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

Phase II Report
Three Dimensional Modeling, Process Analysis and Emissions Sensitivity

Scott Spak[a]
Jaemeen Baek[a]
Jessica Carlson[a]
Gregory Carmichael[a]
Yoo Jung Kim[a]
Nicole Riemer[b]
Charles Stanier[a]

[a]University of Iowa
[a]University of Illinois

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Phase II Report: Three Dimensional Modeling, Process Analysis and Emissions Sensitivity

## Executive Summary

The Phase I report documented analysis of air-quality and meteorology measurements from the LADCO Winter Nitrate Study (WNS) to better understand wintertime episodes of elevated fine particle ($PM_{2.5}$) concentrations in the Midwest. The measurements were taken at Milwaukee (urban) and Mayville (rural) Wisconsin from 1 January - 31 March, 2009. Contemporaneous observations at an urban-rural pairing in Georgia were similarly assessed to understand reasons for regional differences in episode chemistry, aerosol speciation, and intensity. In Phase II of this project, simulations of the study period are performed using the Community Multiscale Air Quality model (CMAQ v. 4.7.1) and the CAMx model (v. 5.2) to answer the following questions:

**How well can models predict fine particle concentrations during observed episodes?** Overall, the level of model skill is judged to be sufficient for (a) understanding what contributes to episodes (after averaging over several modeled episodes); and (b) testing the impact of emission scenarios on average episode frequency and severity. Furthermore, the model is capable of simulating the occurrence (but not exact timing, duration, or severity) of most but not all episodes. Independent simulations for the same location and period conducted by the Wisconsin DNR and LADCO using the CAMx chemical transport model confirmed the main results of the University of Iowa study regarding prediction skill and emission sensitivity; it also highlighted the sensitivity of concentrations to meteorological model configuration.

Key species not simulated as well as others in the Iowa CMAQ implementation during episodes include organic carbon, nitrate, and ammonia (all were underpredicted). Gas species performance ranged from problematic performance (most notably for ammonia) to good or better performance for $NO_x$ and ozone. Comparison of modeled and measured enhancement ratios relative to that of $PM_{2.5}$ indicate that the model is underestimating secondary aerosol (nitrate, sulfate, and possibly SOA) in episodes.

**What processes control ground-level aerosol nitrate amounts?** CMAQ analysis indicates that the nighttime production pathway (involving $N_2O_5$ and wet aerosols or cloud droplets) exceeds the daytime pathway. Furthermore, conversion of $NO_x$ to nitrate (specifically to nitric acid) occurs at peak rates at elevations of 50-200 m above the surface, and over wide geographical areas. The consequence of this is that simulation of wintertime nitrate is difficult because it requires correct simulation of the daytime and nighttime pathways; the nighttime pathway has more chemical steps that have only been recently incorporated into air quality simulations.

**How effective are $NO_x$, $NH_3$, and $SO_2$ emission reductions on $PM_{2.5}$ concentrations?** For the upper Midwest, equal percentage reductions of $NH_3$ emissions and $NO_x$ emissions do not result in equal reductions in $PM_{2.5}$, and the spatial patterns of the reductions are also different. $NH_3$ emissions reductions lead to larger $PM_{2.5}$ reductions than the corresponding $NO_x$ controls by a factor of about four for Mayville and Milwaukee. $NO_x$ reduction leads to $PM_{2.5}$ reductions mainly west of the Mississippi in ammonia-rich regions. Ammonia controls are simulated to have reductions mainly east of the Mississippi river. These features (of $NO_x$ and $NH_3$ reductions) are predicted in both the CAMx and CMAQ model runs. The

higher effectiveness of $NH_3$ emission reductions is explained by the simulation result that $NH_3$ controls decrease total nitrate ($TNO_3$) in Southern Wisconsin more than the $NO_x$ controls. Pure $NO_x$ reductions cause small reductions in nitrate (up to 4% nitrate reduction from a 30% NOx reduction), offset by sulfate increases in some areas.

The simulated impact of a 2015 proxy emission scenario, designed to approximate near-term changes in mobile $NO_x$ and effects of the Cross-State Air Pollution Rule (CSAPR) on coal-fired power plant $NO_x$ and $SO_x$ emissions, is slightly less than that of 30 percent ammonia controls. If the sensitivity of further $NO_x$ and $NH_3$ emission reductions is assessed starting from a 2015 proxy emission, sensitivity of $PM_{2.5}$ to ammonia decreases slightly and the sensitivity to $NO_x$ controls is enhanced; however, ammonia reductions retain significantly more leverage on $PM_{2.5}$ than $NO_x$ reductions even after the reductions associated with the 2015 proxy case. These results are applicable to the upper Midwest and will vary in regions with different relative amounts of ammonia, nitrate and sulfate.

Localized reductions of both $NH_3$ and $NO_x$ were simulated. Reductions of $NH_3$ within 250 km and 60 km of Milwaukee are simulated to have 80 and 30 percent of the effect compared to domain-wide controls, respectively. Localized $NO_x$ controls have relatively small impacts on $PM_{2.5}$ and nitrate concentrations, due to a lack of sensitivity of total nitrate to local $NO_x$ reductions.

**What is the conceptual model of wintertime episodes?** Modeling and further analysis of episodes support the conceptual model that episodes are initiated by meteorological conditions, with episodes characterized by high-pressure systems that tend to persist longer than usual, creating stagnant conditions and often strong inversions that allow pollutant concentrations to build up. The atmospheric moisture and stagnant conditions may have important contributions from snow cover and snow melt, as many of the episodes occurred under conditions of snow cover, and many episodes ended with partial or complete snowmelt. Episodic increases in $PM_{2.5}$ concentrations often begin with a combination of transport of aerosols and their precursors, as well as localized production of nitrate and accumulation of local primary aerosols, particularly organic aerosols in urban locations. Episodes progress partially through widespread production of nitric acid aloft (peaking at elevations from 50-200 meters), with a significant contribution from nighttime chemical pathways. Episodes reach peak concentrations from a combination of transport and local accumulation of both primary and secondary species. Enhanced solar radiation over bright snow surfaces likely enhances OH, aerosol $NO_3$, and $SO_4$ concentrations during some episodes. Feedbacks involving ammonia, $NO_x$, and nitrate were identified by 3D modeling, which should be incorporated into the conceptual model.

**How can episode prediction and analysis be improved in the future?** A ranking of model aspects where future performance improvements would lead to improved $PM_{2.5}$ model skill highlights boundary layer meteorology and nitrate processes (chemistry, emissions, deposition and transport) for Milwaukee episodes prediction. For Mayville, nitrate processes and organic aerosols are thought to be areas where increases in model skill will best translate to increases skill in $PM_{2.5}$ episode prediction. Other areas of future emphasis should include measurements and modeling of boundary layer height, a greater range of $NO_y$ measurements, resolving and evaluating CMAQ predictions of other aerosols, and obtaining a greater range and higher time resolution of organic aerosol measurements. Improvements in the prediction of solar radiation intensity over snow, and in ammonia emissions and deposition are needed. High temperatures and high ammonia concentrations coincide with one another in the observations, and the association is only partially reproduced by models. This, coupled with the persistent model underprediction of ammonia and sensitivity of $PM_{2.5}$ to ammonia, provide a rationale for a future emphasis on ammonia.

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Phase II Report: Three Dimensional Modeling, Process Analysis and Emissions Sensitivity

## Technical Summary

The Phase I report documented detailed analysis of air-quality and meteorology measurements from the LADCO Winter Nitrate Study (WNS) to better understand wintertime episodes of elevated fine particle ($PM_{2.5}$) concentrations in the Midwest. The measurements were taken at Milwaukee (urban) and Mayville (rural) Wisconsin from 1 January - 31 March, 2009 and included high time resolution (hourly) measurements of important air quality variables related to wintertime episodes, including gas and particulate nitrate and ammonia. Contemporaneous observations at an urban-rural pairing of Southeastern Aerosol Research and Characterization (SEARCH) sites at Atlanta (Jefferson Street) and Yorkville, Georgia, were similarly assessed to understand reasons for regional differences in episode chemistry, aerosol speciation, and intensity.

In Phase II of this project, simulations of the study period are performed using the Community Multiscale Air Quality model (CMAQ v. 4.7.1) and meteorology from the Weather Research and Forecasting model (WRF ARW v. 3.3). The simulation utilizes a north central U.S. subdomain with 12 km resolution. Objectives of the simulations are to:

- Assess the capability of the CMAQ model in predicting fine particle concentrations at urban and rural locations during periods with observed episodes;
- Quantify the contribution of nitrate formation pathways and transport processes to particulate episodes;
- Estimate the efficacy of $NO_x$, $NH_3$, and $SO_2$ emission controls on reducing episode intensity, identify important emission sources during wintertime episodes, and determine whether they are local or a result of regional transport; and
- Refine the conceptual understanding of these episodes.

**How well can the CMAQ model predict fine particle concentrations during observed episodes?**
Overall, the level of model skill is judged to be sufficient for (a) understanding what contributes to episodes (after averaging over several modeled episodes); and (b) testing the impact of emission scenarios on average episode frequency and severity. Furthermore, the model is capable of simulating the

occurrence (but not exact timing, duration, or severity) of most but not all episodes. An independent set of simulations for the same location and period was conducted by the Wisconsin DNR (WRF meteorology) and LADCO (CAMx chemical transport model). This set of model runs had diurnal temperature profiles more closely matching observations, and showed overall similar model performance as the CMAQ model, with more instances of overprediction, less instances of underprediction, and an excessive (relative to observations) diurnal variation in $PM_{2.5}$.

A detailed assessment of CMAQ $PM_{2.5}$ performance shows appreciable skill in capturing observed synoptic scale variability. Average absolute concentrations and relative contributions are reproduced well by the model. Episodes are not as well predicted and (on average) show a negative bias (i.e.. underprediction). Key species not simulated as well as others during episodes include organic carbon (negative bias), nitrate (negative bias), and ammonia (negative bias). Gas species performance during episodes for Milwaukee was classified as problematic for $NH_3$ (large negative bias), excellent for $NO_x$ and $NO_y$, and average for $O_3$. For Mayville, $NH_3$ was problematic during episodes (negative bias), $O_3$ was good, and $NO_y$ and $SO_2$ showed average performance. EC predictions vary from unbiased to positively biased, which when coupled with negative bias for OC, lead to systematically low OC/EC ratios. Comparison of modeled and measured enhancement ratios relative to that of $PM_{2.5}$ tell a consistent story, that the model is underestimating secondary aerosol (nitrate, sulfate, and possibly SOA) in episodes. Despite the low ammonia prediction, the gas ratio prediction during episodes is only slightly low (due to offsetting negative bias in both sulfate and nitrate). Gas ratios are significantly underpredicted during non-episode periods (model at 1 to 1.5, and observations at 2 to 3).

As documented in the Phase I report, the Georgia episodes were fewer in number and severity, had low fractions of ammonium nitrate, and high fractions of organic aerosol. Episodes coincided with low wind early morning hours. The University of Iowa CMAQ simulation (at 36 km spatial resolution) for this period had some negative bias for predicting these episodes (model mean of 24.6 $\mu g\ m^{-3}$, observation mean of 29.7, and fractional bias of -0.23). For organic carbon, the principle enhanced species during the episodes, the performance statistics were not as good (model mean 5.3 $\mu g\ m^{-3}$, observed mean 11.6, and fractional bias -0.75). Underprediction of organic carbon during the episodes was the most important limiting factor for better episode prediction by CMAQ for the Georgia sites.

**What processes control ground-level aerosol nitrate amounts?**

Integrated process rate (IPR) analysis and integrated reaction rate analysis (IRR) show that aerosol nitrate at the surface is formed by a combination of chemical and transport processes. Nitric acid is produced 50-200 m above the surface and subsequently transported to the surface via vertical diffusion, where aerosol

nitrate is formed, and aerosol nitrate is then removed largely by dry deposition and transported upwards via vertical diffusion. The aerosol production rate is significantly higher for episode periods (by ~33 percent) and both daytime and nighttime chemical pathways are important. At Milwaukee near the ground the daytime formation pathway for nitric acid is larger than the nighttime pathways (0.08 ppb/h versus 0.04 ppb/h). Regarding the nighttime pathway, the heterogeneous hydrolysis reaction of $N_2O_5$ is found to exceed the homogeneous hydrolysis pathway by a factor of four. The importance of the daytime pathway decreases for higher altitudes. For Mayville, the relative magnitude of the nighttime pathways is larger than that of the daytime pathway, 0.10 ppb/h versus 0.04 ppb/h. The spatial distribution of aerosol nitrate formation is found to vary significantly spatially and on synoptic time scales.

**How effective are $NO_x$, $NH_3$, and $SO_2$ emission reductions on $PM_{2.5}$ concentrations?**

For the upper Midwest, equal percentage reductions of $NH_3$ emissions and $NO_x$ emissions do not result in equal reductions in $PM_{2.5}$, and the spatial patterns of the reductions are also different. $NH_3$ emissions reductions lead to larger $PM_{2.5}$ reductions (~5-12 percent over Milwaukee and Mayville) than the corresponding $NO_x$ controls (~1-3 percent). $NO_x$ reduction leads to $PM_{2.5}$ reductions mainly west of the Mississippi in ammonia-rich regions. Ammonia controls are simulated to have reductions mainly east of the Mississippi river. These features (of $NO_x$ and $NH_3$ reductions) are predicted in both the CAMx and CMAQ model runs. Assuming that the 3D-modeled fractional changes in total ammonia, total nitrate, and total sulfate are correct, the directly-modeled sensitivities are likely accurate for episodes in Southern Wisconsin, based on comparison of the observationally constrained and direct model sensitivities. The higher effectiveness of $NH_3$ emission reductions is due to the unanticipated result that domain-wide $NH_3$ controls decrease total nitrate ($TNO_3$) in Southern Wisconsin more than the $NO_x$ controls. Pure $NO_x$ reductions have a complicated impact on $PM_{2.5}$. The directly-modeled all-hours sensitivity is for a small decrease in $PM_{2.5}$ (up to 4 percent on average) in the more northern and western portions of the domain (which are ammonia-rich). A small $PM_{2.5}$ increase (mostly from sulfate) is modeled from a pure $NO_x$ reduction, and this occurs in the southern portion of the domain.

The simulated impact of a 2015 proxy emission scenario, designed to approximate near-term changes in mobile $NO_x$ and effects of the Cross-State Air Pollution Rule (CSAPR) on coal-fired power plant $NO_x$ and $SO_x$ emissions, is less than that of 30 percent ammonia controls, with episode inorganic $PM_{2.5}$ decreasing by 4-8 percent (a 2-5 percent decrease in total episode $PM_{2.5}$). Sulfate is a smaller contributor to episode concentrations. If the sensitivity of further $NO_x$ and $NH_3$ emission reductions is assessed starting from a 2015 proxy emission, sensitivity of $PM_{2.5}$ to ammonia decreases slightly and the sensitivity to $NO_x$ controls is enhanced; however, ammonia reductions retain significantly more leverage on $PM_{2.5}$ than $NO_x$ reductions even after the reductions associated with the 2015 proxy case. These results

are applicable to the upper Midwest and will vary in regions with different relative amounts of ammonia, nitrate and sulfate. The gas ratio is found to vary greatly across the region, and also to be a good predictor of the spatial variability in sensitivity to emission reductions.

Localized reductions of $NH_3$ are simulated to cause localized impacts on $PM_{2.5}$ that are relatively large and occur in the area of the $NH_3$ reduction. Reduction of $NH_3$ within 250 km of Milwaukee is simulated to have 80 percent of the effect as domain-wide controls, and reduction of $NH_3$ within 60 km of Milwaukee is simulated to have 30 percent of the effect as domain-wide controls. Localized $NO_x$ controls have relatively small impacts on $PM_{2.5}$ and nitrate concentrations, due to a lack of sensitivity of total nitrate to local $NO_x$ reductions. Based on comparison to an observationally-constrained method the CMAQ directly-modeled sensitivities are fairly skillful for the LADCO WNS study sites during episodes, but with some significant errors during other periods associated with errors in modeled gas ratio.

**What is the conceptual model of wintertime episodes?**

Modeling and further analysis of episodes support the conceptual model that episodes are initiated by synoptic meteorological conditions, with episodes characterized by high-pressure systems that tend to persist longer than usual, creating stagnant conditions and often strong inversions that allow pollutant concentrations to build up under the limited mixing height. The atmospheric moisture and stagnant conditions may have important contributions from snow cover and snow melt, as many of the episodes occurred under conditions of snow cover, and many episodes ended with partial or complete snowmelt. Episodic increases in $PM_{2.5}$ concentrations often begin with a combination of transport of aerosols and their precursors, as well as localized production of nitrate and accumulation of local primary aerosols, particularly organic aerosols in urban locations. Episodes progress partially through widespread production of nitric acid aloft (peaking at elevations from 50-200 meters), with a significant contribution from nighttime chemical pathways. Episodes reach peak concentrations from a combination of transport and local accumulation of both primary and secondary species. The transported component to the peak concentrations usually occurs when a surface low-pressure system disperses boundary layer aerosols in front of the incoming surface high, leading to surface-level transport of pollution toward the end of episodes. Enhanced actinic flux over high albedo (snow) surfaces likely enhances OH, aerosol $NO_3$, and $SO_4$ concentrations during some episodes, an effect not represented in CMAQ 4.7.1. Feedbacks were identified by 3D modeling, which should be incorporated into the conceptual model. Ammonia controls are simulated to decrease nitrate lifetime, and $NO_x$ controls are predicted to increase sulfate and (especially locally near NO sources) increase ozone. Additional feedbacks involving other factors such as aerosol pH and size distribution, have not yet been investigated, but may exist.

A ranking of model aspects where future performance improvements would lead to improved $PM_{2.5}$ model skill of the U of I CMAQ implementation based on analysis of model bias and sensitivities shows the following:

- Milwaukee (all hours and episodes): boundary layer meteorology > nitrate/$NO_y$ chemistry, emissions, deposition and transport > organic aerosols > ammonia > sulfate
- Mayville (all hours): organic aerosols > nitrate/$NO_y$ chemistry, emissions, deposition and transport > sulfate > ammonia > boundary layer meteorology.
- Mayville (episode hours): nitrate/$NO_y$ chemistry, emissions, deposition and transport > organic aerosols ~ sulfate > ammonia ~ boundary layer meteorology

Reducing the uncertainty in these processes requires both additional observations and model improvements. Future observational studies would benefit from adding measurement of the boundary layer evolution through co-located instrumentation such as LiDAR, ceilometer, or SODAR. Measurements of a greater range of compounds in the $NO_y$ system, including elevated measurements, would be useful constraints, including OH, $HO_2$, $N_2O_5$, $NO_3$ radical and HONO. Organic species have a large contribution to episodes, particularly at the urban location, and measurements suitable for source apportionment of OC would aid in further advancing the conceptual model. Modeling indicates a large contribution of "other" modeled primary aerosol mass during episodes, and time-resolved measurements of metals and a wider range of cations would help quantify this contribution to episodes and test the models representation of "other PM" sources, such as road and agricultural dust. Progress in forecasting and simulation lies in improved boundary layer prediction, changes in photolysis modules, $NH_3$ fluxes (net emissions and bi-directional deposition), and data assimilation of meteorological variables. High temperatures and high ammonia concentrations coincide with one another in the observations, and the association is only partially reproduced by models; we anticipate that high time resolution meteorology and ammonia measurements can be used in the future to evaluate enhanced ammonia modeling algorithms. Further model refinements of nitrate formation pathways and the role of organics in episodes, informed by measurements, are also needed.