especially during the earlier (January/February) episodes.

The analysis regarding the thermodynamic sensitivity of episode concentrations to hypothetical changes in sulfate, nitrate, and ammonia concentrations (through thermodynamic box modeling), and to changes in SO_2, NO_x, and ammonia emissions (through 3-D chemical transport modeling) are ongoing and subject of a forthcoming publication.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/11037/2012/acp-12-11037-2012-supplement.pdf.

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