Episodic Air Pollution in Wisconsin (LADCO Winter Nitrate Study) and Georgia (SEARCH Network) during January-March 2009

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Phase I Report

Executive Summary

Analysis of air quality and meteorology measurements obtained during the LADCO Winter Nitrate Study (WNS) was performed in order to better understand wintertime episodes of elevated fine particle ($PM_{2.5}$) concentrations in the Midwest. The analysis evaluated and compared 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. Contemporaneous observations at an urban-rural pairing of Southeastern Aerosol Research and Characterization (SEARCH) sites at Atlanta (Jefferson St.) and Yorkville, Georgia were similarly assessed to understand reasons for regional differences in episode chemistry, aerosol speciation, and intensity.

Refined conceptual model of wintertime nitrate PM episodes: The observations support a refinement of the current episode conceptual model. Wintertime fine particle episodes in the Upper Midwest occur when low pressure systems move into the region, and are marked by a shallow, stable planetary boundary layer, with increases in temperature and relative humidity, light southerly winds, and cloud cover. Strong late-season episodes occur in the presence of regional snow cover at temperatures near freezing, when snow melt and sublimation generate fog and strengthen the boundary layer inversion. These meteorological conditions alone raise concentrations of locally-emitted primary pollutants in urban areas to more than double seasonal background levels, and lead to further increases in the concentrations of secondary nitrate and ammonium aerosols due to preferential partitioning to the aerosol phase and ongoing conversion of NOx to nitrate during episodes. The rural response to episode meteorology is marked by less enhancement of primary pollutants due to lower local emissions, and by greater fractional contributions of ammonium nitrate. Nitrate, NOx for further nitrate production, and ammonia seem to be present in sufficient quantities so that these are not limiting; therefore, substantial $PM_{2.5}$ concentration increases are likely to ensue each time the required meteorological conditions occur. However, total ammonia and total nitrate (and, by extension, NOx) influence episode intensity. Controls of ammonia or nitrate are likely to decrease episode concentrations. Substantial contribution to nitrate production from nighttime chemistry of ozone and NO_2 to N_2O_5 and nitric acid is likely and can be investigated through

modeling of the field data. The refined conceptual model should probably include a decrease in ammonia availability as ammonium nitrate episodes progress to higher $PM_{2.5}$ concentrations. Confirmation of this shift would require corroboration by additional measurements, but the current evidence includes the two sites in the current study and multiple sites in a previous independent analysis of the Midwest Ammonia Monitoring network data. Finally, contribution of local urban emissions, particularly of organic aerosols from combustion, is important in urban locations and control of these emissions would decrease the urban excess that is observed.

The largest remaining uncertainties in the conceptual model are the variability from episode-to-episode in ammonia emissions, the balance of daytime and nighttime nitrate production, the relationship between NOx controls and 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 meteorological causes.

Additional policy-relevant findings include:

Episodes in Wisconsin showed strong enhancements in both primary and secondary aerosol compounds. The increase in $PM_{2.5}$ over typical conditions was due primarily to secondary nitrate and ammonium, which increased by a factor of 2-3 as a result of production and accumulation of nitrate together with preferential partitioning of nitrate and ammonia to the aerosol phase at low temperatures and high humidity. Increases in sulfate (factors of 2.2-2.9), organic carbon (factors of 1.4-1.7), and elemental carbon (factors of 1.9-2.0) were also noted. Analysis of nine years of organic carbon filters from the Wisconsin sites confirms the conceptual view that increases in wintertime organic carbon concentrations are from primary and not secondary sources.

There are significant differences in wintertime $PM_{2.5}$ episode frequency and chemical composition between urban and rural sites, and between Wisconsin and Georgia. Total $PM_{2.5}$ mass increased more during episodes at Mayville than at Milwaukee, but peak and average episode concentrations were higher at Milwaukee. All seven episodes at Mayville were coincident with episodes at Milwaukee, but Milwaukee also had six additional local late-winter episodes. Nitrate increased more at Milwaukee, near local sources, while ammonium increased more at Mayville. Preliminary analyses indicate that local sources of NOx (e.g., nearby highways) are important at Milwaukee, and regional sources of ammonia affect both Milwaukee and Mayville. Episode enhancements in $PM_{2.5}$ at the urban site in Georgia were as strong as in Milwaukee, but were less frequent during the study period. Episodes at both Georgia sites were due primarily to increases in organic matter, without such strong enhancements in other aerosol species.

Fine particle episodes during the WNS all began under similar synoptic conditions, with the arrival of a surface low pressure system. Episodes were marked by inversions with warm, moist air and low wind speeds. Snow cover and fog caused by sublimation of snow pack were both correlated with episode intensity; 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. Accurate predictions of boundary layer height, lapse rate, and surface wind speed are important for forecasting wintertime episode intensity.

Wintertime fine particle events in the upper Midwest vary year-by-year. The frequency, severity, and spatial extent of episodic $PM_{2.5}$ particle pollution in the upper Midwest varies from one year to the next depending on meteorology. Conditions (and episodes) during the Jan-Mar 2009 WNS were found to be above normal based on data for the period 2001-2009. Areas affected by wintertime $PM_{2.5}$ episodes include eastern Iowa, southeastern Minnesota, northern Illinois, and much of Wisconsin. (Note, the study did not examine wintertime events east of Lake Michigan.)

Several nitrate production pathways were important during episodes, and the thermodynamic sensitivity of episodes indicated that the importance of changes in ammonia and nitrate was affected by sulfate levels. During Wisconsin episodes, ammonium nitrate concentrations increased from a combination of stagnant inversion conditions, a shift in partitioning toward the condensed phase, and continued chemical production of nitric acid from NO_x. Preliminary analysis of potential nitrate production pathways and nitrate and ozone diurnal patterns were consistent with nitrate from both nighttime (O_3) and daytime (OH) pathways. Decreased solar insolation and decreased ozone during episodes, together with high RH and frequent fog, suggest that aqueous and heterogeneous pathways of aerosol production are as important (or more) than photochemical pathways during episodes. Thermodynamic sensitivity analysis found episodes sensitive to either ammonia or nitrate reductions. However, sensitivity was found to be different, especially at Mayville, during episode conditions than during average conditions, with a decrease in ammonia availability. This result was consistent with a reanalysis of previous thermodynamic sensitivity studies in the Upper Midwest. The relative effect of nitrate and ammonia on $PM_{2.5}$ was sensitive to sulfate levels. Decreases in sulfate (or nitrate) associated with ongoing implementation of the Clean Air Act decreased sensitivity of $PM_{2.5}$ levels to ammonia, and increased sensitivity to nitrate. In contrast, episodes in Georgia were associated with early morning $PM_{2.5}$ peaks, with organic carbon as the most prominent species leading to the buildup.

In Phase II, atmospheric chemical transport modeling with CMAQ and CAMx will be used to confirm these findings from a process-based perspective, and to:

- Identify important emission sources during wintertime episodes and determine whether they are local or a result of regional transport;
- Quantify the contributions of thermodynamic processes impacting $PM_{2.5}$ levels and their rural-urban gradients
- Determine the degree to which photochemical models can accurately predict $PM_{2.5}$ concentrations during observed wintertime episodes; and
- Understand how specific daytime and nighttime photochemical pathways contribute to nitrate formation