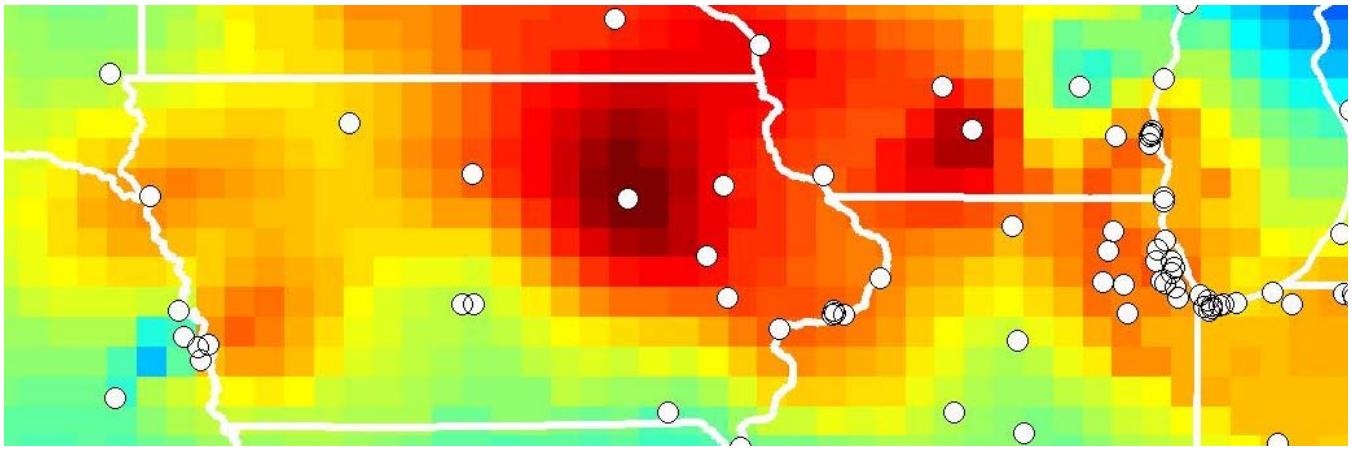
Understanding Episodes of High Airborne Particulate Matter in Iowa



Center for Global and Regional Environmental Research at the University of Iowa
Charles Stanier, Editor

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A report commissioned by the Bi-State State Regional Commission (www.bistateonline.org)

Alex Bender[1]
Gregory Carmichael[1,2]
Adam Beranek-Collins[1]
Morgan E. Brown[2]
Tracey Holloway[3]
Aditsuda Jamroensan[2]
Sang Rin Lee[2,5]
Pallavi Marrapu[1,2]
Alicia Pettibone[1],
Sinan Sousan[1,2]
Scott Spak[2,3,4]
Charles Stanier[1,2,5]

[1] Department of Chemical & Biochemical Engineering, University of Iowa
[2] Center for Global & Regional Environmental Research, University of Iowa
[3] Center for Sustainability and the Global Environment (SAGE), Nelson Institute for Environmental Studies, University of Wisconsin – Madison
[4] Department of Atmospheric & Oceanic Sciences, University of Wisconsin – Madison
[5] IIHR- Hydroscience & Engineering, University of Iowa

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available online at

http://www.engineering.uiowa.edu/~cs_proj/iowa_pm_project/iowa_pm.htm

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Understanding Episodes of High Airborne Particulate Matter in Iowa

by Alex Bender[1], Gregory Carmichael[1,2], Adam Beranek-Collins[1], Morgan Brown[2], Aditsuda Jamroensan[2], Tracey Holloway[3], Sang Rin Lee[2,5], Pallavi Marrapu[1,2], Alicia Pettibone[1], Scott Spak[2,3,4], Sinan Sousan[1,2], and Charles Stanier[1,2,5]

[1]Department of Chemical & Biochemical Engineering, University of Iowa
[2]Center for Global & Regional Environmental Research, University of Iowa
[3]Center for Sustainability and the Global Environment (SAGE), Nelson Institute for Environmental Studies, University of Wisconsin – Madison
[4]Department of Atmospheric & Oceanic Sciences, University of Wisconsin – Madison
[5]IIHR- Hydroscience & Engineering, University of Iowa

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EXECUTIVE SUMMARY

Introduction. The 2006 United States standard for particulate matter smaller than 2.5 microns ($PM_{2.5}$) under the Clean Air Act is 35 micrograms per cubic meter of air ($\mu g\ m^{-3}$) taken over a 24 hour average. This standard was a revision of a previous standard of 65 $\mu g\ m^{-3}$. Many locations around the country were in compliance with the earlier 65 $\mu g\ m^{-3}$ limit, but not with the new value of 35 $\mu g\ m^{-3}$. The rationale for the standard is for the protection of human health, especially sensitive individuals such as the elderly, infants, and those with cardiovascular and respiratory disease.

Two $PM_{2.5}$ monitors in the state of Iowa have 2005-2007 values that are above the 35 $\mu g\ m^{-3}$ attainment threshold (Scott Country/Davenport Wellman St., and Muscatine's Garfield School). Furthermore, many other Eastern Iowa monitors are just below the standard. While it is widely accepted that pollution levels at individual sites are the combination of regional episodic processes, urban scale pollution, and local source impacts, an in depth investigation of these elements for Iowa sites was desired as part of overall efforts to deal with $PM_{2.5}$ levels at or near the 35 $\mu g\ m^{-3}$ threshold.

Final attainment or nonattainment status will be heavily influenced by 2006-2008 monitoring data (which has the two sites in question below the attainment threshold). However, the objectives and results of this work are applicable regardless of attainment status. Furthermore, as the report shows, unless ongoing decreases are achieved in the contributing impact categories identified herein, future years of non-attainment are likely

Objectives. The University of Iowa was contracted by the Bi-State Regional Commission to (1) review published reports and papers on the topic of wintertime Midwestern particulate matter formation; (2) analyze available $PM_{2.5}$ monitoring data; (3) analyze meteorological conditions

associated with episodes; (4) separately analyze local episodes (those at single monitors) and regional episodes (those at multiple monitors); and (5) discuss scientific uncertainties regarding wintertime PM formation and its prediction in air quality models.

Results.

Episode Occurrence and Frequency

- An analysis of the available peer-reviewed literature on Midwestern particulate matter formation, and an analysis of seven years of Iowa and Midwestern meteorological and particulate matter monitoring data, reaffirms the conceptual model for Midwestern PM discussed in the literature. Multi-day episodes of elevated $PM_{2.5}$ levels are an important factor in air quality, especially when considering peak concentrations as the 24-hour average $PM_{2.5}$ regulations do.

- PM episodes occur during both warm and cold seasons. The warm and cold weather episodes are important to attainment/nonattainment of both the annual and daily $PM_{2.5}$ standards. For the period 2002-2008, the cold weather episodes had a small edge in both number and severity.

- Depending on the surrounding land use, population density, and level of industrialization, each monitor is additionally impacted by locally emitted primary particulate matter. At the Muscatine and Davenport Wellman St. locations, the local impacts are severe enough to add to the regional background at levels sufficient to cause nonattainment with the 35 $\mu g\ m^{-3}$ standard during some years.

- A comprehensive list of 44 regional PM episodes (with $PM_{2.5}$ elevated for at least three Iowa monitors) was created for the years January 2002 – July 2008, along with a companion list of non-regional episodes. Detailed time series of pollution levels and meteorological variables were created and are available in appendices to the main report. A time series of daily $PM_{2.5}$ values for the period January 2002 – July 2008 was created from the median of Eastern Iowa monitors. This Eastern Iowa median concentration is useful for evaluating local impacts relative to a regional background value.

- Statistical analysis shows that regional episodes in excess of 35 $\mu g\ m^{-3}$ are unlikely to put monitors in Eastern Iowa into noncompliance unless they experience additional impact from local sources. The accuracy of this conclusion is predicated on the assumption that the period 2002-2008 is representative of future conditions.

Episode Chemistry and Meteorology

- Analysis of speciated $PM_{2.5}$ data during episode and non-episode periods confirms a major role for ammonium nitrate during wintertime episodes, with nitrate rising to ~45% by mass of the total $PM_{2.5}$. During episodes, concentrations of all species increase, but the increase is strongest for ammonium nitrate.

- There is insufficient evidence to definitively mark either nitric acid or ammonia as limiting during wintertime episodes. The best available studies to date have the sensitivity of ammonium nitrate concentrations balanced between the influences of ammonia and nitric acid in Iowa during wintertime. There is likely variability from place-to-place within Iowa and from episode-to-episode on which compound is more limiting to aerosol formation.

- Nitric acid from the NO_3 radical and N_2O_5 is likely to be important in Iowa in winter. The kinetics of this process are uncertain.

- One area of interest for this study was the relationship between $PM_{2.5}$ ammonium nitrate episodes and fog. The literature review identified one paper that studied this relationship; in that study, fog was found NOT to be a contributor.

- Cold weather regional episodes generally occur on the back end of a warm front. Signature meteorological trends during high $PM_{2.5}$ events are a sudden change in wind direction (to be predominately easterly in flow), pressure decrease, rising temperature, dew point, and relative humidity, and a decrease in wind speed.

Model Performance During Episodes

- Two episodes in 2002 were compared to their corresponding model predictions from a regional implementation of the CMAQ air quality model. Even though this model was not configured for urban scale predictions, the model reproduced the episodes fairly well. Spatial patterns of total $PM_{2.5}$ and nitrate, as well as temporal patterns agree fairly well. The model showed high bias during some periods (predicting too high a concentration), for example sometimes predicting > 40 $\mu g\ m^{-3}$ on an hourly basis when less than 10 $\mu g\ m^{-3}$ were registered by the monitor. However, the agreement is sufficient to explore control scenarios for reducing average and peak daily concentrations. If combined with observations of inorganic aerosol speciation, accurate scenarios for reducing PM through NOx and or ammonia controls could be developed.

Quantification of Local Source Impacts

- At the Davenport Wellman St. monitor, conditional probability analysis of hourly wind direction vs. hourly $PM_{2.5}$ showed a strong local impact when the wind was from 210 degrees. This bearing is consistent with what would be expected from emissions from Blackhawk Foundry, which is located approximately 400 meters from the monitor. The magnitude of the conditional probability function is that 20% of hours with wind from 210° have $PM_{2.5}$ values of 30 μg m^{-3} or more above the estimated regional background level. Analysis of the hourly $PM_{2.5}$ readings shows that daily peaks (in hourly $PM_{2.5}$) in excess of 50 μg m^{-3}, and sometimes in excess of 100 μg m^{-3}, are not uncommon; they occur most frequently in morning or midday. Regression analysis of hourly wind direction vs. daily $PM_{2.5}$ levels gives a similar result, with evidence of a local source when wind blows from between 160 and 260 degrees. At the most impacted direction (220 degrees) the average increment over background is 10 μg m^{-3} over a 24 hour period.

- Statistical sampling of attainment vs. nonattainment probabilities at the Davenport Wellman St. monitor puts a **preliminary estimate** of future attainment at 25% under the status quo, and at 81% under elimination of the above background PM that is coming from the 160 to 260 degree direction. The confidence of this preliminary estimate is low because the lack of definitive source apportionment data for the site.

- At the Muscatine monitor, regression analysis of hourly wind direction vs. daily $PM_{2.5}$ levels indicates a strong source impact when wind blows from between 60 and 130 degrees, with the strongest impact at 100-110 degrees. This direction is consistent with the local impact originating from Grain Processing Corp. At the most impacted direction, the average increment over background was 25 μg m^{-3} over a 24 hour period.

- Statistical sampling of attainment vs. nonattainment probabilities at the Muscatine monitor puts a **preliminary estimate** of future attainment at 43% under the status quo, and at 98% under complete control of the above background PM that is coming from the 60 to 130° direction. The confidence of this preliminary estimate is low because of the lack of definitive source apportionment data for the site.

- Evidence of significant local source impacts at other locations was not found, with the exception of a moderately large impact at Clinton (23rd and Camanche) when wind blew from the south (150 to 230°). The average magnitude of this source, as determined by similar regression analysis to that used at Muscatine and Davenport Wellman St., was 20 μg m^{-3} over background levels for a 24 hour stable south wind. This impact is consistent with the local impact originating from the nearby ADM corn processing facility.

Recommendations

- Additional data analysis of speciated $PM_{2.5}$ data from the Midwest ammonia monitoring project is warranted, in concert with thermodynamic partitioning computer modeling in use at the University of Iowa, to determine whether nitric acid or ammonia is limiting during episodes.

- A modest program of regional air quality modeling is warranted to investigate the spatial scales for effective control of SO_2, NOx and ammonia. Special focus would be given to the relative impacts of county-specific emissions, as compared to more broad Iowa/Illinois Mississippi river corridor emissions, and to emissions from more distant locations.

- The State of Iowa, and the stakeholders for air quality in Iowa and the Quad Cities, should take a proactive stance toward further understanding the relative contributions of various air pollution sources to episodes both from a geographical standpoint (where would source controls be effective at reducing episodes), and from a source apportionment standpoint (what source categories should be controlled). A three part effort is recommended: (a) pilot study source apportionment in winter 2010; (b) program of collection and storage of filters for later analysis of episode PM chemistry; and (c) <u>if needed</u> for future air quality management decisions, analysis of the archived filters from b during baseline or episode periods. This would be a cost effective and proactive stance which would be especially important should the EPA lower the annual $PM_{2.5}$ standard to less than 15 $\mu g\ m^{-3}$, or lower the 24-hour standard below 35 $\mu g\ m^{-3}$.

Full report available online at

http://www.engineering.uiowa.edu/~cs_proj/iowa_pm_project/iowa_pm.htm

Direct questions and comments to charles-stanier@uiowa.edu

1.0 INTRODUCTION

Particulate matter smaller than 2.5 microns in diameter is a regulated air pollutant in the United States. Abbreviated as $PM_{2.5}$, the size designation separates $PM_{2.5}$ from larger "coarse" particles. $PM_{2.5}$ particles are small enough to enter the lung; most larger particles are retained in the upper airways such as the nose and throat. Major sources of $PM_{2.5}$ include *primary* sources, where particles are emitted directly to the atmosphere (smoke, vehicle exhaust, dust, sea salt), and *secondary* sources where the particulate matter (PM) is formed in the air from chemical reactions. Major secondary PM types include ammonium sulfate, ammonium nitrate, and secondary organic aerosol. All three are important components of $PM_{2.5}$ in the Midwest.

The 2006 United States $PM_{2.5}$ standard under the Clean Air Act has two separate limits for $PM_{2.5}$. There is a short term limit, which applies to concentrations averaged over 24 hour periods [35 micrograms per cubic meter of air ($\mu g\ m^{-3}$)]. There is also a limit on the annual average concentration (15 $\mu g\ m^{-3}$). This work deals almost entirely with the short term standard, also called the daily limit or 24-hour average standard. The limit of 35 $\mu g\ m^{-3}$ was a revision of a previous standard of 65 $\mu g\ m^{-3}$. Many locations around the country were in compliance with the earlier 65 $\mu g\ m^{-3}$ limit, but not with the new value of 35 $\mu g\ m^{-3}$. The annual average standard was not revised in 2006, but rather remained at 15 $\mu g\ m^{-3}$. The rationale for the standard is for the protection of human health, especially of sensitive individuals such as the elderly, infants, and those with cardiovascular and respiratory disease. Figure 1-1 shows areas that are were classified as nonattainment based on 2005-2007 monitoring data.

Immediate health implications of PM exposure include decreased respiratory and lung functions, as well as aggravating asthma conditions. Long term exposure to fine particulate matter can lead to chronic bronchitis, heart attacks, and premature death in people with heart or lung disease (EPA 2008). Smaller particles yield more serious health implications (than larger particles) because they are more likely to become deeply embedded in the lungs as well as enter the blood stream (EPA 2008).

Attainment or nonattainment within the Clean Air Act is determined by the measured concentration at air quality monitoring stations. The Iowa DNR measures $PM_{2.5}$ concentrations at a number of locations around the state, and attainment or nonattainment of the Clean Air Act standards is determined by averaging the 98th percentile concentrations over the past three years (e.g. 2005, 2006 and 2007). For monitors with a full complement of 365 daily samples, the 98th

percentile rule means that the 8th highest value in a given year determines attainment. Detailed discussion of the procedure for determining compliance can be found in section 2.

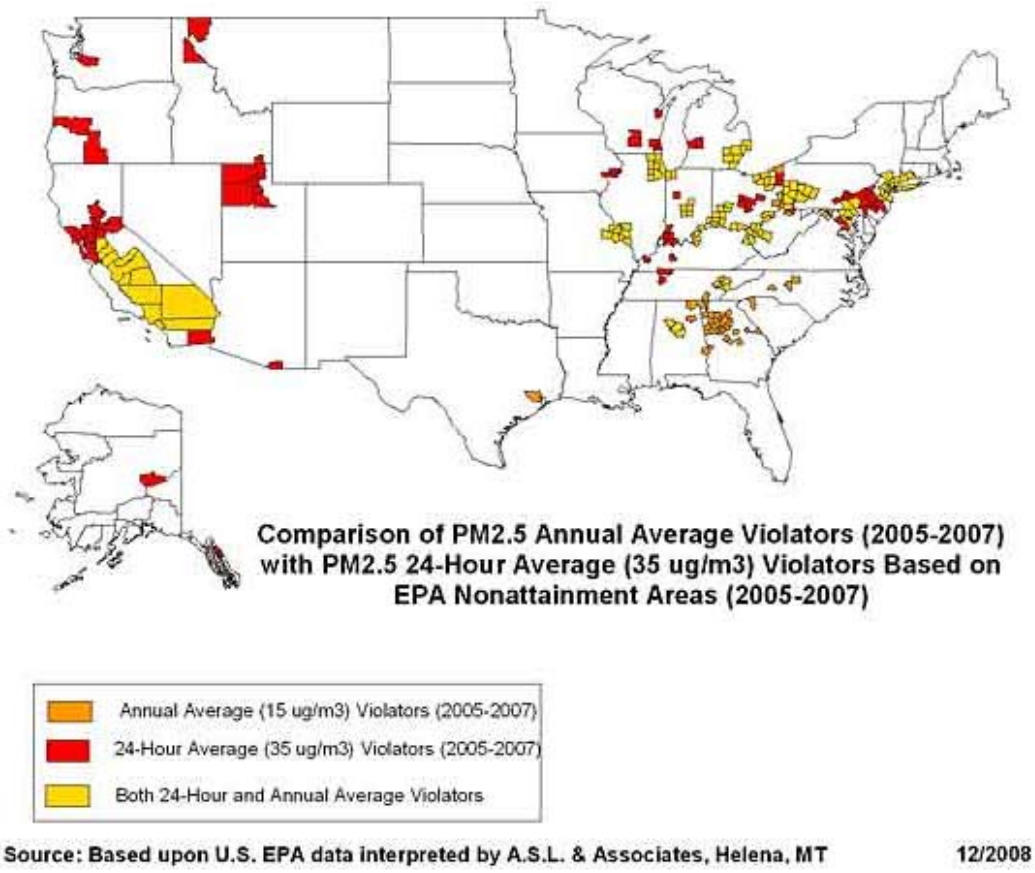

Figure 1-1. $PM_{2.5}$ Nonattainment areas based on 2005-2007 monitoring data. Red areas are mostly areas that were previously in compliance with the $PM_{2.5}$ standards. Scott and Muscatine counties in Iowa were affected. Midwestern areas with similar sitations include areas in Wisconsin (Madison, Appleton, and Milwaukee), Michigan (Grand Rapids), and Indiana (Evansville).

Used with permission. Source: A.S.L. & Associates © 2008, asl-associates.com/map.htm

Two $PM_{2.5}$ monitors in the state of Iowa have 2005-2007 values that are above the 35 μg m^{-3} attainment threshold (Scott Country/Davenport Blackhawk Foundry, and Muscatine's Garfield School). The proposed nonattainment boundaries for these counties are shown in figure 1-2 and 1-3. These were based on 2005-2007 monitoring data. Also proposed by the EPA as nonattainment areas were portions of Rock Island County (including the townships of Black

Hawk, Coal Valley, Hampton, Moline, Rock Island, South Moline and South Rock Island).[1] The latest attainment status is based on 2006-2008 monitoring data, and the Iowa monitors will be in attainment based on 2006-2008 monitoring data (Fitzsimmons 2009). This report is not intended to focus on the regulatory status and regulatory process that IDNR, EPA and the counties have been going through in 2008 and 2009. This report is intended to investigate the general causes of high (greater than 30 μg m^{-3}) levels. However, for readers interested in the detailed regulatory process, several regulatory-related documents have been placed in an appendix. The Bi-state Regional Commission and IDNR can provide significant additional materials along these lines.

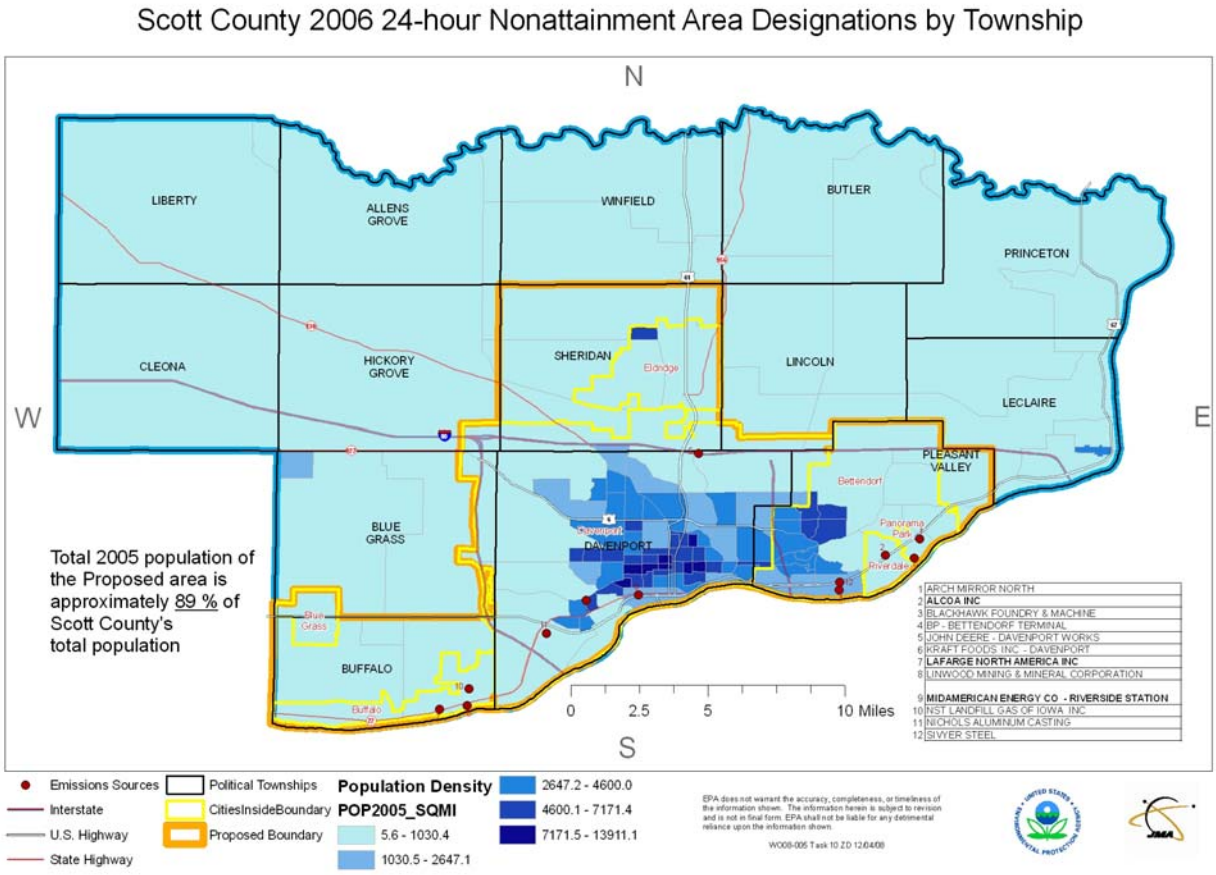

Figure 1-2. $PM_{2.5}$ Nonattainment Proposed by EPA for Scott County

[1] Source: IDNR Press Release, Dec 22 – see appendix K

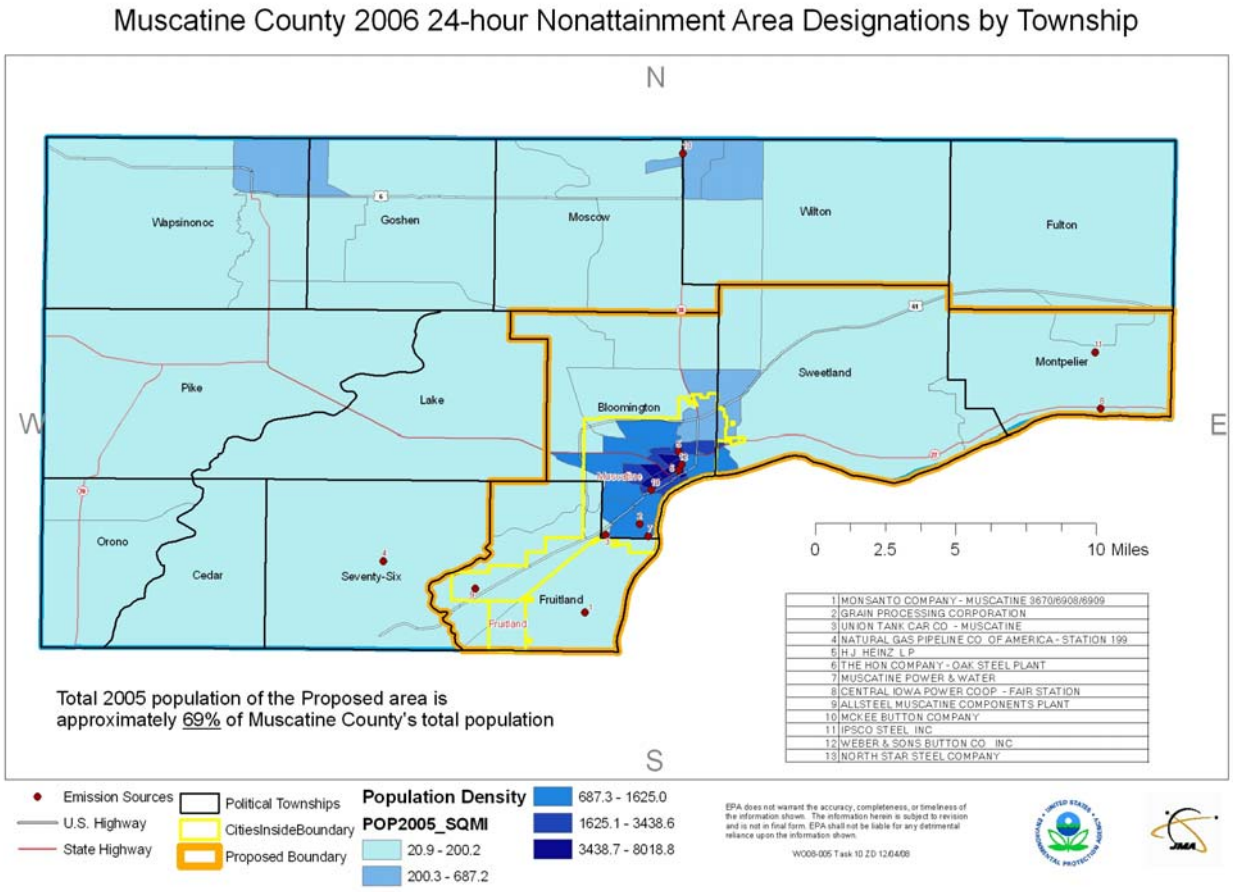

Figure 1-3. $PM_{2.5}$ Nonattainment Proposed by EPA for Muscatine County

As this report shows, high $PM_{2.5}$ levels have two distinct causes. One cause is local emissions of primary $PM_{2.5}$. The other cause is geographically widespread elevations in $PM_{2.5}$ concentrations, usually with a high contribution from secondary PM. This report refers to these as *regional episodes*. While year-to-year variability is large with respect to regional $PM_{2.5}$ episodes, an average year has approximately 3-4 cold season episodes, typically from November to March, where multiple Iowa monitors are above 30 μg m^{-3}. Usually 1-3 of these events have multiple monitors exceeding 35 μg m^{-3}. These episodes have lasted anywhere from 1 to 5 days. One of the longest lasting episodes was for 5 days beginning January 30, 2005. The most polluted episode was a 3 day event in December 2007 with concentrations at more than 4 sites in excess of 55 μg m^{-3}. Summertime 24 hour air quality standard exceedance events also occur, but with somewhat less impact to $PM_{2.5}$ nonattainment during 2005-2007.

According to published literature on $PM_{2.5}$ episodes, meteorology conditions and transport of agricultural NH_3 and nitric acid derived from nitrogen oxides (from combustion) serve as a major contribution for secondary ammonium nitrates throughout the Midwest. In the upper Midwest, some researchers argue that wintertime urban areas are generally most heavily impacted by ammonia transport from rural areas (Lee and Hopke 2006); however, NOx emissions from large cities may drastically increase this effect in the winter (Zhao, Hopke et al. 2007).

Public health, visibility, and economic development are all influenced by these geographically widespread episodes and their leverage on the air quality compliance. Due to the significant contribution from regional sources, multisite episodes cannot be addressed by individual site-specific control measures alone, but require a broad regional control strategy, sometimes aimed at multiple types of pollutants that contribute to $PM_{2.5}$. Good understanding of the sources and particulate matter formation processes that contribute to the episodes is required in order to formulate effective control strategies. Accordingly, a central question for this study is, "how likely is it that a string of winters with above average PM episodes could put large portions of Eastern Iowa out of Clean Air Act compliance?" Some key urban monitor values that show the importance of regional formation events during 2005-2007 are Iowa City, Clinton, Cedar Rapids, and Davenport, with $\mu g\ m^{-3}$ values of 34, 32, 29, and 32 respectively.

The University of Iowa, primarily through the Center for Global and Regional Environmental Research, has a long record of research in particulate pollution and atmospheric science. Helping to solve problems of state priority (such as regional PM exceedances) is part of the core mission of the University and its research centers and faculty members. Therefore, in the fall of 2008, researcher Charles Stanier (a member of the Center for Global and Regional Environmental Research) contracted with the Bistate Regional Commission (http://www.bistateonline.org/index_ns.shtml) to study PM episodes in Iowa. The objectives of this phase of the study were to:

- Review published reports and papers on cold season Midwestern PM episodes.
- Analyze $PM_{2.5}$ data from 2002 through September 2008.
- Analyze $PM_{2.5}$ speciated data from 2002 through September 2008.
- Analyze meteorological conditions favorable for $PM_{2.5}$ episodes.
- Discuss local vs. regional episodes.
- Discuss scientific uncertainties in $PM_{2.5}$ formation.

Section 2 of this report lays out some of the methods and data sources used within the project.

Section 2 also includes some photographs of sites of interest within the report. Section 3 includes an explanation of how the ammonia-sulfate-nitric acid-water aerosol system works, a literature review regarding Midwestern PM formation, and a conceptual model of the processes at work determining the concentration at a given monitor. Section 4 contains the main data analysis of $PM_{2.5}$ mass data. Section 5 presents some results on the chemically resolved, or "speciated" data collected by IDNR and EPA. A discussion of event meteorology for the regional events can be found in section 6. Section 7 presents our results on separating monitor PM loadings into regional and local source contributions. Section 8 contains our analysis of the skill of a 3D air quality model (a sophisticated computer simulation) at representing the cold weather PM formation events. Section 9 contains discussion of some of the points in the previous section, and conclusions.

An extensive set of appendices has been prepared. The appendices include the relevant site lists, episode lists, photographs, time series plots, meteorology plots, model results. The review process that this report has undergone is also described in the appendix. Questions and comments about this report should be addressed to the corresponding author and editor, Charles Stanier, charles-stanier@uiowa.edu, 319-335-1399. The report and appendices are available at http://www.engineering.uiowa.edu/~cs_proj/iowa_pm_project/iowa_pm.htm after registration. Users are encouraged to register to receive update notifications from the University of Iowa on issues surrounding Midwestern $PM_{2.5}$, such as revisions to this work, to appendices, or future publications on the topic. Register by emailing charles-stanier@uiowa.edu.

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EPA. (2008). "Particulate Matter, Health and Evironment." Retrieved December 8, 2008.

Fitzsimmons, S. (2009). 2008 PM2.5 Design Values. Stanier.

Lee, J. H. and P. K. Hopke (2006). "Apportioning sources of PM2.5 in St. Louis, MO using speciation trends network data." Atmospheric Environment **40**: S360-S377.

Zhao, W., P. K. Hopke, et al. (2007). "Spatial distribution of source location for particulate nitrate and sulfate in the upper-midwestern United States." Atmospheric Environment **41**: 16.

2.0 METHODS

Descriptions of data sources, data analysis methods, and geographical domain of study

2.1 Geographical Domain. The main geographical unit of interest for this study is that of Eastern Iowa. However, since particulate matter pollution extends over a broader region, the boundaries for mapping and data analysis in this work will extend to approximately St. Louis in the south, Chicago in the east, Minneapolis in the North, and Omaha in the West.

The latitude and longitude parameters that define our domain are as follows: southern boundary is 37.35 north; northern boundary is 45.5 north; eastern boundary is -86.5; eastern boundary is -97.7. This region is shown as a map in figure 2-1.

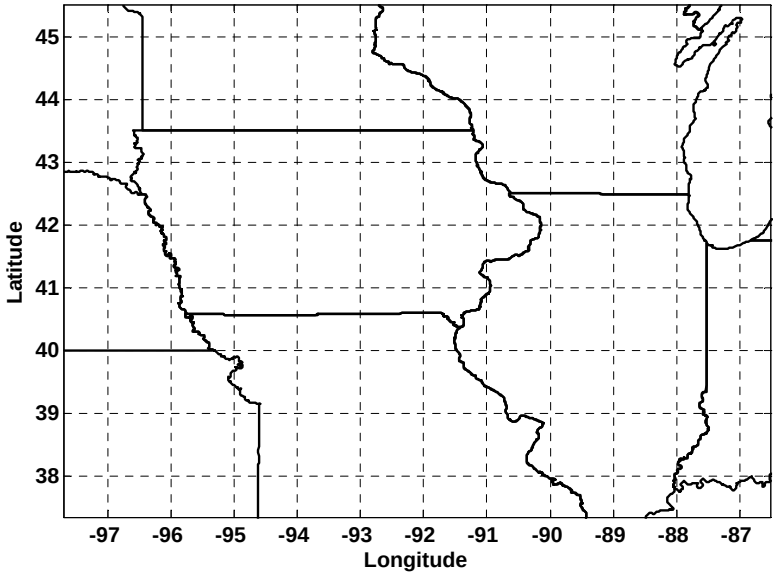

Figure 2-1. Domain considered for this study

2.2 Data sources. Air pollution and meteorology data for this study were taken from a variety of publicly available sources. The Iowa Department of Natural Resources Air Quality Monitoring group was instrumental in providing multiple years of PM monitoring data.

Data	**Description** (content, duration, temporal resolution, spatial coverage)	**Source**
IDNR $PM_{2.5}$ monitoring data	2002-2008 daily filter (FRM) $PM_{2.5}$ for ~15 sites. Hourly $PM_{2.5}$ for ~8 sites by a variety of automated methods.	All Iowa $PM_{2.5}$ data, gases, and some meteorology data is provided by the Iowa Department of Natural Resources (IDNR) with courtesy of Sean Fitzsimmons and John Gering.
IDNR monitoring data for meteorology and air quality monitoring data other than $PM_{2.5}$	2002-2008 wind speed, wind direction, RH, and temperature at most Iowa DNR sites	
CMAQ air quality modeling data, 2002	Simulated $PM_{2.5}$ for the year 2002 from the CMAQ/Models-3. 36 km spatial resolution.	Spak and Holloway (in press 2009)
$PM_{2.5}$ data for sites outside of Iowa	2002-2008 EPA FRM $PM_{2.5}$	Accessed from EPA website.[1]
Speciated $PM_{2.5}$ composition	Speciation Trends Network data for years 2003-2007 for Cedar Rapids, Davenport, and Des Moines	Obtained from Visibility Information Exchange Web Site (VIEWS)
Hourly meteorology data for Eastern Iowa	2002-2008 wind speed, wind direction, temperature, dew-point, surface pressure, cloud cover, precipitation, and visibility	Iowa Environmental Mesonet (IEM). Archived data for Automated Surface Observing System (ASOS) airport locations for the State of Iowa is retrieved from website[2]
Locations of Potential $PM_{2.5}$ Local Sources	Locations of Title V Major Air Pollution Sources with $PM_{2.5}$ Emissions	Iowa 9-Factor Analyses for Scott and Muscatine Counties. Also EPA AirData website.[3]
Aerial Photography	1x1 meter resolution aerial photography over Iowa	Iowa Geographic Map Server http://ortho.gis.iastate.edu/map.html

Table 2-1. Main Data Sources

Air quality and meteorology data is limited to 2002 – September 2008. The remainder of Iowa's 2008 data has been submitted to the EPA AQS database. That data, if accepted and finalized without any changes, will put the Scott and Muscatine monitors into attainment with the daily standard (Fitzsimmons 2009). The results of this work are robust to whether the data record stops in September 2008 or December 2008. Some figures, such as 2008 wind and pollution roses (section 4), figure 4-5 and 4-6, and attainment probabilities in sections 4 and sections 7 would change slightly if new data were added.

Appendix C has maps and photos of some sites of interest for this work, and some IDNR monitoring trailers. (A small selection of photos can be found at the end of this chapter).

[1] Measurement code 88101 data downloaded from http://www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm
[2] Retrieved from http://mesonet.agron.iastate.edu/request/download.phtml.
[3] http://www.epa.gov/air/data/

Appendix D includes a table listing the location, site ID, latitude, and longitude of the monitoring sites used in this study.

2.3 Data Analysis Methods. Data analysis methods employed in this study include wind roses, pollution roses, statistical "box and whisker" diagrams, kriging, linear regression, and conditional probability functions. In addition to these, a major emphasis was placed on combining meteorological and PM monitoring data in high quality time series that would allow data visualization of the PM episodes.

Wind roses and pollution roses are widely used in environmental engineering. Since some readers of the work may not be familiar with these important tools, examples are given here.

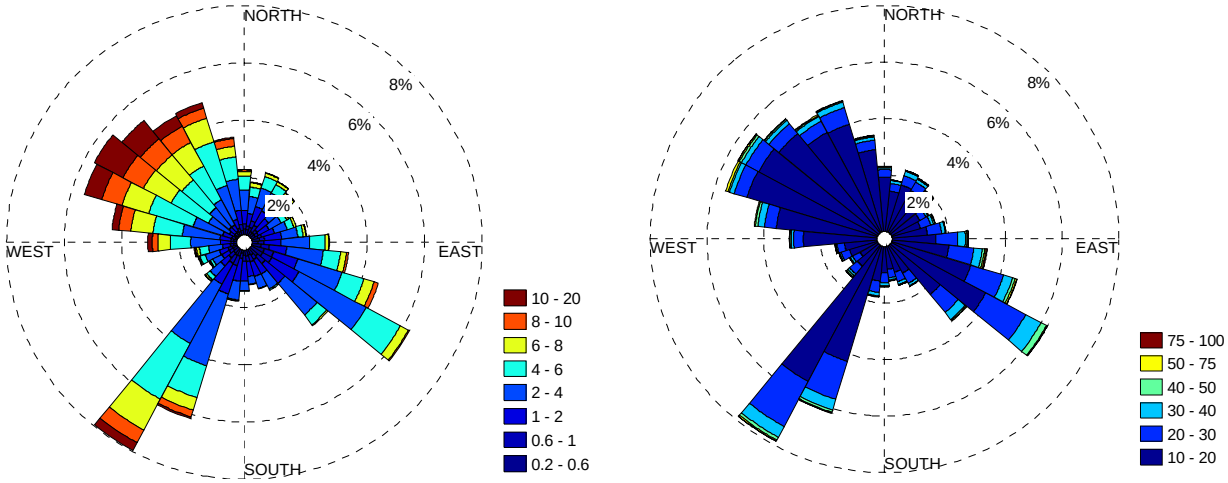

Figure 2-2. Both for the same site (Davenport 10th & Vine, Years 2006-2008), figure a (left) shows the wind rose, while figure b (right) shows the pollution rose for $PM_{2.5}$. See text for explanation.

The wind rose (figure 2-2a) combines two pieces of information, (1) the frequency of wind blowing from a specific direction – this is denoted by the length of the spokes that extend from the center; and (2) the wind velocity – this is denoted by the color scale. The rings are at 5%, 10%, and 15% frequency, and the wind rose could be summarized by statements such as, at this site, winds are most common from the northwest, southeast, and southwest, and are infrequent from the northeast. Strong winds tend to come preferentially from the west. Winds from the southwest at this site have a preference for specific headings of around 210°. The pollution rose (figure 2.2b) plots wind direction again, but the color scale is changed from wind velocity to an air quality parameter, in this case $PM_{2.5}$ concentration. The most salient feature of

the example pollution rose is that high $PM_{2.5}$ levels (50-75 µg m^{-3}) preferentially arrive with winds coming from the east.

Wind rose and pollution rose plots in this document are generated using a modified version of the MATLAB script wind_rose available from the free MATLAB Central file exchange.

Box and whisker diagrams are standard statistical plots used to summarize the features of a distribution of data. An example is shown in figure 2-3.

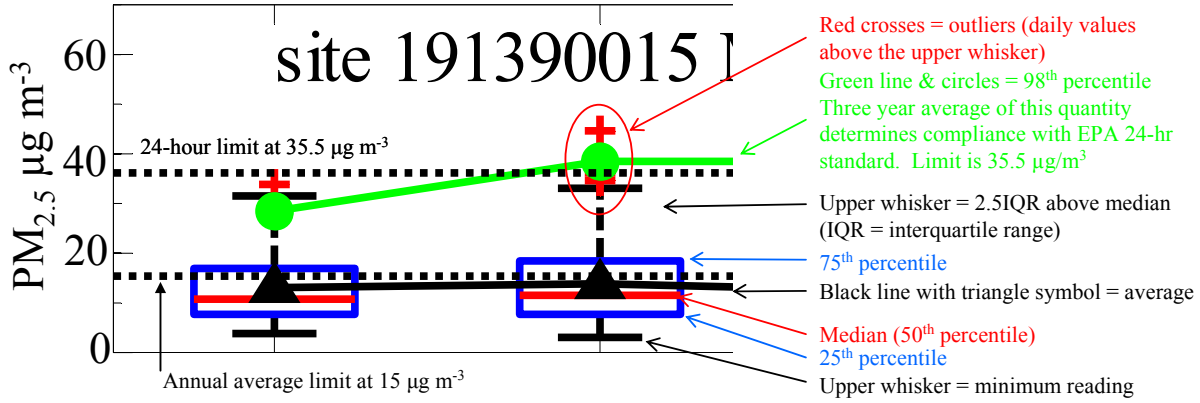

Figure 2-3. Example of a box and whisker diagram, which can summarize the range, distribution, mean, and median of a sampled variable. In this work, this is applied to annual measurements of $PM_{2.5}$ at each monitoring location in Iowa.

Table 2-2. Notes on calculating the "Design Value" (98th percentile for the 24-hour average standard)

In this work, actual 98th percentiles are calculated, and unrounded 98th percentile values are averaged. 98th percentile values are calculated in this work using MATLAB's prctile function and Excel's PERCENTILE function. This will give slightly different values than if the EPA procedures for calculating a design value are used. The procedures can be found at in CFR Title 40, Volume 2 (Revised as of July 1, 2008; From the U.S. GPO via GPO Access; CITE: 40CFR50 App N).

Thus, for a sampler with a full complement of 365 daily samples, it is the 8th highest reading from each of the 3 years, averaged, and then rounded to the nearest full microgram. Therefore, if the average of the 3 values is 35.49 or lower, then compliance with the 24 hour standard is achieved. If the average of the 3 values is 35.50 or higher, compliance is not achieved.

Table 1

Annual creditable number of samples for year ``y'' (cny)	P0.98, y is the nth maximum value of the year, where n is the listed number
1-50	1
51-100	2
101-150	3
151-200	4
201-250	5
251-300	6
301-350	7
351-366	8

An example of a conditional probability function is shown in figure 2-4. The conditional probability function (Kim et al. 2003) is determined by calculating the fraction of observations from a given wind direction that meet a criteria. The criteria used in figure 2-4 is exceedance of a $PM_{2.5}$ concentration of 35 μg m^{-3}. Figure 2-4 would be correctly interpreted by saying that 6% of the samples associated with wind from the east had $PM_{2.5}$ concentrations greater than 35 μg m^{-3}, while only zero to two percent of samples from other directions had $PM_{2.5}$ concentrations in excess of 35 μg m^{-3}. Conditional probability plots are routinely used in determining if specific wind directions are associated with pollution.

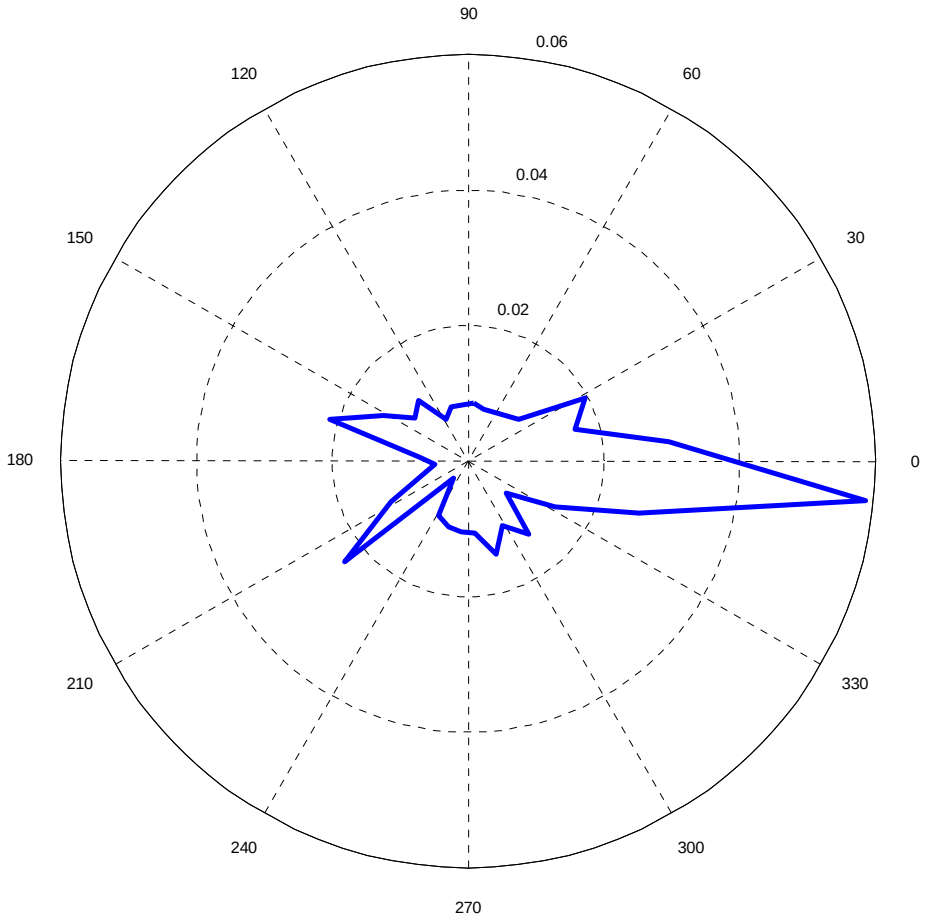

Figure 2-4. Example conditional probability function plot. Blue trace denotes the probability of the measured quantity (e.g. $PM_{2.5}$) exceeding a threshold when binned according to wind direction using 32 bins. See text for more information.

Related techniques of potential source contribution function and quantitative transport bias analysis (QTBA) are not employed in this phase of the study. They extend the source

contribution function approach to account for longer travel paths of air parcels (out to 100s of kilometers) as estimated by meteorological models and observations.

Spatial smoothing, or "interpolation" of irregularly spaced measurement data, to form concentration contour maps, was performed by statistical Kriging in the ArcGIS software package. Smoothed contour maps need to be used carefully. They play important roles of guiding the eyes to quickly note the spatial scale of pollution episodes, and the movement of the high and low concentration zones from day to day as an episode unfolds. But Kriging and other interpolation techniques can introduce artifacts and patterns in the data that are not real. It should be noted that while the Kriged maps do not denote this, the surfaces have considerable uncertainty to their exact height (concentration) and shape (precise location and shape of iso-concentration contour lines).

Spatial smoothing is done in both MATLAB and in ArcGIS. In ArcGIS, ordinary prediction map kriging is used in ArcGIS v. 9 (ARC Map 9.3) for interpolating data. In both cases, the following parameters are used: sill value of (C_{avg}^2)/5.5 where C_{avg} is the mean concentration of the variable being smoothed; nugget values of 10% of the sill for particulate matter and 20% for nitrate; lag size (spatial smoothing distance) is 2 degrees; semivariogram type: Gaussian.

Some photos of Iowa locations to be discussed in this work are below. More maps and photos can be found in Appendix C.

	
Garfield Elementary (Muscatine) with Samplers on School Roof, GPC in background	GPC Plant (Muscatine) – photo taken from Garfield Elementary School

	
GPC Plant (from west)	Stacks along Mississippi in Muscatine
	
GPC plumes going over Mississippi River	Impaired Visibility over Mississippi at Muscatine
	
IDNR Monitors at Blackhawk Foundry	IDNR Monitors at 10th and Vine

	
Blackhawk Foundry and Machine Company	Blackhawk Foundry and Machine Company

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Spak, S. and T. Holloway (in press 2009). Seasonality of Speciated Aerosol Transport over the Great Lakes Region. University of Wisconsin-Madison, Center for Sustainability and the Global Environment.

3.0 LITERATURE REVIEW

3.1 Background on chemistry of nitrate aerosols and related nitrogen species

One key topic of study in this work is the sulfate-nitrate-ammonia-water inorganic aerosol system. Species in this system can respond in complicated ways to changes in temperature, relative humidity, and total concentrations of these pollutants. These species are important, because, together with organic aerosols from motor vehicles, they are the dominant species in winter. The complexity of this system is due to the chemical interactions between these species, and the fact that three of the four species (nitric acid, ammonia, and water) can easily move between the gas phase and the aerosol phase in response to changes in temperature, relative humidity, or in the chemical environment. Complicating matters is fact that nitrate and ammonium are difficult species to measure in the aerosol and gas phase (they tend to be lost during sampling, and this problem is given the technical name of a negative artifact). Simultaneous measurements of both the aerosol and the gas phase (in other words nitrate and nitric acid, or ammonium and ammonia) are rare, and subject to large errors.

Figure 3-1 shows our conceptual model for particulate matter formation and concentrations in Iowa. There are three important points that one should know about Midwestern PM formation:

- **Key point #1. Aerosols are a mixture of different chemical compounds, coming from a variety of locations** ranging from very local sources (shown in the diagram by the brown factory symbol), nearby but "fresh" emissions (shown in the diagram by the Local County emissions box), and regionally transported pollutants that can come from 100s of miles away.
- **Key point #2.** During wintertime regional episodes, ammonium nitrate aerosol is the most prevalent aerosol species. A key component in ammonium nitrate is nitrate. Nitrate is the form that nitric acid (a gas) takes when it enters the particles. Nitric acid is formed from atmospheric chemical reactions of NOx, and NOx is emitted during combustion. Therefore, **the ultimate source of much ammonium nitrate is combustion sources such as automobiles, other mobile sources, and power generation (gas, oil, and coal) plants**.
- **Key point #3. Ammonium nitrate is (a) semivolatile and (b) requires a specific balance of ammonia and nitric acid.** This is shown in the diagram by the see-saw in the "Ammonia-Nitric Acid Balance" box. When there is too little ammonia, ammonium nitrate formation will stop when all the ammonia is gone, leaving nitric acid gas, and creating what is termed an ammonia limited scenario. Conversely, when there is too little nitric acid, ammonium nitrate formation will stop when all the nitric acid is gone, leaving ammonia gas, and creating what is termed a nitric acid limited scenario. Finally,

ammonium nitrate is sensitive to temperature and relative humidity. For example, it can evaporate when entering a heated space (such as a house) on a cold day.

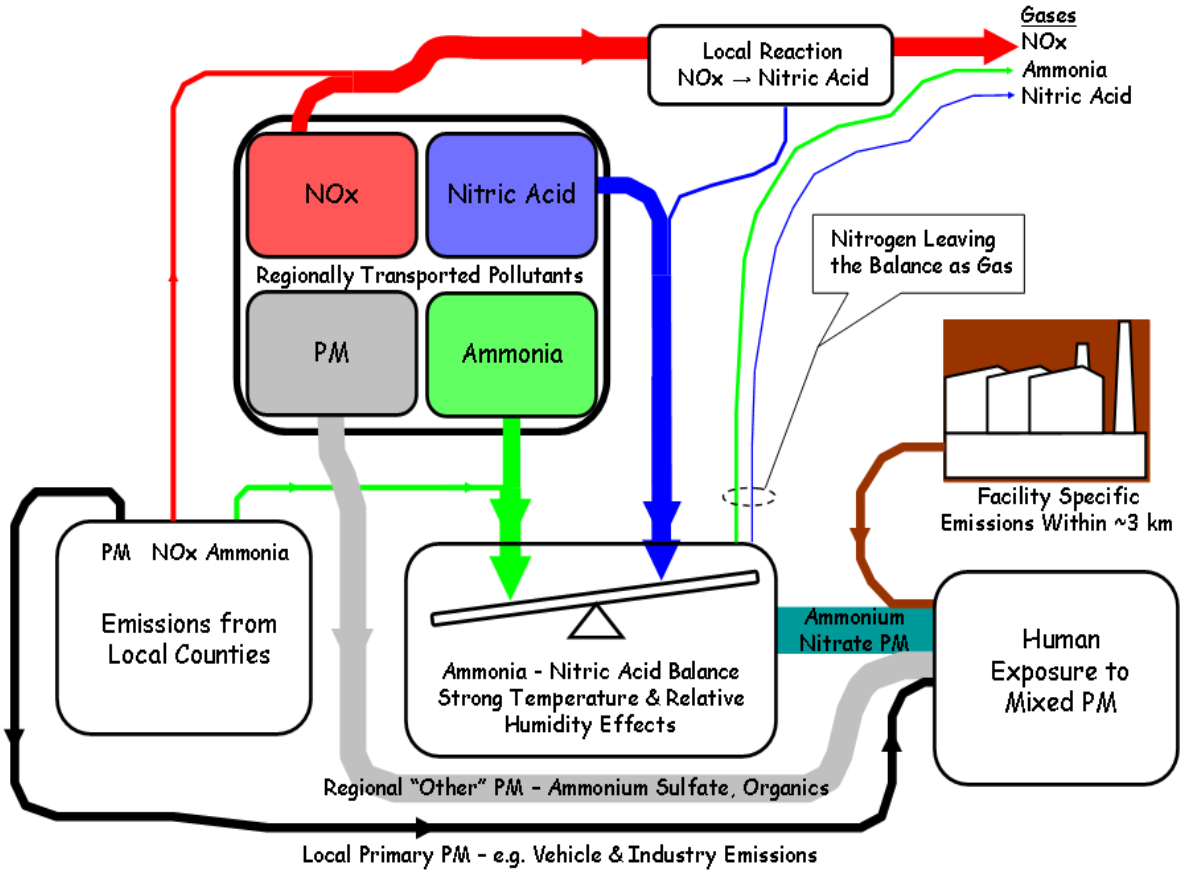

Figure 3-1. Conceptual model for particulate matter formation and concentrations in Iowa.

Much of the literature review consists of summarizing published work where authors have looked at various parts of this conceptual diagram.

A guide to different forms of nitrogen in the atmosphere can be found in Table 3-1. Nitrogen species can be conveniently grouped into NO_x species ($NO + NO_2$) and NO_y species (NO_x plus all reactive oxidation products of NO_x). NO_y includes HNO_3 and aerosol nitrate. Measurements are often reported in two different units: mass concentration (e.g, microgram per cubic meter, $\mu g\ m^{-3}$) and mixing ratio [e.g. part per billion (ppb), part per trillion (ppt)]. The conversion from one to the other depends on the molecular weight of the species in question and the temperature. A reference to these conversions can be found in Table 3-2.

Table 3-1. List of Ambient Nitrogen Containing Compounds

Compound	Name	Oxidation State & Molecular Weight	Group	Typical Conc	Source
NOy	**"NO-y"**	**Various +2 to +5**	**NOx plus all reactive oxidation products of NOx**	0.2-10 ppb	Seinfeld & Pandis, page 74
N_2O_5	Dinitrogen pentoxide (also referred to as nitrogen pentoxide)	+5 / 108.01	NOy	can reach similar levels as HNO_3 at night	
HNO_3	Nitric acid	+5 / 63.01	NOy	1-4 μg m^{-3} 0.3-1.4 ppb	Wittig et al. (2004) Blanchard (2008)
NO_3- (sometime as ammonium nitrate NH_4NO_3)	Nitrate ion (aerosol only)	+5 / 62.00	In NOy but requires aerosol phase measurement	Wintertime = 1-20 μg m^{-3}	this work
PAN [RC(O)OONO2]	Peroxyacetal nitrate	+5 / 135.08 (with R as CH_3)	NOy	0-1 ppb 20% of NOy in Michigan summer 0-6 ug m^{-3}	Thornberry et al. (2001)
$RONO_2$	Alkyl nitrates	+5 / 77.04 (with R as CH_3)	NOy	5-40 ppt or 1-2% of NOy for ∑C3-C8 $RONO_2$	Thornberry et al. (2001)
$ROONO_2$	Peroxyalkyl nitrates (also peroxynitrate)	+5 / 93.04	NOy	not reported in Thornberry et al. (2001)	
NO_3•	Nitrate radical	+5 / 62.00	NOy	Daytime max ~0.6 ppt (Seinfeld and Pandis p. 253) Up to 100 ppt at night if sufficient O_3 and NO_2 Lifetime is strong function of RH – high RH = short lifetime due to nitric acid formation	
HNO_4	Peroxynitric acid	+5 / 79.01	NOy	not reported in Thornberry et al. (2001)	
NOx	**"NOX"**	**+2 and +4**	**NO + NO_2**	5-100 ppb ~8-170 μg m^{-3}	Seinfeld & Pandis p. 72
NO_2	Nitrogen dioxide	+4 / 46.01	NOx	~1/2 of NOx. NO favored in fresh emissions. NO_2 favored in aged emissions but also linked to O_3 and sunlight.	(Wittig, Takahama et al. 2004) Lesser of NOx species emitted from combustion
HONO	Nitrous acid	+3 / 47.01	NOy	90-200 ppt or ~5% of NOy in Michigan summer 0.2-0.4 μg m^{-3}	Thornberry et al. (2001)
NO_2^-	Nitrite ion (aerosol only)	+3 / 46.01	In NOy, but requires aerosol phase measurement	will be in equilibrium with HONO. 30-200 ppt in Michigan summer	Thornberry et al. (2001)
HOONO	Peroxynitrous acid	+3 / 63.01	NOy	not reported in Thornberry et al. 2001	
NO	Nitric oxide	+2 / 30.01	NOx	~1/2 of NOx. NO favored in fresh emissions. NO_2 favored in aged emissions.	Wittig et al (2004) Main NOx species emitted from combustion
N_2O	Nitrous oxide	+1 / 44.01	Mostly inert – no role in aerosol pollution		
N_2	Nitrogen	0 / 28.01	Completely inert		
Organic nitrogen	(e.g. proteins, urea)	-3	Mainly found in soil and water, not in atmosphere. May be component of some organic aerosols.		
NH_4^+	Ammonium ion (aerosol only)	-3 / 18.04	Major component of ammonium nitrate	0-4 μg m^{-3} 0-5 ppb	Blanchard (2008)
NH_3	Ammonia (gas only)	-3 / 17.03	Non reactive, but converts easily to ammonium ion in presence of sulfate or nitrate	0.08 – 8 μg /m^3 0.1 – 10 ppb	Blanchard (2008)

Table 3-2 Conversions between mass concentrations and mixing ratios

Compound	Molecular Weight	1 ppb when converted to $\mu g\ m^{-3}$ (assuming 273 K) $\mu g\ m^{-3}$ = ppb x (# below) x T (K) / 273	1 $\mu g\ m^{-3}$ when converted to ppb (assuming 273 K) ppb = $\mu g\ m^{-3}$ x (# below) x 273 / T (K)
Ammonia (NH_3)	17.03	0.76	1.32
Nitric Acid (HNO_3)	63.01	2.81	0.36
Nitric Oxide (NO)	30.01	1.34	0.76
Nitrogen Dioxide (NO_2)	46.01	2.05	0.49
Water (H_2O)	18.02	0.80	1.24
Sulfuric Acid (H_2SO_4)	98.07	4.38	0.23
Ozone (O_3)	48.00	2.14	0.47
Sulfur Dioxide (SO_2)	64.06	2.86	0.35
Ammonium Nitrate (NH_4NO_3)	80.04	3.57	0.28
Ammonium Sulfate $(NH_4)_2SO_4$	132.13	5.90	0.17
Nitrate Radical (NO_3)	62.00	2.77	0.36
Dinitrogen pentoxide (N_2O_5)	108.01	4.82	0.21

There are four atmospherically relevant sources of nitric acid. Full equation sets for nitric acid can be found in model documentation for CMAQ and CAMx, as well as in Pandis and Seinfeld (1989) and Zhang, Wu et al. (2008). The pathways are:

- OH + NO_2 (main gas phase pathway)
- NO_3 radical reaction with hydrocarbons
- NO_3 conversion to N_2O_5 followed by hydrolysis to HNO_3 on aqueous aerosols
- Aqueous processing of nitrate radical to form nitrate ion

Minor pathways, generally not considered important in previous studies, may involve compounds including HONO, HOONO, alkyl nitrates, and peroxy nitrates (Vayenas, Takahama et al. 2005). Takahama et al. (2005) divide these pathways into two pathways. A daytime OH + NO_2 pathway, and a nighttime pathway where every O_3 + NO_2 reaction leads to a nitric acid through a conversion of the NO_3 radical.

The NO_2 + O_3 reaction is the only major source of nitrate radical in troposphere, and the equilibration with NO_2 and NO_3 (to form N_2O_5) is rapid, ~1 min [Seinfeld and Pandis, page 253, ed 1 (1998)].

The figure below (Wittig, Takahama et al. 2004) illustrates how total and aerosol nitrate behave during the four seasons. The figure is based on measurements in Pittsburgh, Pennsylvania, but temperature and relative humidity are similar enough that the qualitative features of the nitrate system are the same as in Iowa. In January, 100% of nitrate is in the aerosol phase. Also, the diurnal pattern does not look like a photochemical species (as total

nitrate looks like in July 2001). Concentrations increase at night, indicating a nighttime production route of nitrate. The decrease in the day is from the increase in the mixing height, and could be coupled with daytime production of nitrate as well.

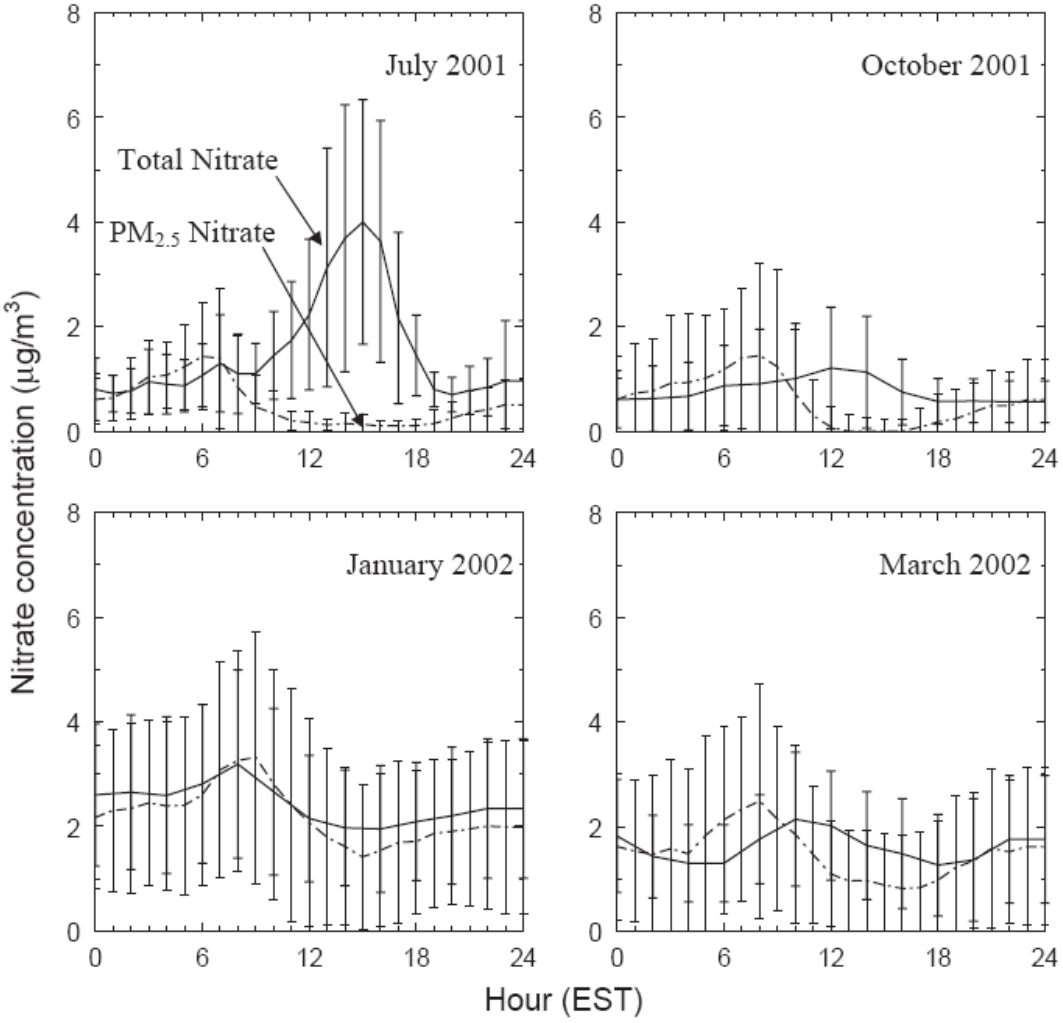

Figure 3-2. Example of diurnal gas-to-particle partitioning for nitric acid (gas) vs. nitrate aerosol (particle) in July 2001, Oct 2001, Jan 2002, and March 2002 (Pittsburgh PA). Also shown is the standard deviation of the hourly measurements used to compute both monthly average diurnal profiles.

A common view in many academic journal articles is that nitrate episodes in the upper Midwest are completely neutralized and that there is free excess gas phase ammonia. The evidence for these types of statements is usually weak, and below some recent measurement-based studies that are likely more accurate are reviewed below.

However, assuming ammonia in excess, the formation of ammonium nitrate is limited by available nitric acid. This is important for this work for three reasons: (1) the ability of models

to reproduce the episodes will be linked to the skill of the models at managing the wintertime nitric acid formation and loss pathways (model skill is also influenced by the quality of the emissions inventory and transport of NO_x); (2) to reduce PM, one must reduce total nitrate (nitric acid + nitrate), and thus the sensitivities of total nitrate to various controllable emission categories, as well as the response of nitric acid lifetime to uncontrollable factors such as temperature and RH, are important; and (3) expected continuing decreases in sulfate and SO_2 can interact with the nitric acid balance. In some parts of the country, decreases in sulfur levels will lead to increased levels of aerosol nitrate (increases in particulate nitrate due to the freeing up of NH_3). If ammonia is truly in excess, then there will be no nitrate replacement in the upper Midwest, and the Midwest can expect the full benefit of reductions in sulfate.

3.2 A review of peer-reviewed and air quality planning/research publications with a focus on Midwestern PM formation.

A literature search was conducted to find papers and publications in the following areas: Midwestern ammonium nitrate formation events; modeling of regional air pollution episodes in the U.S.; sensitivity of the ammonia-nitrate-sulfate-water aerosol system to controls in the eastern and Midwestern U.S.; and nitric acid formation chemistry, including nitrate radical and N_2O_5 reactions. While most of the literature review of the paper is included in this section, some specific areas are discussed both here and in the results and discussion sections. This includes papers that cover the skill of models at reproducing PM episodes (covered in section 8.0), and the chemistry and thermodynamics of the regional ammonia-nitrate-sulfate-water system (see section 9.0).

Key papers for this work are listed in Table 3-3. Except for the names of monitoring networks (e.g. STN, IMPROVE, CASTNet), chemical species (e.g. SO_2, NH_3, etc.), model names (CMAQ, CAMX), and one common source apportionment technique (PMF[1]), abbreviations have been spelled out in table 3-3.

[1] PMF = Positive Matrix Factorization

Table 3-3. Guide to key papers.

Paper	Title	Methods	Conclusions Most Relevant to This Work
Appel, K.W. (2008)	Evaluation of CMAQ 4.5: Sensitivities impacting model performance; part II - particulate matter	Evaluation of CMAQ against STN (average performance) with regional subanalyses	See text for synopsis of authors conclusions on CMAQ for the Great Lakes
Bae et al. (2004)	Hourly and Daily Patterns of Particle-Phase Organic and Elemental Carbon Concentrations in the Urban Atmosphere	Demonstrate the use of 1-in-6 day organic carbon and elemental carbon samples to identify weekday-weekend trends in carbonaceous aerosol sources	Could potentially be used as a source apportionment tool in Eastern Iowa
Blanchard et al. (2008)	Chemical characterization of the organic fraction of atmospheric aerosol at two sites in Ontario, Canada.	Ran box model on extensive ammonia and nitrate measurements from midwestern sites taken 2003-2006	Relevant sites include Lake Sugema, IA, Bondville, IL, and Mayville, WI.
Buzco-Guven et al. (2007)	Analysis and Apportionment of Organic Carbon and Fine PM at Multiple Sites in the Midwestern US	PMF Analysis of STN and IMPROVE filters at various sites including Chicago and Bondville	Limited work on nitrate. Some insights into rural / urban organic aerosols.
Chu, S.H. (2004)	$PM_{2.5}$ Episodes as Observed in the Speciation Trends Network	Using STN aerosol chemistry filters from 2000-2002 to understand regional episodes (nationwide scope)	In winter, high values occur during stagnant, high-pressure systems usually on the backside of the system. In urban areas, meteorology and aerosol thermodynamics are as important (if not more important) as the photochemistry in determining high $PM_{2.5}$ concentrations.
Dawson et al. (2007)	Sensitivity of $PM_{2.5}$ to climate in the Eastern U.S.	Model sensitivity runs to future climate scenarios	No direct relevance to this work, but the nitrate system in particular in winter displays several sensitivities (e.g. temperature, relative humidity)
Dennis et al. (2008)	Observable indicators of the sensitivity of $PM_{2.5}$ nitrate to emission reductions - Part II: Sensitivity to errors in total ammonia and total nitrate of the CMAQ-predicted non-linear effect of SO_2 emission reductions	Sensitivity studies looking at nitrate and sulfate concentrations under NH_3 emissions uncertainty, NOx emissions uncertainty, and N_2O_5 reaction uncertainty	The object of the main interest in the eastern U.S. (nitrate replacement of sulfate, quantified by the nitrate relative response), is most sensitive to uncertainty in ammonia emissions. On the other hand, the study demonstrates that in Chicago (and presumably farther west), the N_2O_5 and NOx uncertainties account for large percentage uncertainties in modeled total nitrate.

Paper	Title	Methods	Conclusions Most Relevant to This Work
Karydis, V. A. (2007)	Evaluation of a three-dimensional chemical transport model (PMCAMx) in the eastern United States for all four seasons	Evaluation of a 36x36 grid application of PMCAMx over the U.S. for July 2001, Oct 2001, Jan 2002, and Apr 2002	See text for evaluation of nitrate predictions in July and January cases.
IDNR (2008)	Technical Support Document. Response to EPA's Proposed Nonattainment Boundarires for Scott County, Iowa, and Rock Island County, Illinois and Muscatine County, Iowa. October 20, 2008	Proposed nonattainment boundaries and extensive modeling and data analysis to support them, using AERMOD dispersion model, source apportionment using CAMx PSAT; also includes extensive discussion of controls at Blackhawk Foundry submitted by Blackhawk Foundry	Extensive similarities between this work and the IDNR work. Many similar conclusions reached by completely independent analysis by IDNR and University of Iowa. See special section in text on conclusions.
LADCO (2004)	$PM_{2.5}$ in Urban Areas in the Upper Midwest	Excellent overview of urban PM in the midwest, mainly drawing from LADCO and EPA sampling and analysis.	Important result in terms of information relevant to Iowa. See text.
Lee and Hopke (2006)	Apportioning sources of PM2.5 in St. Louis, MO using speciation trends network data	PMF and Potential Source Contribution Function of speciated filters	Methods would be applicable to Iowa hotspots. Link between urban nitrate and rural ammonia put forward in this paper.
Lee et al. (2006)	Source identification of airborne $PM_{2.5}$ at the St. Louis-Midwest Supersite	In a source-rich location (East St. Louis) $PM_{2.5}$ filter data analyzed by PMF.	10 source categories resolved, including local industrial factors such as zinc smelting and steel processing. Winter samples, nitrate leading factor at 4-5 $\mu g\ m^{-3}$.
Lillis, D. (1999)	Production and removal of aerosol in a polluted fog layer	Model and measurement study of high pH fogs with high nitrate in California	Removal of nitrate during fogs (3 events studied) was larger than production. Production and removal more balanced for sulfur.
McMurry, P., et al. (2004)	Conceptual Models of PM for North American Regions. Particulate Matter Science for Policy Makers: A NARSTO Assessment	Review Paper	Influential document that gives conceptual models for PM formation and high PM episodes in 9 different parts of North America. Regional wintertime events in the Midwest were not well studied at the time and aerosol measurements (both of mass and especially speciation and hourly mass) were much more limited at this time.
Phillips and Finkelstein (2006)	Comparison of Spatial Patterns of Pollutant Distribution with CMAQ Predictions	Compared spatial patterns for 2001 CMAQ run with smoothed STN and CASTNet data	Over long (1 month or greater) averaging periods spatial patterns agree between measurements and models for speciated PM components, although in 2001 the data in the midwest were very sparse
Pinder et al. (2007)	Ammonia Emission Controls as a Cost-Effective Strategy for Reducing Atmospheric Particulate Matter in the Eastern U.S.	A 3D air quality model (PMCAMx) is combined with economic functions for the costs of controls on NOx and SO_2 sources, and this together is used to calculate the opportunity to control a regulated air pollutant ($PM_{2.5}$) by controlling a nonregulated gas (NH_3)	Pinder calculates that ammonia reductions in winter would be effective (sulfur reductions are more effective in summer) and that the ammonia reductions would be cost competitive if they could be achieved for around \$8,000 per ton of NH_3 or lower.

Paper	Title	Methods	Conclusions Most Relevant to This Work
Pinder et al. (2008)	Observable indicators of the sensitivity of $PM_{2.5}$ nitrate to emission reductions - Part I: Derivation of the adjusted gas ratio and applicability at regulatory	Combined 3D modeling and thermodynamic box modeling to show that the adjusted gas ratio is a good indicator of nitrate relative reduction behavior in many CMAQ grid cells	The technique of calculating total inorganic species budgets (by 3D model) but relying heavily on observations for the base case thermodynamic state of the system, is applicable in the midwest.
Spak et al. (2008)'	Seasonality of Speciated Aerosol Transport over the Great Lakes Region	Model evaluation of CMAQ 2002	Good agreement, especially for winter nitrate. See text and section 8 of this work.
Takahama et al. (2004)	Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study	Testing thermodynamic model and predicting sensitivity of summer and winter aerosols to changes in total nitrate, total sulfate, total ammonia, and relative humidity and temperature	Technique is applicable to upper midwest. Results for high ammonia cases during winter show a strong positive sensitivity to relative humidity, and moderate sensitivities to both total ammonia and total nitrate.
Tesche et al. (2006)	CMAQ/CAMx annual 2002 performance evaluation over the eastern US	Evaluation of CMAQ with 12 km eastern U.S. nest against speciation data	Poor performance for wintertime nitrate, with January bias relative to STN sites at + 55%, and fractional error at 118%. Diurnal changes in nitrate too strong during winter as well.
Vayenas et al. (2005)	Simulation of the thermodynamics and removal processes in the sulfate-ammonia-nitric acid system during winter: Implications for $PM_{2.5}$ control strategies	Construct a new model, TMR or thermodynamic model with removal, so simulate the partitioning, production and loss of nitric acid constrained by measurements from Pittsburgh. Then used to model sensitivity to changes in total nitrate, total sulfate, total ammonia	Simple but promising technique for use in Midwest, becauses nighttime nitric acid formation is set by measurements. Predicted wintertime peaks in nitric acid and nitrate at 8 AM due to nighttime production of nitric acid, low temperatures, and high relative humidity. Estimate of net generation/transport of 0.7 $\mu g\ m^{-3}$ -hr of total nitrate during the hours from 5 PM to 8 AM and net generation/transport of 0.1 $\mu g\ m^{-3}$ -hr during the day, due to chemical production of ~0.3 $\mu g\ m^{-3}$ -hr and simultaneous entrainment of clean air into the mixed layer.
Wittig et al. (2004)	Semi-continuous $PM_{2.5}$ inorganic composition measurements during the Pittsburgh Air Quality Study	Evaluating nitric acid partitioning, and measurement using semiconiuous analyzers	See text for summary of nitric acid partitioning by season and time of day.
Wu et al. (2007)	Modeling atmospheric transport and fate of ammonia in North Carolina -- Part II: Effect of ammonia emissions on fine PM formation	Model based sensitivity study	Technique is subject to errors described in Dennis et al. 2008, and hybrid model-measurement-box model approach of Pinder (2008) is more accurate
Zhang et al. (2008)	Modeling agricultural air quality: Current status, major challenges, and outlook	Review article of challenges and approaches to modeling agricultural air quality	Good review of special challenges including, spatial scales, specialized emissions inventories, nitrogen balance, and odor-irritant chemicals
Zhao et al. (2007)	Spatial distribution of source locations for particulate nitrate and sulfate in the upper-midwestern United States	Back trajectory analysis of nitrate and sulfate data to identify source regions impacting Chicago, St. Louis, and other areas farther east.	Methods would be applicable to Iowa hotspots. Indicates "self-pollution" by urban NOx during winter is important in St. Louis, Chicago, and the Ohio River Valley, and that urban influence is comparable to a broad regional impact (from rural NH3 sources)

3.2.1 Literature review on CONCEPTUAL MODELS & METEOROLOGY

A number of publications summarize the well known finding that meteorology and high $PM_{2.5}$ episodes in the Midwestern U.S. are tightly linked. In the 2004 NARSTO PM Assessment (Chapter 10, Conceptual Models for PM for North American Regions), the highest $PM_{2.5}$ values usually occur in the upper Midwest during summer and winter months, rather than the spring and fall. Episodes occur under stagnant high-pressure systems when there is shallow turbulent mixing (Chu 2004).

The section on the Upper Midwest – Great Lakes Area is not specific to Iowa, but is rather focused on the Great Lakes and Chicago. At the time of the NARSTO assessment, nitrate and ammonia data were not available to show the extent of the short term winter episodes, nitrate is listed as 11% of the annually averaged regional composition (McMurry et al., page 363), and nitrate events are mentioned only in passing. In summary, the upper Midwest, in the lens of the 2004 assessment, was viewed as clean and comparatively uninteresting from a PM formation standpoint.

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

Chu (2004) furthermore showed that nitrate events were concentrated in the Nov-Feb period. Chu (2004)'s analysis ends in February 2002, but there is a 2 month overlap with the episode identification process done in this work. Focusing on a nationwide analysis, Chu (2004) identifies high PM nitrate events on Jan 2 and 5; on Jan 14, 17 and 20; on Jan 26, 29 and Feb 1, 4, and 7; on Feb 13, 16, and 19. The alternation of days is from the fact that the sampling network operates 1 day in 3. Thus Chu (with a national scope) identified nitrate events in 5 episodes during the Jan/Feb 2002 period. Of these episodes, only 1 (Feb 6-8) is identified as an episode in this work (see section 4). However, the Feb 6-8 episode was strong enough for Chu (2004) to analyze in detail. Within the Midwest and Great Lakes, peak $PM_{2.5}$ occurred in Chicago with 34 $\mu g\ m^{-3}$, and concentrations in Iowa ranged from 18-26 $\mu g\ m^{-3}$. Approximately

40% of the filter mass in Iowa was nitrate, and peak nitrate was in Chicago. Chu further found that ammonia levels were almost sufficient for full neutralization of nitric acid in the Midwest, and acidic conditions occurred only southeast of the Ohio River.

One key issue of the conceptual model (figure 3-1) is the amount of split between regionally transported pollutants and local emissions. This is difficult to determine, but it is an important value, and considerable work has been done in Chicago and St. Louis on this topic. Although these are larger metropolitan areas than are found in Iowa, this is perhaps the best available data on the wintertime urban-regional split. The percentage contribution from local sources (often approximately 20% in large cities) does not fall proportionately with the size of the urban area. In other words, a city of 100,000 will not have 1/10th of the local impact (e.g. 2%) relative to a city 1,000,000. This is because pollutants can get trapped by weak winds (especially during the night) and by stagnant meteorological conditions. Under those types of conditions, the local impact will scale roughly by population density, not by total population. Thus, the Chicago, St. Louis, and Indianapolis urban-regional split values are of high relevance to Iowa.

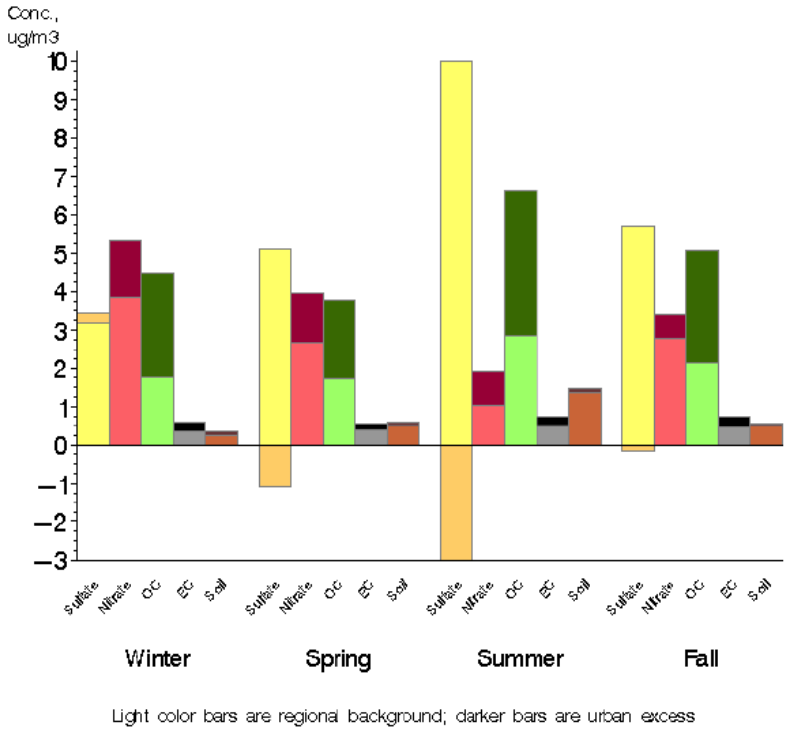

Figure 61. Urban-Regional Contributions to $PM_{2.5}$ Concentrations in Chicago MSA

Figure 3-3. Urban-regional split (by season) from LADCO (2004). All seasons have substantial (> 10%) local impacts of nitrate and organics.

Figure 3-3, from LADCO (2004), splits out regional and local aerosols according to season and species. For Chicago, on an annual basis, the split is reported at ~12 (regional) and ~4 (local) μg m^{-3}.

Results for St. Louis (not shown) show strong variability from site to site around the St. Louis area, especially in organic carbon, and nitrate. This is indicative of variable and local sources. St. Louis wintertime nitrate is ~25% local. Site to site variability in nitrate follows that of elemental carbon, also indicative of local pollution from the same sources that are emitting the elemental carbon, presumably vehicles and industry. Similar patterns (also not shown) of variability and site-to-site correlation are seen with EC for wintertime local nitrate and organics in Chicago.

3.2.2 Literature review on SOURCE APPORTIONMENT

In a source-apportionment study of St. Louis, Lee and Hopke (2006) emphasize the importance of transport of agricultural NH_3 as a major contribution for nitrates for St. Louis. The link between urban nitrate in St. Louis and agricultural ammonia was identified in a potential source contribution function (PSCF) analysis. High nitrate concentrations in St. Louis were linked to air parcel trajectories from Iowa, Kansas and, to a lesser extent, a broad region of the upper Midwest. Related results from the Hopke group at Clarkson include Zhao et al. (2005), which provides an extensive analysis of the source regions that influence nitrate levels in St. Louis, Chicago, and several other locations farther to the east. Zhao et al. (2007) outlines a wintertime phenomenon where urban sources of NO_x and NH_3 mix with a wider regional NH_3 source to create urban scale nitrate elevations, especially in the Ohio River valley. The same phenomenon might be at play in Iowa's urban areas. In a 2005 work from the Hopke group along with LADCO authors, Kim et al. (2005) analyze over 250 filters from Bondville, IL and determine the source loadings for that site. Wintertime loadings are consistent with the speciation results shown in section 5 of this work (nitrate > sulfate > primary organics). Lee et al. (2006) focus the PMF method on filters collected at an industrially-impacted site in St. Louis during the St. Louis EPA supersite study.

In a different source apportionment study, Brook et al. (2007) used source-receptor modeling of monitoring data to apportion aerosol loading into local sources (mainly motor vehicles) and regional transport. While the Toronto split is not necessarily applicable to other

cities, 30-45% of $PM_{2.5}$ was of local origin and the remainder was from regionally transported $PM_{2.5}$.

Buzco-Given et al. (2007) also conducted source apportionment using the positive matrix factorization (PMF) method at multiple Midwestern sites (including Northbrook, IL which is north of Chicago, and Bondville IL). Their IMPROVE[2] and STN[3] filter data processed through PMF yields insights about the differences in the organic aerosol fraction between a pair of urban (Chicago) and the rural site (Bondville). The information on the nitrate factor is difficult to interpret because the analysis in the paper is not segregated by season. In another Midwestern source apportionment study, Bae et. al. (2004) show that weekday-weekend trends (that can be used to infer source categories) can be identified with long term records of 1-in-6 day samples, such as those collected in the STN and IMPROVE networks.

3.2.3 Literature Review on MEASUREMENT AND BOX MODELING STUDIES

Box modeling studies aim to assess the sensitivity of the nitrate-ammonia-sulfate-water system to changes in total nitric acid, total ammonia, temperature, and/or relative humidity. In other words, they focus on modeling the "see-saw" box of the conceptual model in figure 3.1. These studies begin with measured data for the gas, aerosol, or total (gas + aerosol) concentrations of the species. They then simulate changes to the makeup of the mixture (e.g. removal of 25% of the ammonia due to controls on upwind ammonia sources) and then thermodynamic models simulate the resulting aerosol mass. This technique is necessary because the nitrate-ammonia-sulfate-water system can respond in complicated ways to changes in composition. This is due to the chemical interactions between these species, and the fact that three of the four species (nitric acid, ammonia, and water) can easily move between the gas phase and the aerosol phase in response to changes in temperature or in the chemical environment. Complicating matters is the fact that nitrate and ammonium are difficult species to measure in the aerosol phase (they tend to be lost during sampling, and this problem is given the technical name of a negative artifact). Further complication arises from the fact that measurements of both the aerosol and the gas phase (in other words nitrate and nitric acid, or

[2] Interagency Monitoring of Protected Visual Environments, http://vista.cira.colostate.edu/improve/ -- A PM monitoring network focused on visibility in National Parks.
[3] Speciation Trends Network, An acronym for the EPA-state PM filter network for tracking of PM chemical speciation – network coverage is weighted toward urban and nonattainment locations.

ammonium and ammonia) are rare, and subject to large errors. This is accounted for in the box modeling studies by repeating the analysis assuming a large degree on uncertainty in the measurements themselves.

Box modeling studies are predicated on having available good measurements of total, aerosol, and gas nitrate, ammonia, and sulfate. These measurements are difficult to perform and require special instrumentation. One successful study aimed at a mass balance on the inorganic composition system was conducted by Wittig et al. (2004) during the Pittsburgh EPA Supersite study. The January 2002 aerosol nitrate profile, as measured by semicontinuous analyzers, peaked at 3.5 μg m^{-3} at 8 AM, and had an afternoon minimum of 1.3 μg m^{-3}. In January 2002, nitrate was 90-100% partitioned to the aerosol phase. Even in July, nitrate was partitioned to the aerosol phase almost 100% in the early morning (and 100% to gas phase from ~10AM until 7 PM), and in October and March, the behavior was intermediate between these limits.

Takahama et al. (2004) used a box model in conjunction with detailed hourly measurements of total nitrate and total ammonia to assess the sensitivity of partitioning to changes in total nitrate, sulfur, and ammonia that may occur due to changes in upwind emissions. They also assess the agreement between the thermodynamic model and the observations, testing a number of assumptions in these thermodynamic models, such as the crystallization state and mixing state of particles.

Vayenas et al. (2005) extended the thermodynamic equilibrium box model to include chemical production, entrainment, and deposition of nitric acid. Thus a full mass balance on nitric acid could be achieved. This is a simple but promising technique for use in Midwest, because nighttime nitric acid formation is set by measurements, and could be particularly valuable in conjunction with hourly measurements of nitrate and ammonia, such as from the Midwest Ammonia Network (Blanchard 2008) or the LADCO ongoing wintertime nitrate study (LADCO 2008). Vayenas et al. predicted wintertime peaks in nitric acid and nitrate at 8 AM due to nighttime production of nitric acid, low temperatures, and high RH. They estimate a net generation/transport of 0.7 μg m^{-3}-hr of total nitrate during the hours from 5 PM to 8 AM and a net generation/transport of 0.1 μg m^{-3}-hr during the day, due to chemical production of ~0.3 μg m^{-3}-hr and simultaneous entrainment of clean air into the mixed layer.

Blanchard (2008) in collaboration with LADCO has recently published a comprehensive study of PM sensitivity to total ammonia and total nitrate using extensive filter data taken as part

of the 2003-2006 Midwest Ammonia Monitoring Project. Sites in Blanchard's analysis include Lake Sugema, IA, Bondville, IL, and Mayville, WI. Key results from this study include: (1) eastern Iowa appears to have, on average, an excess of ammonia in winter. Thus, reductions in nitric acid are more effective than reductions ammonia, although variability around the mean was not analyzed. However, one episode (Feb 2005) was analyzed and during that period, the Iowa sites shift to a more balanced ammonia-nitric acid relationship, such that aerosols are equally sensitive (considering uncertainty in the analysis) to nitric acid or ammonia reductions. Blanchard's large dataset shows that Eastern Iowa in winter may not have as large an excess of ammonia as other articles suggest. There is a tendency to lump all seasons and all parts of the upper Midwest together into an area strong and persistent agricultural ammonia surplus.

Blanchard further has robust results on urban-rural paired measurements for site pairs that are similar in size and location to Iowa towns and cities, such as Bondville and Indianapolis. The urban excess runs at approximately 20% from site to site.

Finally, it should be noted that in areas of concentrated NO_x emissions, there may be a local ammonia limitation. It should also be noted that urban NH_3 emissions are uncertain and may also play an important role.

3.2.4 Literature Review of 3D MODELING STUDIES

Air quality models, also called 3D chemical transport models, perform simultaneous calculation of aerosol chemistry, gas chemistry, and transport. These models are driven by large data input files that include meteorology that is developed on a custom basis for each model run. These models can be used for a variety of air quality planning purposes. Most relevant to this work are (1) the prediction of episodes; and (2) the sensitivity of episodes to controls of different species (NO_x, NH_3, primary $PM_{2.5}$) from different source regions. Once it has been determined (for example, by box modeling – see above) that local $PM_{2.5}$ concentrations can be reduced during episodes by lowering the concentration of a specific compound (e.g. ammonia), 3D chemical transport models can be used to say where does the ammonia reduction need to be done, and to what level does the cut need to be?

Many modeling studies are focused on the issue of sulfate replacement. This is the process by which SO_2 reductions (which are continuing on a large scale under the Clean Air Act) lead to reductions in SO_4 aerosols, but at the same time potentially free up ammonia that would

have previously formed ammonium sulfate, thereby allowing it form ammonium nitrate aerosol. The net effect of this is that a reduction in SO_2 does not fully translate to a reduction in $PM_{2.5}$ aerosol, depending on the amount of nitrate replacement. If ammonia is limited (as it is in summertime in the eastern and southeastern U.S.) this process can be quite important.

For example, Dennis et al. (2008) use CMAQ to simulate January 2002 conditions in paired set of simulations, one with standard emissions, and one with a 25% imposed reduction in SO_2 emissions across the U.S. The model predicts a drop in sulfate aerosol concentration relative to the base case of 10-11% in the Midwest, and a drop of 14-15% in the Southeast. At the same time, nitrate concentrations increase by 15% in the Southeast, and by much less in the Midwest (with zero increase in nitrate over a region centered on Iowa because of high availability of NH_3). Focusing on the Chicago and St. Louis results, Dennis et al. predict a sulfate drop of 7-10% (in response to the nationwide cut in SO_2), which amounts to ~0.4 $\mu g\ m^{-3}$during winter. Nitrate concentrations are unchanged (to within 0.1 $\mu g\ m^{-3}$) for these locations. Dennis et al. further predict that in January nitric acid is partitioned heavily toward the aerosol phase due to cold temperature and sufficient ammonia – 98% partitioning to aerosol phase in Chicago, and 88% partitioning to aerosol phase in St. Louis. Ammonia emissions are highly uncertain in the models, but for the calculation of nitrate replacement, the uncertainty only matters in locations that are in an ammonia limited condition. Dennis et al. (2008) also investigate the N_2O_5 pathway for nitrate, which is accepted as (1) very important to nitrate production during winter; (2) uncertain; and (3) too high in CMAQ, at least relative to measurement-model comparison from Pittsburgh. Changes in the accommodation coefficient of N_2O_5 by a factor of 10 changed modeled total nitrate in Chicago from 3.8 (low γ) to 5.9 $\mu g\ m^{-3}$ (high γ). Similarly, nitrate in Chicago was sensitive to domain-wide changes in NO_x. 25% increases and decreases in NO_x, changed nitrate by 13 to 15% in Chicago. They also mention other important sensitivities, including the relationship between NO_x and O_3, and between nitrate phase and nitrate lifetime.

Phillips and Finkelstein (2008) investigate the agreement of monthly average smoothed contours of major aerosol species on a nationwide domain. They find broad agreement. However, they did not investigate sub-monthly averages and episodes.

Zhang et al. (2008) report that chemical species in air quality models are not very representative of agricultural air quality concerns. Therefore, there are caveats to consider when considering model studies for the upper Midwest.

In a model-based sensitivity study using PMCAMx, Pinder et al. (2007) calculates that ammonia reductions in winter would be effective (sulfur reductions are more effective in summer) at reducing average $PM_{2.5}$ levels in the eastern U.S. The ammonia reductions would be cost competitive if they could be achieved for around $8,000 per ton of NH_3 or lower.

Tesche et al. (2007) evaluate the 36 and 12 km CMAQ results against a wide variety of filter samples. Among all CMAQ species, NO_3 is particularly badly modeled, with overestimation in winter and underestimation in summer. January bias relative to STN sites at + 55%, and fractional error at 118%. Diurnal changes in nitrate were too strong during winter as well.

In a similar evaluation, PMCAMx was tested by Karydis et al. (2008). Underestimation of nitrate in summer is explained by too low production of nitric acid during summer nights via N_2O_5 pathway. In January, paired model measurement values for the rural IMPROVE network have a overprediction (+25%) and versus the urban STN network an underprediction (-43%). Thus the performance is significantly better than in Tesche et al. (2006).

Appel et al. (2008) evaluated CMAQ with a focus on predicting seasonally averaged concentrations by region. For Great Lakes, spring performance is excellent, summer shows a small positive bias, and fall shows a large (~4 μg m^{-3} average) positive bias driven by "Other" (mostly primary) PM, and by ammonium nitrate overprediction. During winter, ammonium nitrate prediction is good in the region (on average), but CMAQ has a positive bias of about 5 μg m^{-3} due to "Other" category. Fall nitrate overprediction is attributed to overestimates of NH_3 emissions, and to the N_2O_5 nitrate pathway.

Spak and Holloway (2008) evaluate CMAQ predictions over the Great Lakes for a 2002 model year run and find some problems with nitrate, but overall reasonable performance in simulating spatial patterns, composition, and episodes. Nitrate prediction is classified as “Good” in winter and fall, as is ammonium for all seasons. “Good” is defined as a fractional bias of ± 30% and a fractional error of 50%. Nitrate prediction is classified as “Problematic” in spring and summer, although the absolute magnitudes of these errors are small. January mean bias (nitrate) reported by Spak is -0.01 for STN and +0.13 for IMPROVE samples. This is better than the

other CMAQ evaluations reported in this work. Spak and Holloways modeling results are examined in detail in section 8.

3.2.5 Literature review on COMBINED BOX MODEL AND 3D MODEL

Pinder et al. (2008) deal with the problem of uncertainty in absolute concentration predictions of models by using the 3D model CMAQ to simulate the change in total ammonia, total nitric acid, and total sulfur in response to emission reductions. The model can calculate the fractional change in the total (gas + aerosol) concentrations fairly accurately. The resulting changes in the total species concentrations are then used in a box model (with the base case set to measured concentrations) to get the sensitivity of aerosol concentrations to emissions changes. They further go on to show that a master variable is present in terms of the nitrate-sulfate-ammonia-water system, and that master variable is the adjusted gas ratio, which is equal to:

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

where DSN is the degree of sulfate neutralization

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

The adjusted gas ratio is shown to be somewhat better as a master variable than gas ratio GR (Blanchard, Roth et al. 2000), and the excess ammonia EA (1999).

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

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

3.2.6 Literature review on NITRATE FOGS

Using a model and measurements, Lillis et al. (1999) studied production and removal of aerosols in fogs in the San Joaquin Valley of California, an area with high ammonia, high nitrate, and frequent fogs. Thus, conditions are similar to some Iowa PM episodes. They found that winter fogs in the study area reduce aerosol concentrations of sulfate, nitrate, and ammonium. The reduction occurs even though there is chemical production (oxidation) of NO_x to nitrate and SO_2 to sulfate in the fogs. Chemical production of nitrate was dominated by the N_2O_5 pathway,

but this was much less than nitrate removal from wet deposition (fog droplets landing on surfaces).

The modeling sensitivity work of Pandis et al. (1989) also holds the view that there is no interesting or important chemistry of NO_x or NO_y on aqueous of fog droplets, except for the NO_3/N_2O_5 pathways that are well known and in the current generation of models, even if they are uncertain in terms of kinetics.

3.2.6 Literature review of IDNR Technical Support Document (October 22, 2008)

The IDNR Technical Support Document: Response to EPA's Proposed Nonattainment Boundaries for Scott County, Iowa, and Rock Island County, Illinois and Muscatine County, Iowa, October 20, 2008 (can be downloaded from IDNR at http://www.iowadnr.gov/air/prof/progdev/files/NA_Response_TJD.pdf) contains a wealth of information, modeling, and analysis on the topic of PM2.5 in Iowa. Although this report addresses similar questions (and in some cases using similar methods), this report was prepared completely independent of the IDNR report. The report is essentially the proposal of nonattainment boundaries for Scott and Muscatine counties and their justification through monitor data analysis, air dispersion modeling, CAMx air quality modeling, and CAMx PSAT source apportionment modeling. The document also includes an extensive analysis of source controls at Blackhawk Foundry submitted by Blackhawk Foundry, and a letter of support from Grain Processing Corporation.

At 174 pages, a comprehensive review is not appropriate here. However, this review of the IDNR report is focused on one area:

- Questions addressed independently by both IDNR and the University of Iowa.

Table 3-4. Selected comparisons of IDNR report and this report

Topic	Page reference	Comments
Impact of emissions from local counties	IDNR page 20 this work sections 3.2.1 and 3.2.2	In a 12 km resolution CAMx model run, zeroing out Rock Island primary PM, SO2, and NOx results in only a 2% decrease in modeled PM in the Scott County grid cell. Similar zero-out studies show rural Scott county sources contribute 3% of PM on exceedance days. The Muscatine county rural zero-out result is the same 3%. These results are higher than the upper bound proposed in this work (25% from local counties during exceedances) based on literature review of Chicago and St. Louis data. However, the methodology in the IDNR report is stronger than the methodology used in this work, with the caveat that the 12 km resolution, topographic influences near monitors, and unique meteorology of episodes may cause biases in the CAMx approach.
Impact of emissions from local counties, vs. state of Iowa, vs. long distance transport	IDNR page 33 this work sections 3.2.1 and 3.2.2	Nitrate on high nitrate days is shown (by PSAT) to come from Muscatine/Scott/Rock Island counties (<3%), from other Iowa counties (~11%), from non-Iowa counties relatively close to Iowa (e.g. NW Illinois, SW Wisconsin) ~10%, and from more distant U.S. sources (~76%). These results are higher than the upper bound proposed in this work (25% from local counties during exceedances) based on literature review of Chicago and St. Louis data. However, the methodology in the IDNR report is stronger than the methodology used in this work, with the caveat that the 12 km resolution, topographic influences near monitors, and unique meteorology of episodes may cause biases in the CAMx approach.
Blackhawk Foundry impact	IDNR page 39 this work section 7.6	IDNR AERMOD and this report come to the same conclusion, that substantial reductions in the increment above background would be achieved by source controls.
Sub-county boundary designations	IDNR page 55 this work section 7.6	This work is entirely consistent with sub-county boundaries, since (a) the individual sources have substantial leverage on the attainment or nonattainment status of the monitors in question; (b) the regional background pollution is not sufficient, by itself, to cause nonattainment.
Directional features of $PM_{2.5}$ at Davenport Wellman St. (Blackhawk Foundry) monitor	IDNR page 95 this work section 7.2	Using a different approach, IDNR shows that the impact peaks at a direction of 200-210 degrees, at a magnitude of 25-30 μg m^{-3} above background. This work shows the impact peaking at 200-220 degrees and sometimes reaching 40 μg m^{-3}.

The only discrepancy between the IDNR report and this report identified at the current time concerns the potential impact of local NOx, $PM_{2.5}$, and ammonia sources during episodes. Rural-urban paired samples from other Midwest locations put the potential for local impact around 25%, but the IDNR modeling puts the local impact at less than 3%. However, the methodology in the IDNR report is stronger than the methodology used in this work, with the caveat that the 12 km resolution, topographic influences near monitors, and unique meteorology of episodes may cause biases in the CAMx approach. This could be investigated further in a using existing datasets, particularly of high time resolution nitrate coupled with source tracers

that are locally emitted such as carbon monoxide and elemental carbon. It could also be investigated more using higher resolution modeling, or (with the highest confidence) by source apportionment studies using organic and metal tracers in combination with source fingerprints.

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4.0 DATA ANALYSIS OF $PM_{2.5}$ MASS DATA

As shown in the literature review, and based on the 9-Factor analyses completed for Scott and Muscatine Counties by IDNR in 2008, data analysis of EPA and IDNR data is expected to show wintertime episodes of high $PM_{2.5}$. The aims of this work are not to replicate those, but rather to begin to (1) study the episodes in more detail in order to help the regulated community, local government, and state government fully understand the balance of local (< 50 km), near-local (50-200 km), and regional factors at play; (2) help bridge the gap between the literature review, which is mostly focused on long term behavior (monthly to seasonal averages), and the episodes which are one to five days in duration; and (3) identify areas of key questions where further study may be prudent; and (4) identify methods of modeling, data analysis, and sampling that could play a constructive role in better understanding nitrate levels in Iowa.

Additional analysis plots are located in various appendices, and only highlights are discussed here.

4.1 Monitoring Data

Data for the analysis of $PM_{2.5}$ observing sites for 2002 through September 2008 are provided by the Iowa Department of Natural Resources (IDNR). Figure 4-1 shows the location of these monitors. More detailed maps of the Davenport monitors are shown in figures 4-2 and 4-3. Extensive maps of monitoring locations can be found on the IDNR website. Photographs of some monitors can be found in Appendix C. A comprehensive table on information on each monitoring site can be found in Appendix D.

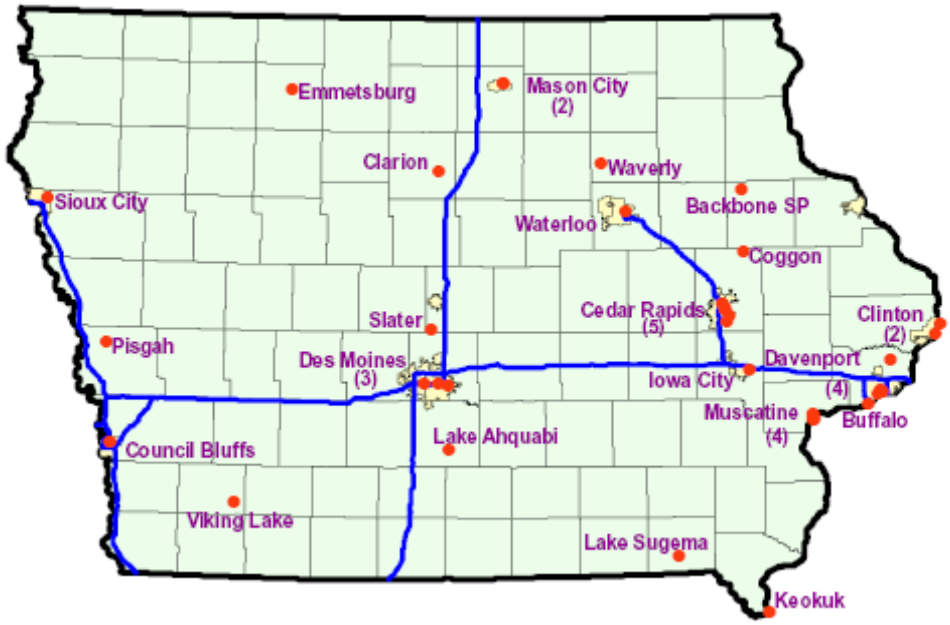


Figure 4-1. Site map of monitoring locations in Iowa.
(http://www.iowadnr.com/air/index.html)

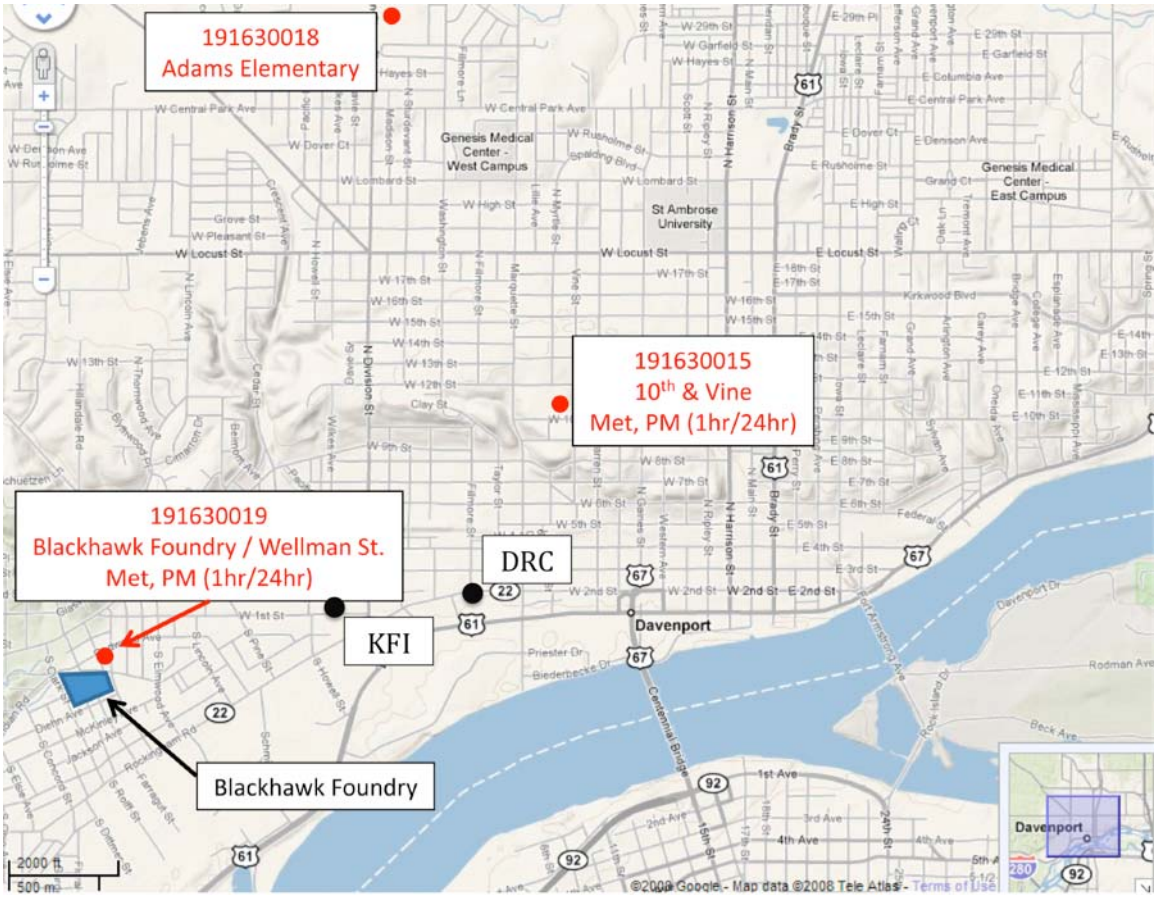


Figure 4-2. Davenport IA. Map of monitoring locations for $PM_{2.5}$.

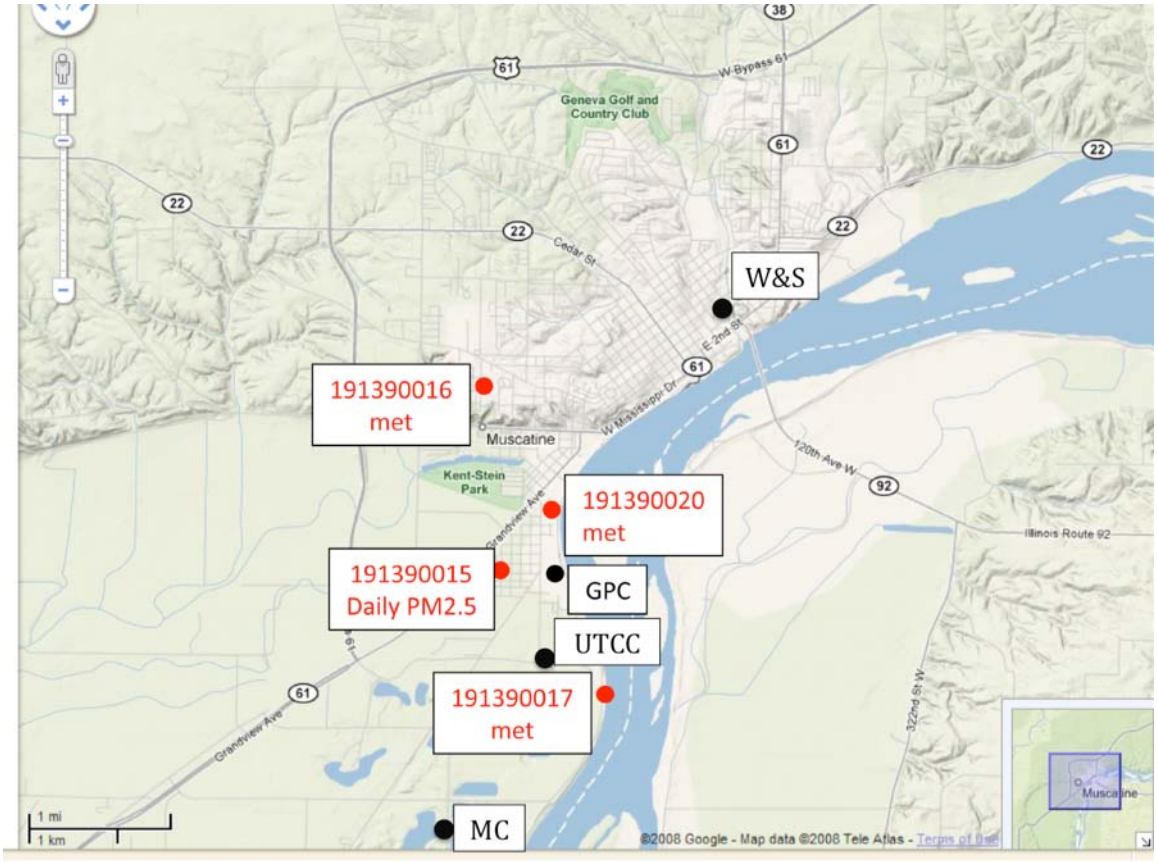


Figure 4-3. Muscatine IA Map with Air Pollution and Meteorological Sensors.

4.2 Analysis of $PM_{2.5}$ Time Series

An example time series recorded at a $PM_{2.5}$ monitoring site is shown in figure 4-4. The unit on the y axis is the "microgram of aerosol per cubic meter of air, abbreviated μg m^{-3}." The blue lines denote the EPA limits on the 24 hour maximum concentration during a year (technically the 98th percentile value), and the annual average limit. These limits are 35 and 15 μg m^{-3}, respectively. At the site used for figure 4-4, there were measurements of $PM_{2.5}$ by two different instruments. The measurement by the 24 hour Federal Reference Method filter-based or "FRM" technique is shown as the stairstepped black line. Because it measures the average concentration from midnight to midnight, the concentration is shown as a flat bar for each day, and variation on shorter timescales cannot be detected by the FRM measurements. The actual concentration changes constantly. This can be seen by the red line, which is made up of hourly measurements from an FDMS TEOM, which is a newer and much faster response technique.

During this period covered in figure 4-4, there were no exceedances of the 24 hour standard (the thick black line never exceeds 35 μg m^{-3}). The grey band labeled 2002-1 is an episode identified by the University of Iowa. These episodes are discussed later.

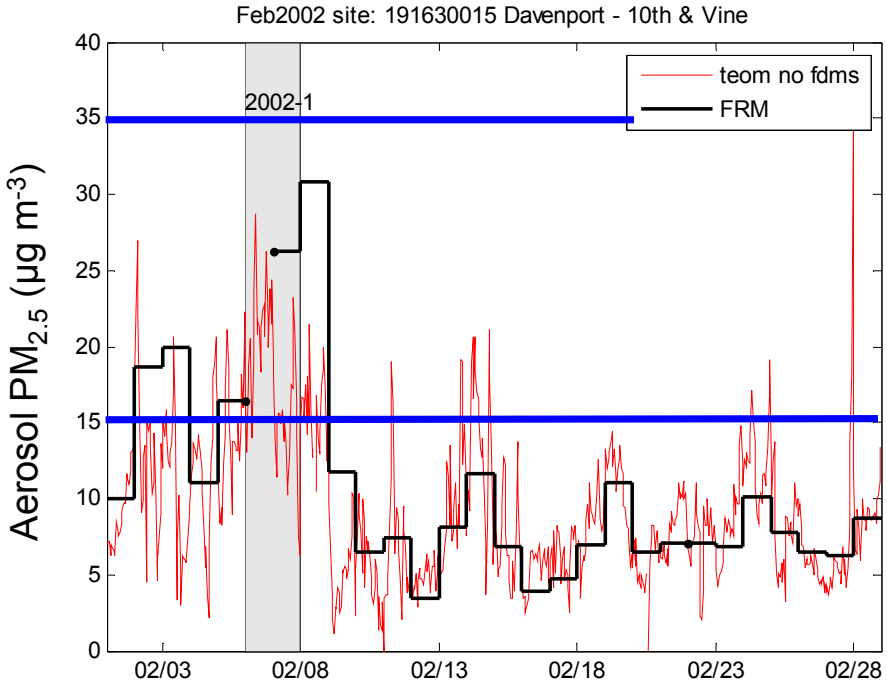


Figure 4-4. Example of a monthly time series of $PM_{2.5}$ measurements from IDNR.

The first main analysis completed using the daily $PM_{2.5}$ values (as measured by IDNR FRM monitors), was to develop box-and-whisker plots showing the year-to-year $PM_{2.5}$ distributions measured at each of the Iowa monitoring locations. Plots for the nine sites with highest median $PM_{2.5}$ levels are shown in figures 4-5 and 4-6. Diagrams for all sites can be found in appendix B. Three lines are added to the plot in addition to the standard values for a box and whisker diagram – the mean $PM_{2.5}$ value (black line, black boxes), the 98th percential (green line), and the compliance threshold (grey line at 35.5 µg m^{-3}). The µg m^{-3} two sites that are most problematic in terms of nonattainment (Muscatine, and Davenport Wellman St.) are shown in figure 4-5.

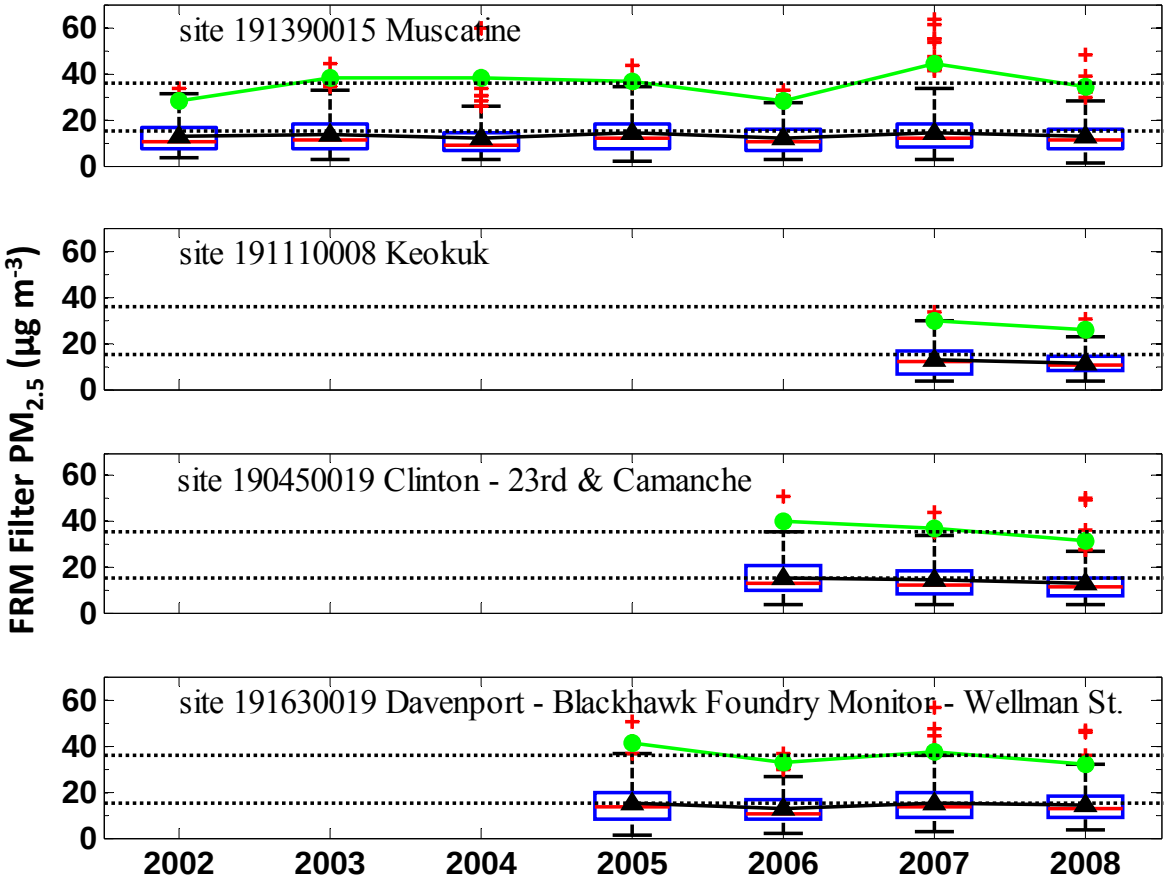


Figure 4-5. Box and whisker plots showing year by year mean, median, and 98th percentile for the 4 monitors in the state with the highest median $PM_{2.5}$ levels. The green line with circles is the 98th percentile and the black line with triangles is the mean. Lower and upper dotted black lines refer to the annual average standard (15 µg m^{-3}) and the 24-hr standard (35.5 µg m^{-3}).

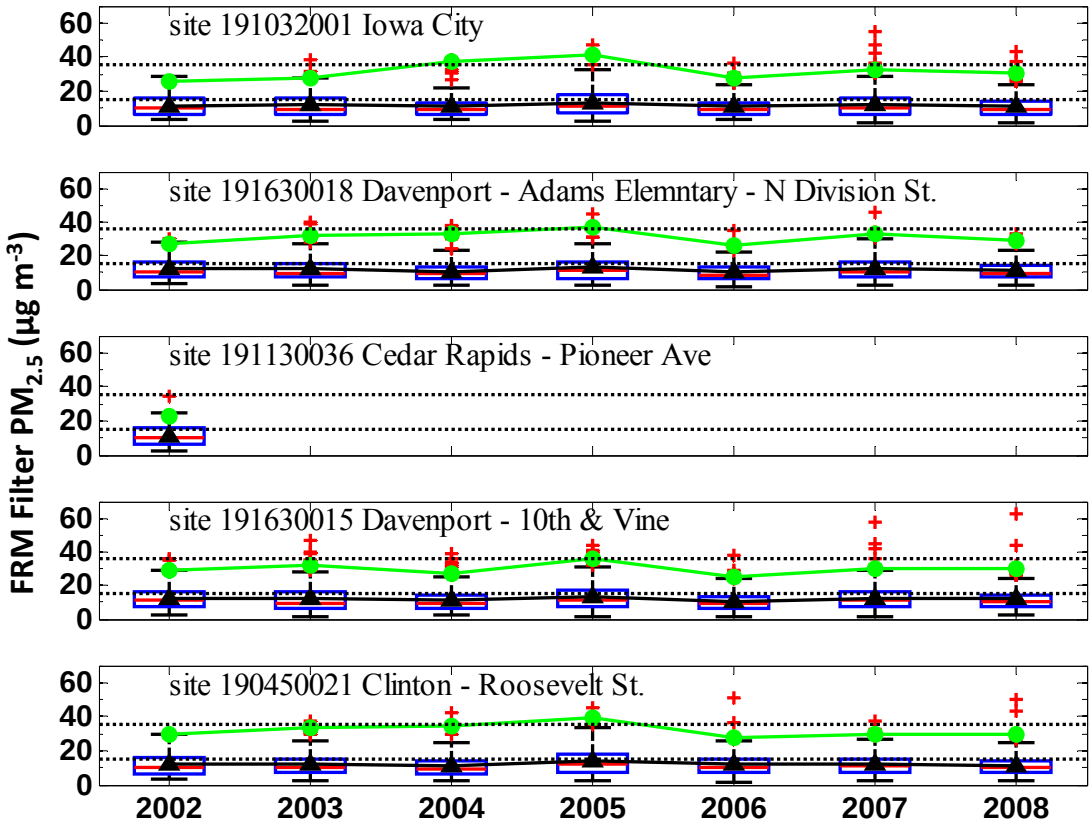


Figure 4-6. Box and whisker plots showing year by year mean, median, and 98th percentile for the 5 monitors in the state ranked 21-25 (out of 29) in median $PM_{2.5}$ levels. The green line with circles is the 98th percentile and the black line with triangles is the mean. Lower and upper dotted black lines refer to the annual average standard (15 µg m^{-3}) and the 24-hr standard (35.5 µg m^{-3}).

Conclusions drawn from the box-and-whisker diagrams are as follows.

- $PM_{2.5}$ is not normally distributed – but rather is skewed such that high PM events are much farther from median levels than low PM events. The skewed distributions cause mean levels to exceed median levels. This is normal for air pollution statistics.
- 98th percentile values are below the compliance thresholds for most sites in most years. However, some of the more polluted sites have 98th percentile values that can fluctuate above and below the threshold.
- Annual average $PM_{2.5}$ is typically below the 15 µg m^{-3} standard at all sites except for the Davenport Wellman St. monitor, where 2005 and 2007 exceeded the 15.0 µg m^{-3} threshold. Mean $PM_{2.5}$ values at that site were 15.21, 13.05, 15.07, and 14.23 for years 2005-2008, with a mean of 14.39 µg m^{-3} and a standard deviation on the annual mean of 0.99. (2008 values through July).
- 98th percentile values fluctuate considerable due to variability in regional pollution (as shown by fluctations correlated from site to site), and also by variability in wind patterns and emission levels of local sources.

- Although no formal statistical tests are employed, there are no obvious long term $PM_{2.5}$ trends in this dataset. Year to year variability exceeds any long term trend present in the data. It should be noted that average, peak, and 98th percentile $PM_{2.5}$ need not have the same trends. Furthermore, $PM_{2.5}$ trends could potentially differ by season.

4.3 – Episode Lists

The second major data analysis activity was to develop graphical time series of daily PM levels spanning multiple sites. These can be used to find "regional" events where multiple monitors share the same temporal pattern for $PM_{2.5}$. A comprehensive set can be found in Appendix B. These figures are not used directly for any analysis, but rather provide (a) some quality control on the data processing done by the University of Iowa team; and (b) context for other analysis, such as the development of a comprehensive episode list.

These time series in Appendix B enabled the development of a comprehensive episode list. Similar to that done by the IDNR in the 9-factor analysis, the $PM_{2.5}$ records were analyzed systematically using MATLAB scripts to identify episodes that include days meeting the following descriptions.

Table 4-1. Episode classification criteria.

Event Classification	Description and Criteria
1-R	Regional PM event with 3 or more monitors exceeding 35 μg m^{-3}. These are typically multiday episodes. The criteria is employed such that on the peak day of the episode, 3 or more monitors must exceed 35 μg m^{-3}.
1-N	Non-regional event with 1 monitor exceeding 35 μg m^{-3}.
2-R	Regional PM event with somewhat lower peak levels than a 1R event. Peak monitor must exceed 32 μg m^{-3f}, 2nd highest must exceed 30 μg m^{-3}, and 3rd highest must exceed 28 μg m^{-3}.
2-N	Non regional PM event, with a single monitor exceeding 32 μg m^{-3}.

Please note that the Table 4-1 criteria were used as a guideline, but not as an absolute rule in event classification. For example, in 2002, it was necessary to identify episodes to compare against available 2002 PM model predictions. Applying the strict criteria above would give no regional episodes in 2002. Therefore, for 2002, the criteria were relaxed. Second, non-regional events were examined using the time series in Appendix B. If multiple monitors all rose and fell together on the day of the 1-N or 2-N event, but the formal criteria for a regional episode were not met, a subjective decision was made on whether the event was "more regional" or "more local" in its character. Finally, the events should properly be understood not as regional in the sense that the events span hundreds of kilometers, but rather that they are multi-monitor events within the IDNR sampling network. Since some cities have multiple sites – elevated PM in a

single city such as Cedar Rapids or Davenport is sufficient to trigger a multisite episode by this criteria. In fact, most episodes are over large scales.

A summary of the strongest regional (or multi-monitor) PM episodes during 2002-2008 are shown in Table 4-2. A comprehensive list can be found in Appendix A. All non-regional $PM_{2.5}$ episodes identified are found in Table 4-3. The non-regional nature of the episodes in Table 4-3 is confirmed by noting the difference between the high monitor, and the next highest 3 monitors in the state. Many of these events have levels that are 20 $\mu g\ m^{-3}$ greater than other monitors across the state.

Table 4-2 skips from the 20^{th} most severe episode, to the 22^{nd}, 24^{th}, 40^{th}, and 50^{th}. This is because the specific episodes were targeted for comparison to available modeling or meoteorological data.

The monthly frequency of episodes is shown in figure 4-7. There are two "seasons" for air pollution – a warm season, and a cold season. Both the warm and cold seasons are important in defining the impact of regional air pollution on compliance with the 24 hour standard. Defining the cold season as November – March, the warm season as June – September, and the months of April, May, and October as transitional, the breakdown of episodes is as shown in Table 4-4. A histogram of episode severity in each of the seasons is shown in figure 4-8.

Table 4-2. Key high PM episodes spanning 3 or more monitors identified by the University of Iowa. Full list in Appendix A.

Ranking (by multi-monitor average)	Univ. of Iowa Episode Code	Season (Cold / Warm)	Estimated Start Date	Estimated End Date	Peak FRM Measurement	Location – Peak FRM Measurement	Multisite (~5) $PM_{2.5}$ Avg.	Notes
1	2007-20	C	12/17/07	12/21/07	63.0	Waterloo	49.6	b, c
2	2006-7	C	11/21/06	11/27/06	50.9	Clinton - 23rd & Camanche	42.6	b,c
3	2005-5	C	1/27/05	2/3/05	53.2	Waterloo	40.3	b,c
4	2005-7	W	7/31/05	8/3/05	50.5	Davenport – Wellman St.	40.1	c
5	2003-6	W	4/15/03	4/19/03	43.9	Muscatine	39.7	
6	2004-4	W	7/1/04	7/4/04	59.3	Muscatine	39.4	
7	2003-9	W	9/6/03	9/11/03	44.0	Cedar Rapids - Wenig Rd Ne	39.4	
8	2004-7	C	12/26/04	12/30/04	42.3	Clinton - Roosevelt St.	39.3	b
9	2008-5	C	2/21/08	2/25/08	50.5	Clinton - Roosevelt St.	38.8	c
10	2004-2	C	2/16/04	2/20/04	42.3	Mason City	38.6	b,c
11	2007-4	C	3/6/07	3/10/07	44.2	Davenport - Wellman St.	37.9	c
12	2005-8	W	9/5/05	9/13/05	40.5	Davenport - Wellman St.	36.5	
13	2005-10	C	12/20/05	12/25/05	39.7	Clinton - Roosevelt St.	36.3	b
14	2003-2	C	2/27/03	3/1/03	39.7	Davenport - 10th & Vine	36.1	b
15	2008-4	C	1/31/08	2/4/08	37.6	Sioux City	35.9	
16	2003-8	W	8/12/03	8/14/03	39.4	Des Moines Iowa - Carpenter	35.7	
17	2003-3	C	3/11/03	3/20/03	48.7	Cedar Rapids - Wenig Rd Ne	35.0	
18	2005-6	W	6/23/05	6/29/05	41.7	Davenport - Wellman St.	34.6	
19	2004-1	C	1/8/04	1/11/04	34.5	Des Moines Iowa - Carpenter	33.1	
20	2004-6	W	10/26/04	10/29/04	34.3	Clinton - Roosevelt St.	32.5	
22	2007-18	W	11/17/07	11/20/07	39.1	Davenport - Wellman St.	32.2	c
24	2002-10	W	8/26/02	9/2/02	36.7	Cedar Rapids - Wenig Rd Ne	31.6	a
40	2002-1	C	2/6/02	2/8/02	30.8	Davenport - 10th & Vine	27.8	a
50	2002-12	C	12/10/02	12/16/02	33.8	Muscatine	23.6	a

Note a – Focus of comparison to CMAQ model Note b – Focus for compositional analysis of episode using STN data
Note c – Focus for examination of spatial patterns

University of Iowa Episode Code	Date	FRM $PM_{2.5}$ ($\mu g\ m^{-3}$)	Monitor	Next 3 Highest $PM_{2.5}$ Levels Measured Statewide on Same Day ($\mu g\ m^{-3}$)		
2002-2	2/12/02	30	Cedar Rapids - Wenig Rd Ne	4	3	
2002-3	2/22/02	29	Council Bluffs	15	13	13
2002-9	7/17/02	35	Davenport - 10th & Vine	28	18	
2002-11	9/27/02	30	Davenport - 10th & Vine	23	15	12
2003-4	4/3/03	34	Clinton - Roosevelt St.	31	28	26
2003-5	4/6/03	35	Muscatine	14	12	12
2003-7	4/24/03	38	Muscatine	15	14	14
2004-3	4/24/04	38	Muscatine	20	20	20
2005-1	1/1/05	34	Muscatine	12	12	10
2005-3	1/16/05	34	Council Bluffs	18	16	16
2005-9	9/13/05	41	Davenport - Wellman St.	24	24	23
2006-1	3/1/06	34	Des Moines Iowa - Carpenter	19		
2006-3	8/6/06	32	Clinton - 23rd & Camanche	28	27	27
2007-1	2/23/07	44	Muscatine	16	15	15
2007-2	2/24/07	53	Muscatine	11	10	9
2007-3	2/28/07	55	Muscatine	21	19	19
2007-5	5/3/07	42	Muscatine	22	18	17
2007-6	5/4/07	61	Muscatine	26	19	16
2007-7	5/5/07	63	Muscatine	27	23	23
2007-8	5/6/07	34	Muscatine	17	15	14
2007-12	6/18/07	33	Davenport - Wellman St.	17	16	15
2007-17	10/29/07	34	Davenport - Wellman St.	9	9	8
2008-1	1/7/08	32	Davenport - Wellman St.	24	24	24
2008-7	3/17/08	34	Muscatine	19	18	17
2008-8	3/20/08	32	Muscatine	17	11	11
2008-9	3/21/08	33	Muscatine	14	14	14
2008-10	4/23/08	36	Muscatine	11	10	9
2008-11	4/30/08	32	Muscatine	22	19	18
2008-12[1]	7/4/08	62	Davenport - 10th & Vine	22	18	11

Table 4-3. All Non-regional PM episodes identified by University of Iowa

[1] This episode has been declared exceptional by IDNR based on evidence that it was caused by Fourth of July fireworks.

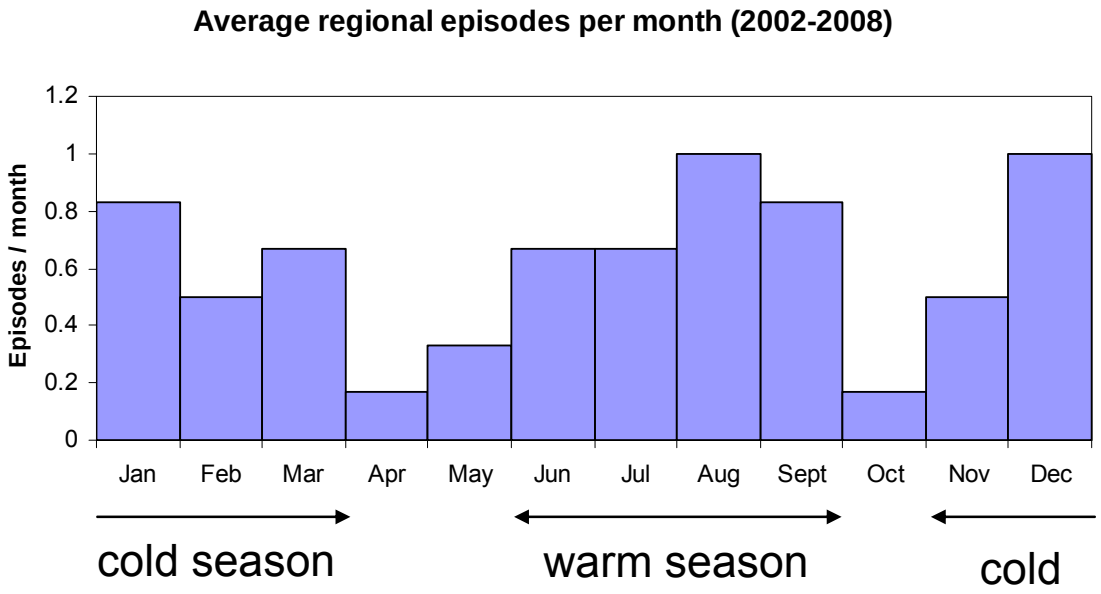


Figure 4-7. Monthly occurrence frequency of multi-monitor episodes with $PM_{2.5}$ > 30 µg m^{-3}

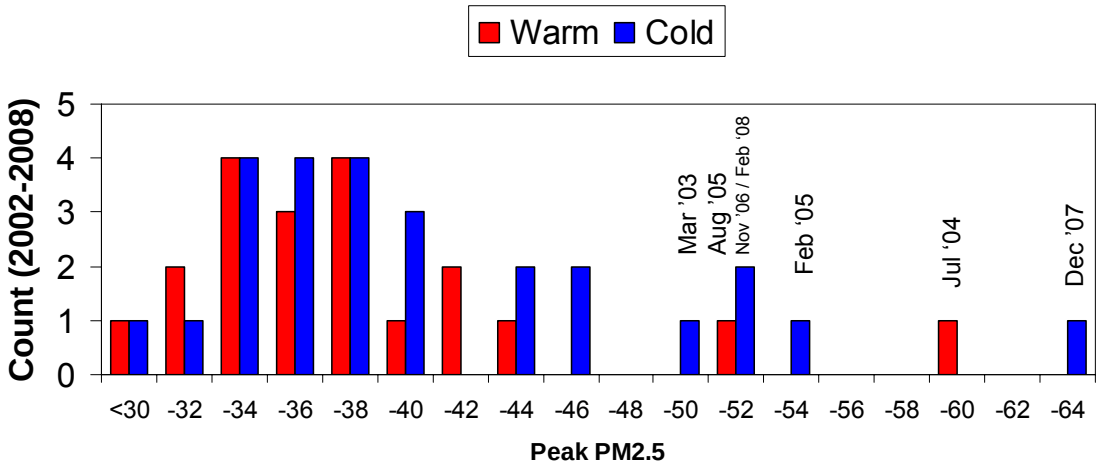


Figure 4-8. Histogram of warm- and cold-weather episode severity.

Table 4-4. Selected statistics about cold and warm season regional episodes

Statistic	Warm Season (June-Sept)	Cold Season (Nov-Mar)
Total number of regional (multiple monitors in Iowa) episodes > 30 µg m^{-3} identified, 2002 – June 2008	19	21
Total number of regional episodes > 35 µg m^{-3} identified	12	18
Number of episodes in the top 12 list	3	9
Mean peak Iowa FRM reading during episode	37.6	40.0
Average monthly frequency (note: transition month episode frequency is 0.22 episodes per month)	0.79	0.70

4.4 Combined meteorological and PM time series

To facilitate the detailed understanding of the progression of each episode, the relationship between meteorology and episodes, and the behavior of the high time resolution hourly meteorology and PM monitors, a series of monthly time series were developed. An example is shown in Figure 4-9.

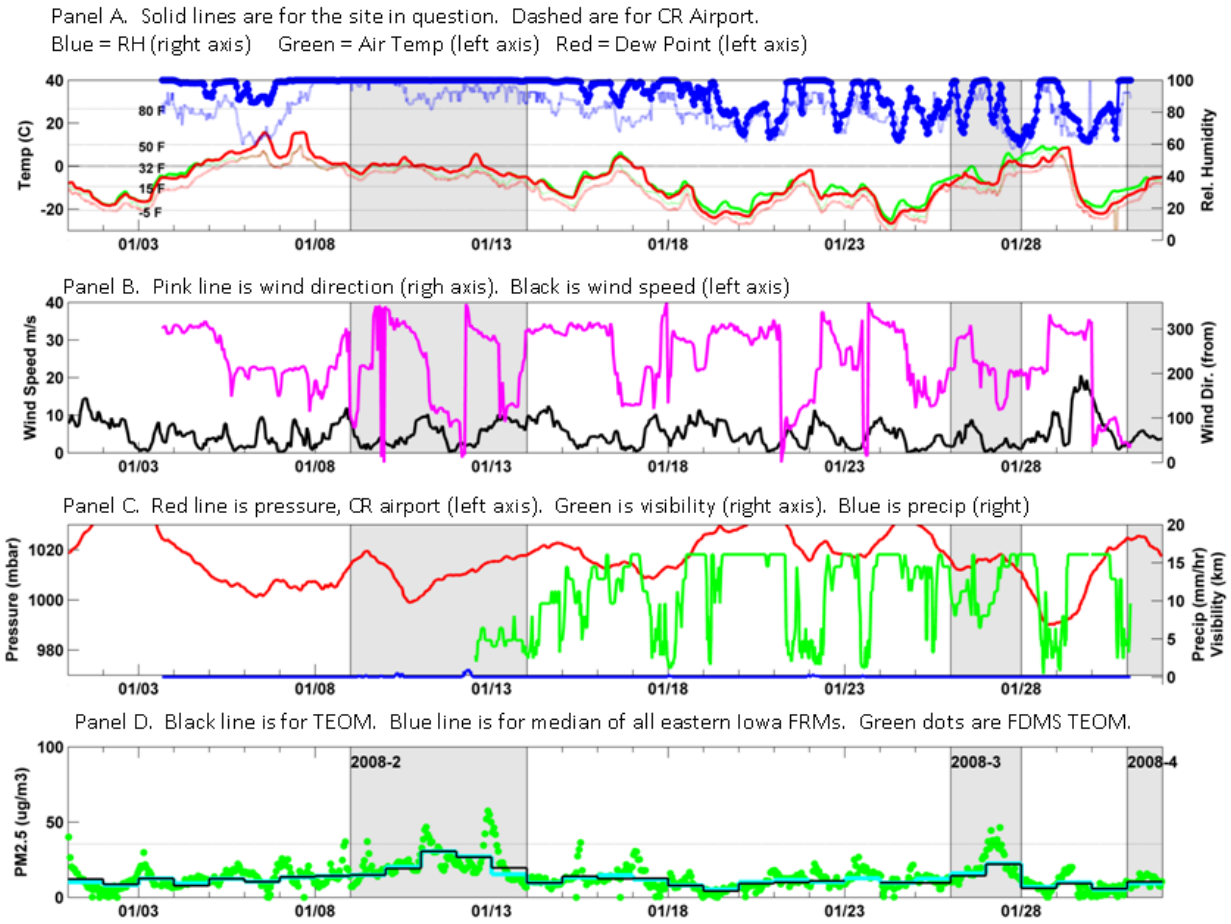


Figure 4-9. Multipanel plot for one month. Data includes met and PM data from Davenport 10th and Vine & meteorology from the Cedar Rapids Airport. Panel A focuses on meteorology including temperature, dewpoint, and relative humidity. Panel B focuses on wind speed and wind direction. Panel C focuses on pressure, visibility, and precipitation. Panel D has daily $PM_{2.5}$, hourly $PM_{2.5}$, and an eastern Iowa median $PM_{2.5}$ for comparison of individual sites to the eastern Iowa median. Multi-monitor episodes are marked in grey.

4.5 Smoothed contour maps

An additional major data analysis activity was to make smoothed contour maps of concentrations during episodes. This can show urban-rural concentration differences, and spatial patterns can give a hint as to the transport and source regions involved in the episodes. An example of such a figure is shown in figure 4-10, and a more comprehensive set of smoothed contour maps can be found in Appendix F.

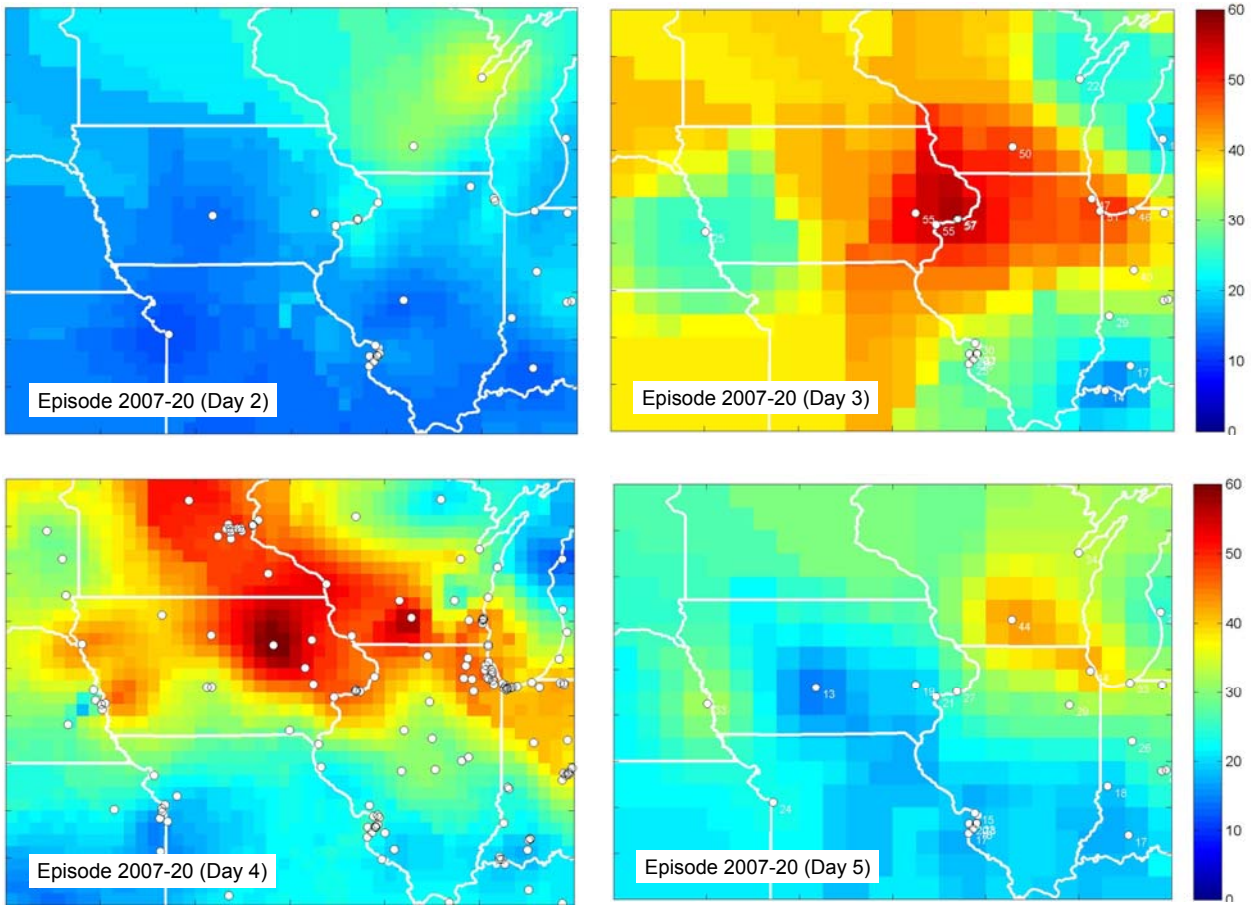


Figure 4-10. Spatial patterns during days 2-5 of an episode during December 2007. This is the strongest episode found in our analysis (University of Iowa episode code 2007-20, with a peak FRM measurement of 63 on day 4, and a five site average $PM_{2.5}$ of 50 on day 4. Pixelation on the smoothing calculation is adjusted up or down based on the number of monitors.

This episode, as viewed in terms of meteorology and from the 10th and Vine location, is shown in figure 4-11.

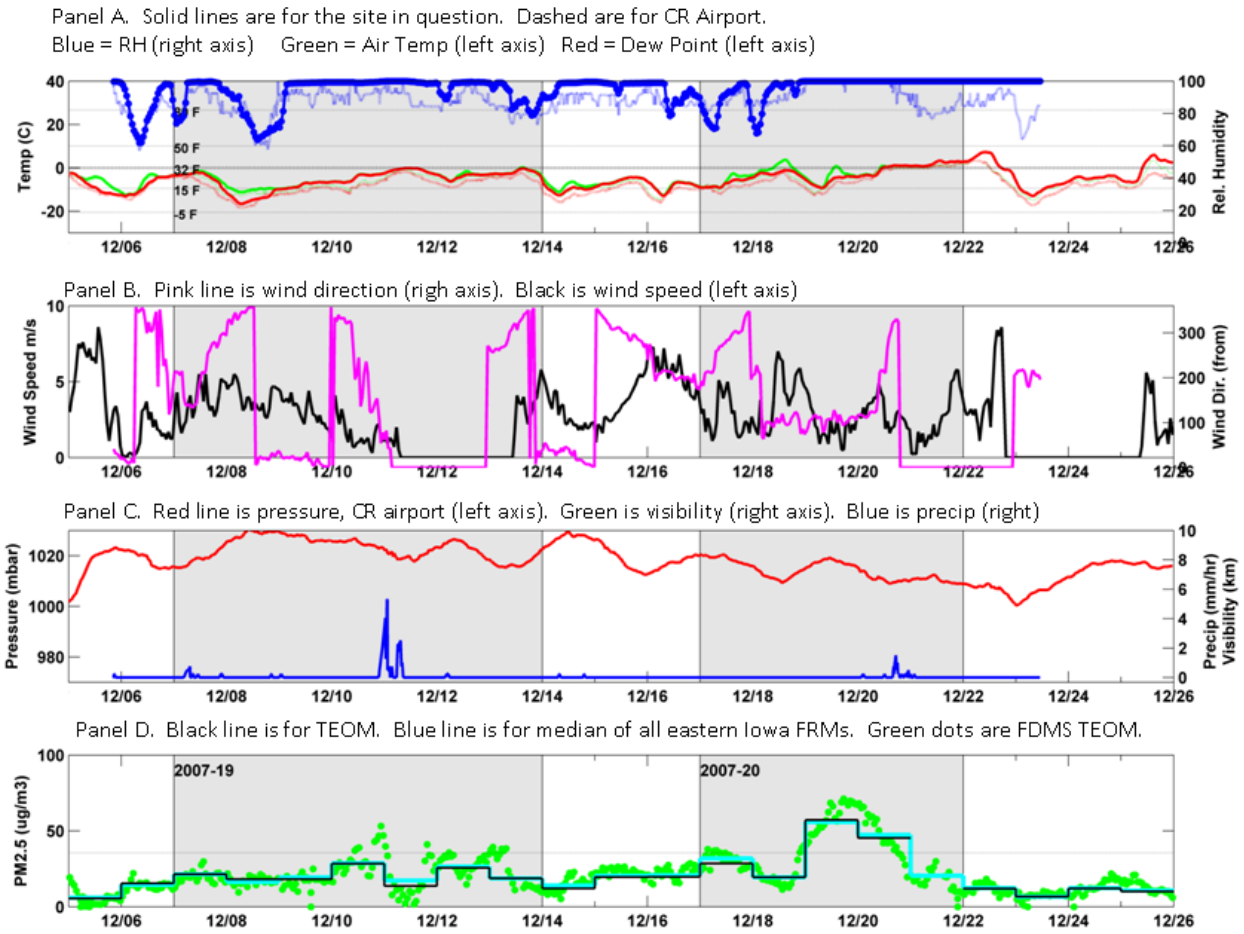


Figure 4-11. Multipanel plot including episode 2007-20 shown in figure 4-10. The grey band for 2007-20 begins on 12/17.

The period is fairly cold (just below 0°C or 32°F) warming to just above freezing during the peak portion of the episode. RH is very high, wind speeds are low, and flow shifts to wind from the east toward the peak of the episode. This is representative of the typical pattern, although the concentrations are atypical. Meteorology's link to episodes is discussed in detail in section 6.

4.6 Statistical Simulation of Attainment and Non-Attainment Likelihood

Using the available FRM measurements at each site from 2002 to 2006, a Monte Carlo type simulation was done to estimate the long term average value of the 98th percentile concentration value at each site in Iowa.

The key classification was: what fraction of years that can be classified as follows:

A. Average of last 3 year's 98th percentile value > or equal to 35.5 (non attainment)

B. Average of last 3 year's 98th percentile value < 35.5 (attainment)

Calculation was done as follows:

1. Load all FRM data for the given site
2. Count the number of valid FRM samples [n_{sample}]
    3. Select a random number *R* between 1 and n_{sample}
    4. Assume the FRM value of our hypothetical day is equal to $PM_{2.5}$ of day(*R*)
    5. Repeat steps 3-4 for 365 times, building up a year of synthetic data
    6. Calculate the 98th percentile
7. Repeat steps 3-6 for 1000 repetitions, building up a list of 1000 hypothetical years, each with a 98th percentile value
8. Calculate the 3 year running average of the 98th percentiles. (this gives a list of 998 values).
9. Classify the 998 values as falling into class A or B (see above).
10. Report an attainment likelihood that is the count of B events / 998

The result of this calculation is shown in table 4-5.

Table 4-5. Estimated likelihood of attainment with 35 μg m-3, from extrapolation of 2002-2008 monitoring values

site	site	I. percent of 3-year averaged in attainment	II. base case + 1 μg m^{-3} added to all samples	III. base case + 1 μg m^{-3} added to all samples and 1 addition episode per year
191471002	Emmetsburg	100.0%	100.0%	100.0%
191370002	Montgomery County - Viking Lake	100.0%	100.0%	99.8%
191532510	Clive	100.0%	100.0%	100.0%
191970004	Clarion	100.0%	100.0%	100.0%
191770005	Lake Sugema State Park	100.0%	100.0%	100.0%
191530030	Des Moines Iowa - Carpenter	100.0%	100.0%	100.0%
191930017	Sioux City	100.0%	100.0%	100.0%
191532520	Des Moines - NE 3rd St - Saylor Twp	100.0%	100.0%	100.0%
191130037	Cedar Rapids - Wenig Rd Ne	99.3%	97.3%	88.1%
191770006	Van Buren County - Lacey Trail	100.0%	100.0%	100.0%
190130008	Waterloo	100.0%	99.8%	97.0%
190550001	Backbone St. Park	84.3%	72.5%	54.7%
191130040	Cedar Rapids - 11st St. Nw	100.0%	100.0%	99.3%
191550009	Council Bluffs	100.0%	100.0%	100.0%
191032001	Iowa City	96.3%	88.1%	72.7%
191630018	Davenport - Adams Elemntary - N Division St.	99.5%	96.6%	89.1%
191130036	Cedar Rapids - Pioneer Ave	100.0%	100.0%	100.0%
191630015	Davenport - 10th & Vine	100.0%	99.8%	97.5%
190450021	Clinton - Roosevelt St.	99.6%	96.0%	85.1%
191390015	Muscatine	42.6%	18.2%	5.2%
191110008	Keokuk	100.0%	100.0%	100.0%
190450019	Clinton - 23rd & Camanche	51.2%	25.1%	9.9%
191630019	Davenport - Wellman St.	24.7%	7.0%	2.4%

The values in the column I of percentages are calculated directly from the IDNR $PM_{2.5}$ data, and form an estimate on the future compliance of Iowa's monitoring sites. The accuracy of these values is predicated on the assumption that the period 2002-2008 is representative of future conditions. The uncertainty is larger than is apparent in the plot. Without considering a wider spatial area (states around Iowa) and a longer time history, it is difficult to gage the stability of the number and severity of episodes. Some sites without full monitoring records have estimates that are less precise than others. More sophisticated methods of performing this forecast are available, and can be employed to Iowa's situation if needed (e.g. more sophisticated statistical

model, using estimation procedures for missing data, and also involving 3D air quality models and/or dispersion models).

Many variations on this calculation can be performed. For example, the following scenarios can be considered:

- Increase (decrease) in frequency or severity of regional episodes
- Increase (decrease) in average $PM_{2.5}$ concentration
- Decrease in levels associated with source controls

In table 4-5, two cases are considered with increases in regional PM pollution. Column II includes an additional 1 $\mu g\ m^{-3}$ on all samples. This impacts attainment at a few of the sites that are closest to the threshold right now, such as Iowa City. Addition of one extra regional episode each year at every monitoring location (column III), makes attainment questionable at multiple sites, including some in Clinton, Cedar Rapids, and Davenport. Addition of two extra regional episodes (not shown) each year brings four Iowa monitors to below 80% attainment, Iowa City, Clinton (Roosevelt), Cedar Rapids, and Davenport (Adams Elementary).

5.0 SPECIATED $PM_{2.5}$ DATA ANALYSIS

The goals of this section are to answer the following questions about cold weather regional PM episodes:

1. What is the absolute concentration and fraction of ammonium nitrate (e.g. nitrate / total PM)? How does this compare to PM composition during non episodes during the same season?
2. How do these quantities vary, from episode to episode, and spatially?
3. In terms of nitrate, what is the balance of local nitrate production, vs. regional nitrate levels?

5.1 Scope of Data Analysis Activities

The EPA Speciation Trend Network (STN) is a made up of over 150 urban monitoring sites located throughout the country. Each site collects 24-hour duration fine particle samples ($PM_{2.5}$) that are analyzed by ion chromatography and other techniques. The species analyzed by the STN are summarized in the table below.

Table 5-1 List of Species Analyzed in Speciation Trends Network (STN) Samples

Aluminum	Chromium	Mercury	Sodium
Ammonium Ion	Cobalt	Molybdenum	Sodium ion
Antimony	Copper	Nickel	Strontium
Arsenic	Europium	Niobium	Sulfate
Barium	Gallium	Nitrate	Sulfur
Bromine	Gold	Phosphorus	Tantalum
Cadmium	Hafnium	Potassium	Terbium
Calcium	Indium	Potassium ion	Tin
Carbon	Iridium	Rubidium	Titanium
Carbon, Elemental Total	Iron	Samarium	Vanadium
Carbon, Organic Total	Lanthanum	Scandium	Yttrium
Cerium	Lead	Selenium	Zinc
Cesium	Magnesium	Silicon	Zirconium
Chlorine	Manganese	Silver	

There were three active STN sites located in Iowa from 2003 to the present. The sites are located in Cedar Rapids (EPA site id# 191130037), Davenport (EPA site id# 191630015), and Des Moines (EPA site id# 191530030). Speciated $PM_{2.5}$ concentrations were obtained from the

Visibility Information Exchange Web Site (VIEWS). The Cedar Rapids (CR) and Des Moines (DM) sites report concentrations every sixth day, the Davenport (DP) site reports concentrations every third day.

The speciated data was analyzed on a relative and absolute basis. The data was broken down into seven categories; Elemental Carbon (EC), Organic Carbon (OC), Nitrate, Sulfate, Ammonium, Metal/Crustal, and Other. The Metal/Crustal categories was assumed to be the sum of the concentration of all species listed in Table 1 excluding elemental carbon, organic carbon, nitrate, sulfate, and ammonium. The Other is calculated as the value necessary to bring the summed components of the STN filter up (or down) to the total value of the paired FRM mass measurement.

5.2 Results for Composition Analysis of Episodes

Speciated data was collected for the winter season (November through March) at each site from 2003 to 2007. From this information a winter season average was determined for each year at each site on a relative and absolute basis. The tables below summarize this analysis.

Table 5-2 November-March Averages of Absolute Speciated $PM_{2.5}$ Concentrations ($\mu g\ m^{-3}$).

SITE	DATE	Total $PM_{2.5}$	EC	OC	NO_3	SO_4	NH_4	Metal/ Crustal	Other
CR	2002-2003	13.633	0.405	2.434	4.478	2.228	2.135	1.356	0.597
CR	2003-2004	12.236	0.180	2.111	4.162	2.110	1.813	1.094	0.765
CR	2004-2005	14.810	0.216	2.131	5.939	2.630	2.653	1.256	-0.015
CR	2005-2006	10.791	0.273	2.025	3.776	2.295	1.896	1.042	-0.516
CR	2006-2007	12.643	0.309	2.464	4.783	2.244	2.203	1.224	-0.584
CR	2007-2008	17.290	0.417	2.505	6.250	2.050	3.093	1.185	1.792
DP	2002-2003	15.320	0.448	3.099	5.190	2.754	2.509	1.546	-0.226
DP	2003-2004	12.356	0.256	2.351	3.671	2.083	1.701	1.183	1.111
DP	2004-2005	14.368	0.327	2.727	5.188	2.464	2.409	1.360	-0.107
DP	2005-2006	10.903	0.348	2.356	3.745	2.296	1.942	1.182	-0.966
DP	2006-2007	12.542	0.405	2.884	4.160	2.090	1.999	1.273	-0.269
DP	2007-2008	14.147	0.468	2.679	4.853	2.135	2.283	1.271	0.458
DM	2002-2003	10.825	0.441	2.765	3.060	1.793	1.495	1.191	0.081
DM	2003-2004	11.929	0.249	2.350	4.158	1.901	1.740	0.987	0.544
DM	2004-2005	12.467	0.282	2.209	4.612	2.119	2.073	1.159	0.013
DM	2005-2006	9.596	0.268	2.034	3.440	2.056	1.744	1.013	-0.959
DM	2006-2007	11.448	0.363	2.320	4.099	1.857	1.829	1.085	-0.105
DM	2007-2008	14.090	0.540	2.515	5.272	1.681	2.405	1.072	0.605

Table 5-3 Seasonal Averages of Relative Speciated $PM_{2.5}$ Concentrations

SITE	DATE	EC	OC	NO_3	SO_4	NH_4	Metal/Crustal	Other
CR	2002-2003	0.0380	0.2317	0.3241	0.1595	0.1472	0.1104	-0.0108
CR	2003-2004	0.0157	0.2131	0.3043	0.1896	0.1400	0.0998	0.0375
CR	2004-2005	0.0183	0.1895	0.3790	0.2006	0.1759	0.0955	-0.0589
CR	2005-2006	0.0358	0.2433	0.3595	0.2213	0.1801	0.1071	-0.1471
CR	2006-2007	0.0270	0.2196	0.3693	0.1926	0.1717	0.1077	-0.0880
CR	2007-2008	0.0282	0.2145	0.3244	0.1298	0.1503	0.0920	0.0609
DP	2002-2003	0.0343	0.2442	0.3141	0.1775	0.1519	0.1117	-0.0336
DP	2003-2004	0.0232	0.2297	0.2701	0.1689	0.1269	0.1023	0.0790
DP	2004-2005	0.0262	0.2244	0.3408	0.1862	0.1619	0.1035	-0.0430
DP	2005-2006	0.0361	0.2644	0.3347	0.2244	0.1763	0.1190	-0.1549
DP	2006-2007	0.0345	0.2543	0.3194	0.1778	0.1540	0.1100	-0.0501
DP	2007-2008	0.0468	0.2515	0.3122	0.1655	0.1517	0.1116	-0.0392
DM	2002-2003	0.0477	0.2819	0.2794	0.1706	0.1343	0.1141	-0.0281
DM	2003-2004	0.0241	0.2382	0.3103	0.1786	0.1368	0.0928	0.0190
DM	2004-2005	0.0265	0.2183	0.3389	0.1872	0.1597	0.1021	-0.0327
DM	2005-2006	0.0338	0.2524	0.3539	0.2204	0.1772	0.1134	-0.1510
DM	2006-2007	0.0377	0.2415	0.3288	0.1779	0.1514	0.1114	-0.0487
DM	2007-2008	0.0466	0.2441	0.3197	0.1283	0.1435	0.0995	0.0184

The speciated concentrations were analyzed during the episodes with the six highest total $PM_{2.5}$ concentrations where data was available for at least two of the three Iowa sites (episode #'s 2007-20, 2006-7, 2005-5, 2004-7, 2007-4, and 2005-10 – see table 4-2). The data was plotted for each episode. The plots included all dates with data within the date range of the episode and a seasonal average of each site. The plots can be seen in the figure 5-1. The identifiers on each plot (2006-7, 2005-5, etc. reference to the University of Iowa episode number).

To summarize table 5-3, the average nitrate fraction, averaging over all winters, is around 33%. The fractional chemistry of the aerosol, averaging over all years is (by mass) nitrate > organics (OC) > sulfate ~ ammonium > metal / crustal > elemental carbon.

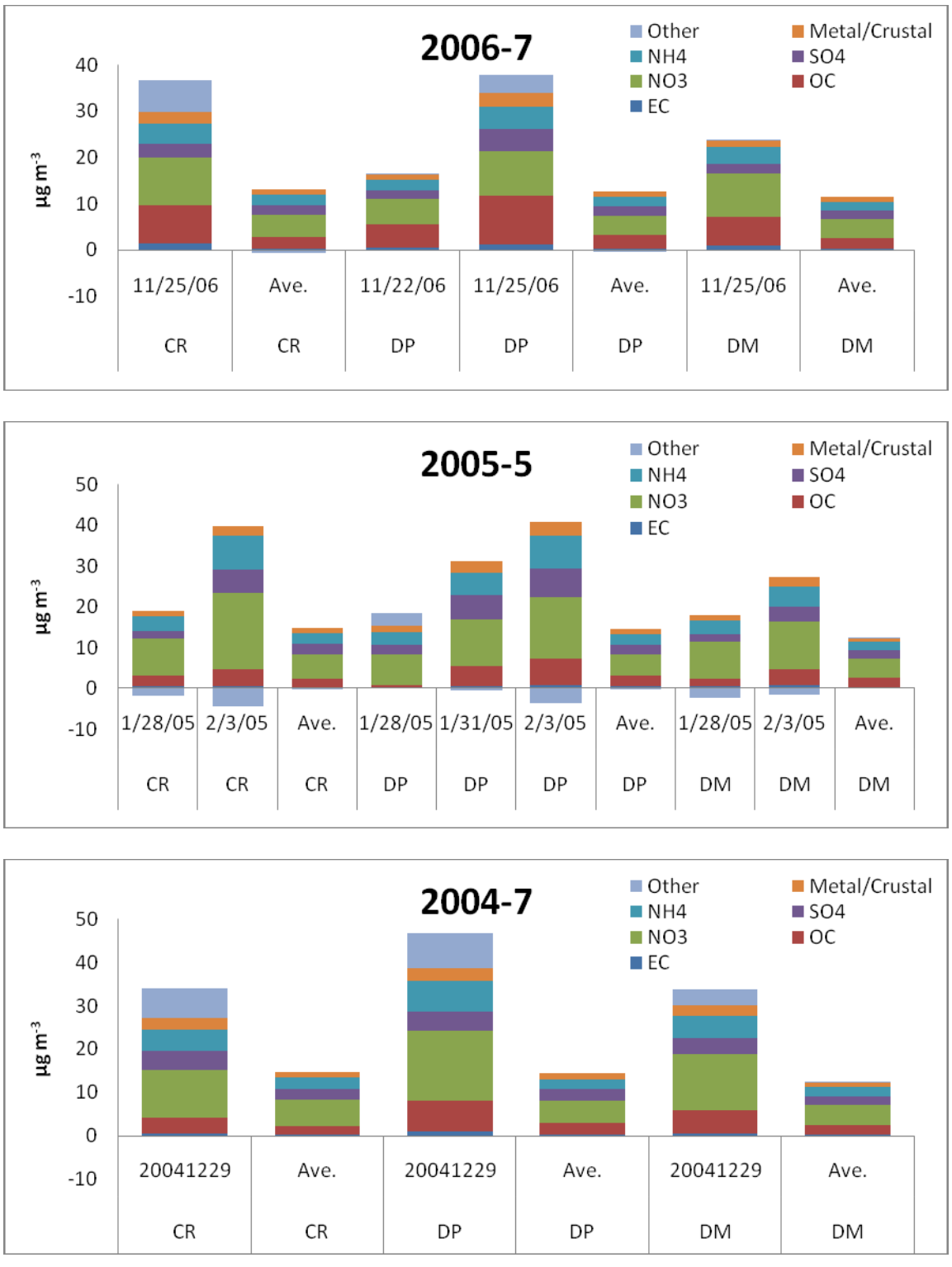


Figure 5-1. Speciated PM2.5 concentrations on specific days during episodes vs. the winter average speciated PM2.5 at Cedar Rapids (CR), Davenport (DP), and Des Moines (DM). Top panel is for episode 2006-7, middle is for 2005-5, and bottom is for 2004-7.

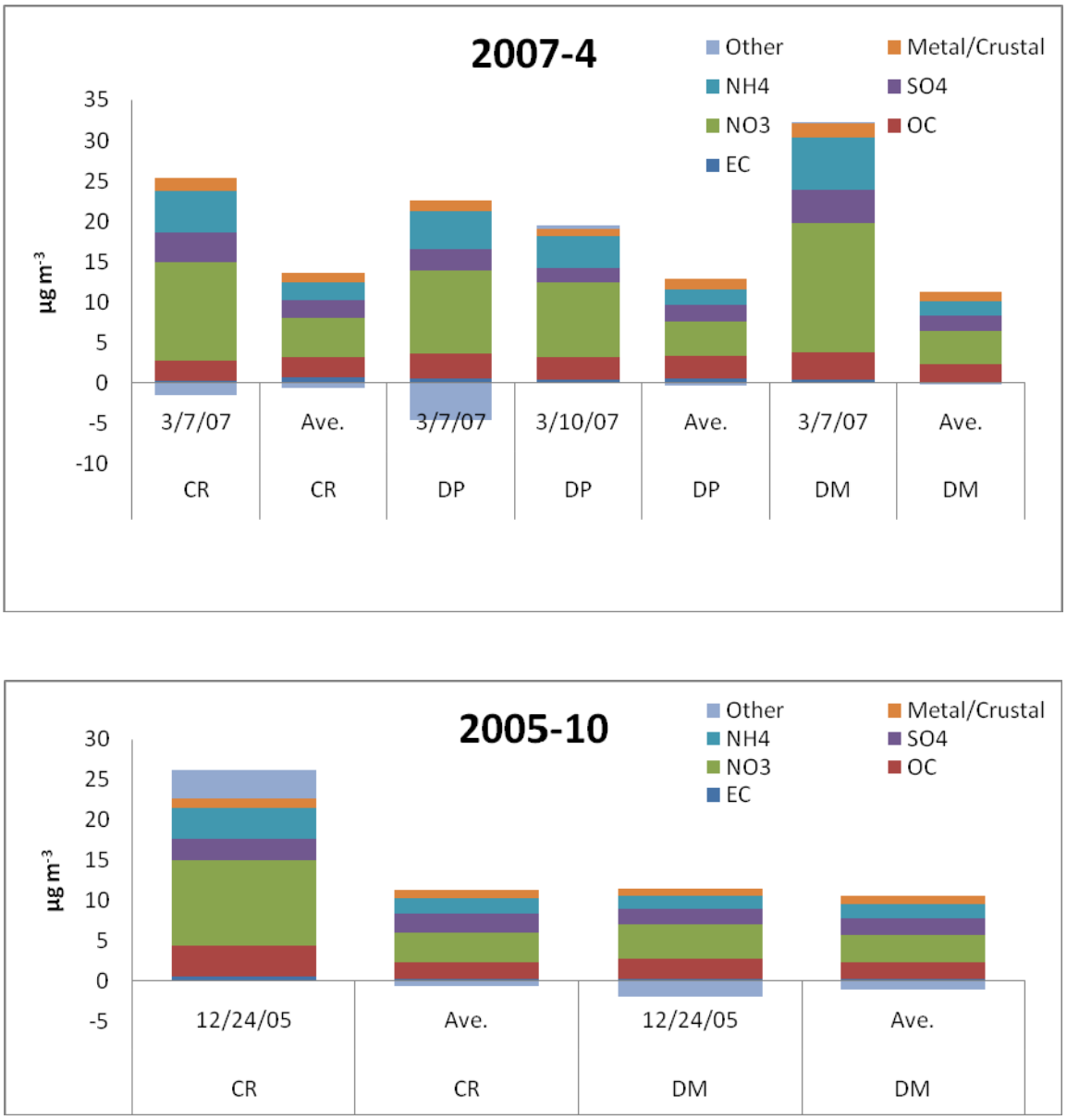


Figure 5-1 continued. Speciated PM2.5 concentrations on specific days during episodes vs. the winter average speciated PM2.5 at Cedar Rapids (CR), Davenport (DP), and Des Moines (DM). Top panel is for episode 2007-4 and bottom is for 2005-10.

The overall average relative concentration of each species category was calculated for the winter season from 2003 to 2007. This was compared to the overall average relative contribution of each species category during the six episodes analyzed. Table 5-4 summarizes these results.

High time resolution nitrate measurements are available at Davenport. However, analysis of these is beyond the scope of the current work. Using high time resolution nitrate (and ammonia, which is also available) can potentially provide significant information on (1) nitrate

formation pathways; (2) local vs. regional nitrate, and (3) sensitivity of nitrate aerosol to nitric acid and ammonia. However, this type of analysis requires extensive consideration of potential instrument errors. An example of the high time resolution nitrate data is shown below. The sharp increase on the night of 11/24 and during the early morning of 11/25 could be local formation of nitric acid, changes in partitioning of nitric acid (due to RH, temperature, or ammonia), or transport of total nitrate.

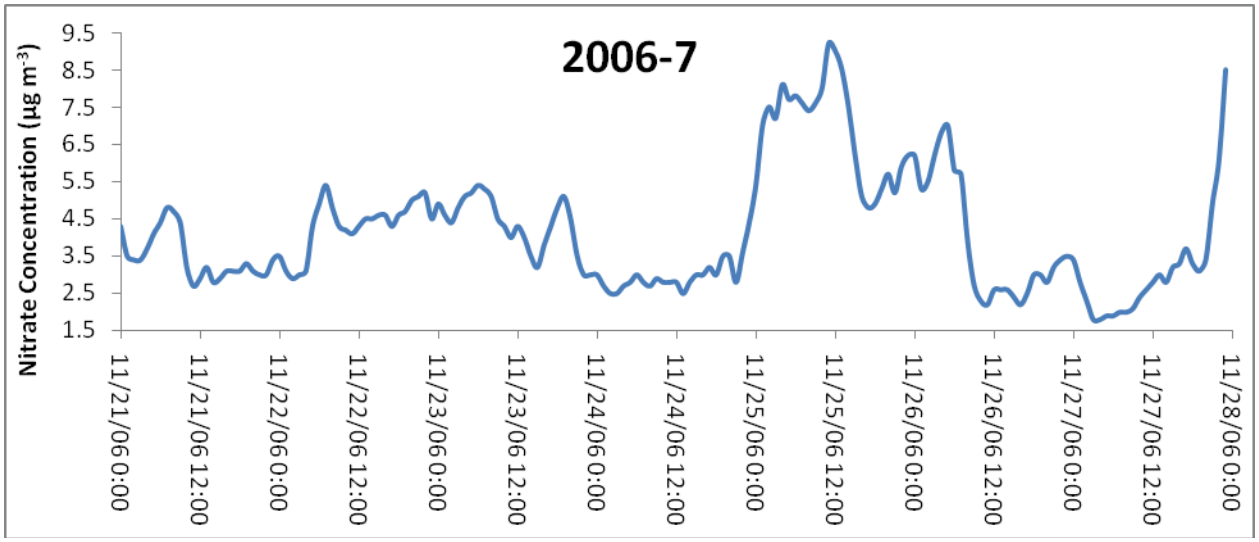


Figure 5-2. High time resolution nitrate (Davenport 10th and Vine) during episode 2006-7. Note rapid increase in nitrate during the early morning of 11/25/2006.

Table 5-4 Average Relative Concentrations During Winter Season and Episodes.

Site	Average	EC	OC	NO_3	SO_4	NH_4	Metal/Crustal	Other
CR	Episodal	0.020	0.128	0.425	0.118	0.184	0.064	0.062
CR	Seasonal	0.026	0.219	0.345	0.189	0.162	0.103	-0.044
DM	Episodal	0.027	0.167	0.461	0.121	0.192	0.070	-0.038
DM	Seasonal	0.034	0.243	0.326	0.183	0.153	0.105	-0.043
DP	Episodal	0.026	0.165	0.400	0.131	0.180	0.071	0.029
DP	Seasonal	0.032	0.243	0.315	0.184	0.153	0.109	-0.036

The main point of table 5-4 is that wintertime episodes can be shown by the data to be associated with enhanced ammonium nitrate. A plot of the ratio of the relative episode concentration to seasonal average (figure 5-3) shows this relationship.

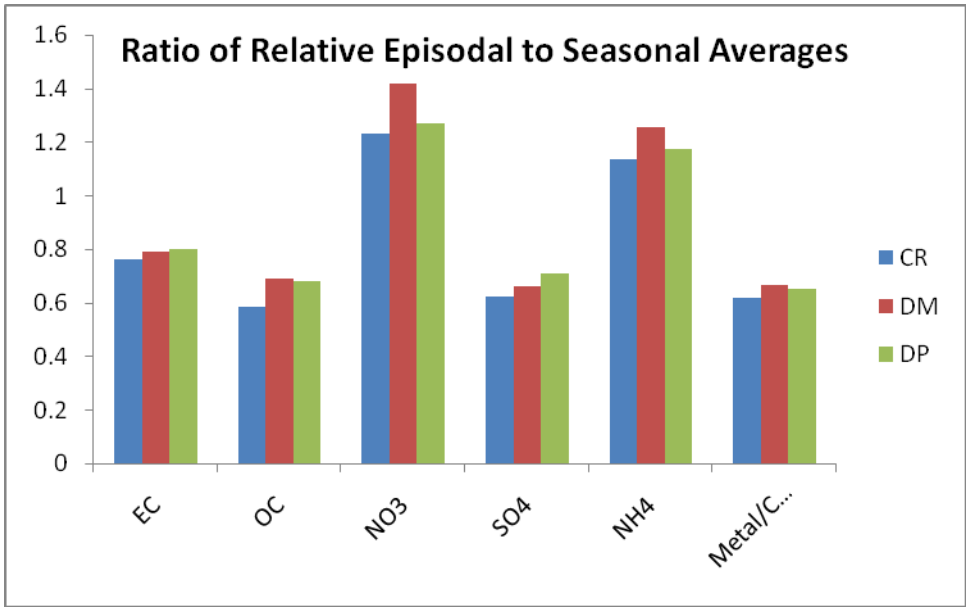


Figure 5-3. Enrichment ratios for six aerosol species during episodes. Values greater than 1 indicate an increase in the fraction of the aerosol attributable to that species during episodes. (e.g. 10% by mass on average, and 15% by mass during episodes would be a ratio of 1.5).

The site to site variation of these ratios was small. The relative concentration of elemental carbon, organic carbon, sulfate, and metals/ crustals was consistently higher during the seasonal averages than during episodal averages. The relative nitrate and ammonium concentrations were significantly higher during episodes compared to the seasonal average. Elemental carbon is depleted on a fractional basis, but not to the same extent as organics and sulfate.

5.3 Results for Local vs. Regional Nitrate

The data analyzed is not of sufficient spatial density to answer the question of local vs. regional nitrate. However, there are some reports in the literature that may be applicable to the Eastern Iowa / Quad Cities area. The most comprehensive result on that front is from LADCO (2004), shown in figure 3-3. For Chicago, the wintertime split of nitrate is ~4.0 μg m^{-3} regional, and ~1.2 μg m^{-3} local. For spring and fall, the total nitrate is a bit lower, but the local fraction is approximately the same. In other words, the ratio of an urban nitrate value to the corresponding rural value is ~1.3 in both Chicago and St. Louis in winter.

St. Louis (not shown) shows strong variability from site to site around the St. Louis area, especially in organic carbon, and nitrate. This is indicative of variable and local sources. Site to site variability in nitrate follows that of elemental carbon, also indicative of local pollution from

the same sources that are emitting the elemental carbon, presumably vehicles and industry. Similar pattern of variability and correlation was reported with EC for wintertime local nitrate and organics in Chicago.

One cannot assume that just because Iowa cities and towns are smaller than St. Louis and Chicago, that the local nitrate contribution will be negligible. Concentrations of NOx can be just as high in Iowa locations, even if the total mass of NOx (when added up over a whole metropolitan area) is different. Because episodes occur during stagnant periods, local fractions may be enhanced during episodes. In other words, an *average* 25% local fraction of wintertime urban nitrate, may be the average of a lower local fraction during low concentration periods, and a higher local fraction during episodes. Recent modeling by IDNR comes to a different conclusion about local contributions during nitrate episodes (less than 3% PM2.5 of local origin). See discussion in section 3.2.6.

More sophisticated modeling and/or source receptor sampling will be necessary to quantify local-regional contributions during episodes. While this discussion has focused on nitrate (and NOx), similar questions arise for ammonia.

References

VIEWS, Visibility Information Exchange Web Site, http://vista.cira.colostate.edu/views/.

LADCO (2004). PM2.5 in Urban Areas in the Upper Midwest. L. M. A. D. Consortium.

6.0 METEOROLOGICAL CONDITIONS

Synoptic weather maps and surface measurement time series were analyzed to determine the types of meteorology associated with cold season regional episodes.

One common pattern for the episodes if for PM to build up on the back end of a warm front. This is shown conceptually in Figure 6-1. Signature meteorological trends during this type of high $PM_{2.5}$ event are a sudden change in wind direction (to be predominately easterly in flow), pressure decrease, rising temperature, dew point, and relative humidity, and a decrease in wind speed. The front can be a cold front (usually shown on the synoptic maps), as shown in figure 6-1, or a dryline (usually not shown on the synoptic maps). A dryline is a front where the temperatures don't change much, but the dewpoint does. Since dry air is more dense than moist air, it acts very much like a cold front in that there are usually storm systems along the frontal system.

Figure 6-3 shows time series and figure 6-4 shows a representative weather map during this type of episode meteorology for episode 2007-4.

A second meteorological pattern associated with air pollution episodes is cold air, under a high pressure system. The “cold-snap” type periods are accompanied by subsidence of high pressure air aloft (keeping pollutants at the surface) and intense nighttime temperature inversions (also tending to keep pollutants at the surface). A cartoon of this type of meteorology is shown in figure 6-2.

A qualitative analysis of weather maps during episodes indicates that the first case (characterized by frontal passage) are associated with ¾ of the nonattainment episodes, while the remaining ¼ of the cold season events are associated with high pressure conditions.

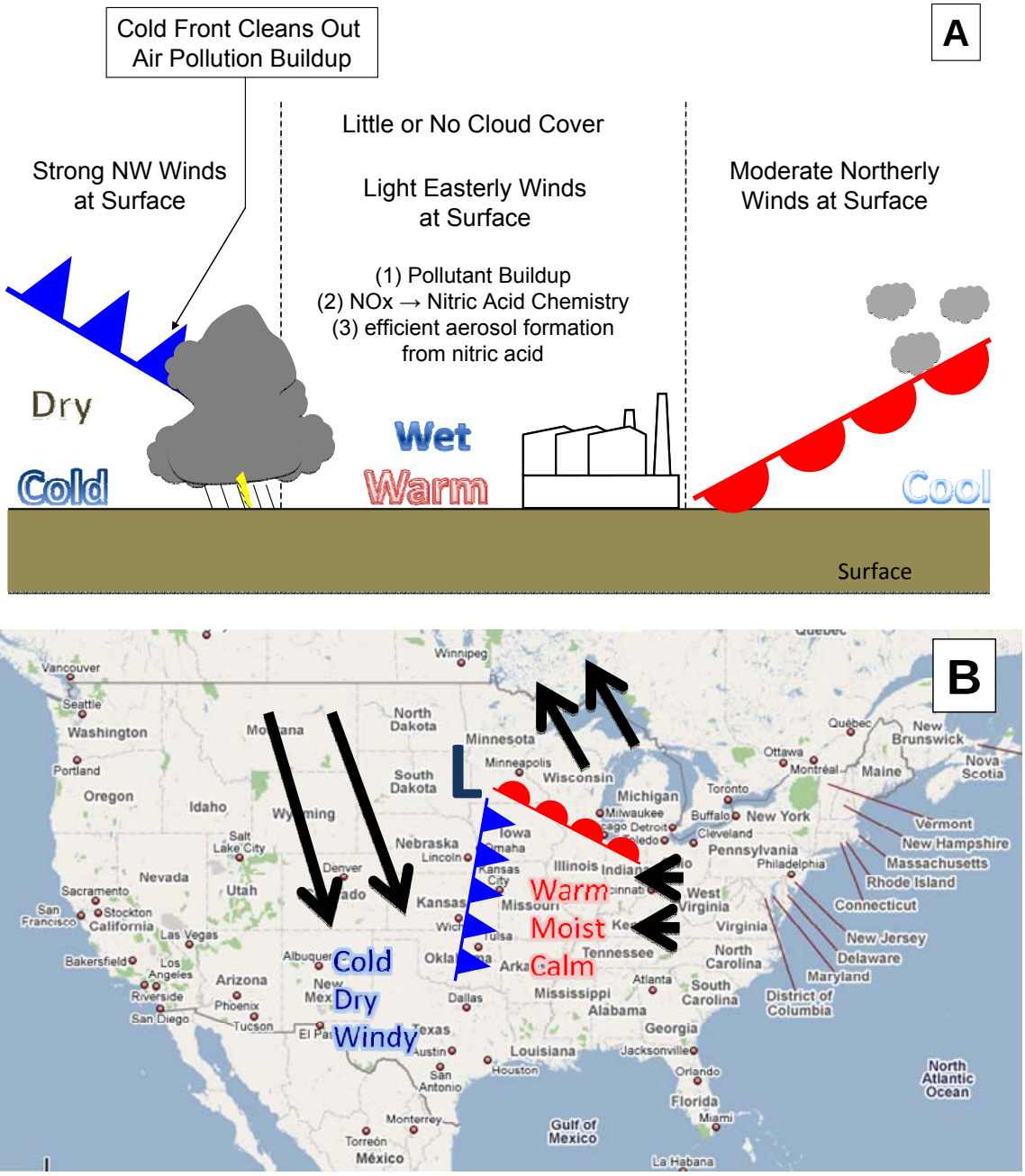


Figure 6-1. Conceptual model for approximately 75% of Iowa's regional wintertime PM episodes. Panel A has a view looking from South to North at the surface. Panel B has a surface map.

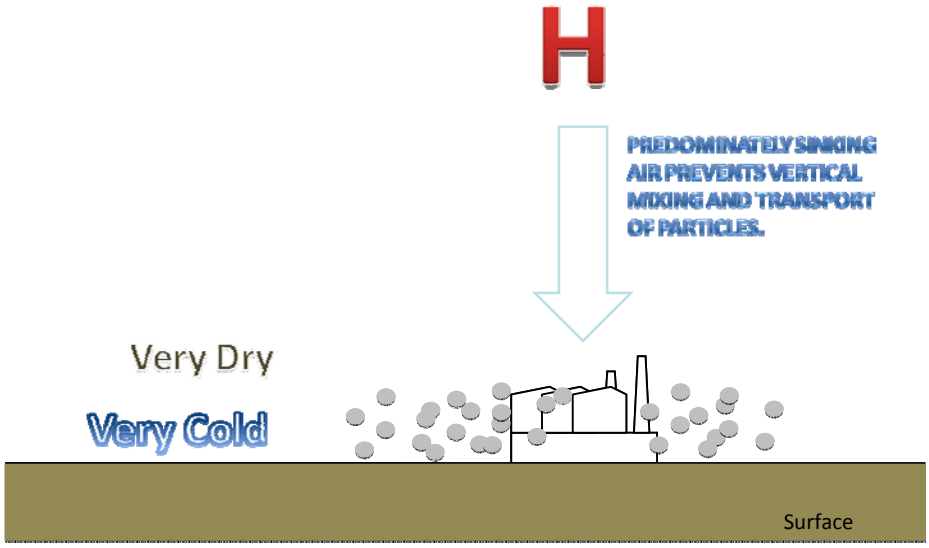


Figure 6-2. Conceptual diagram of high pressure / subsidence / inversion driven episode.

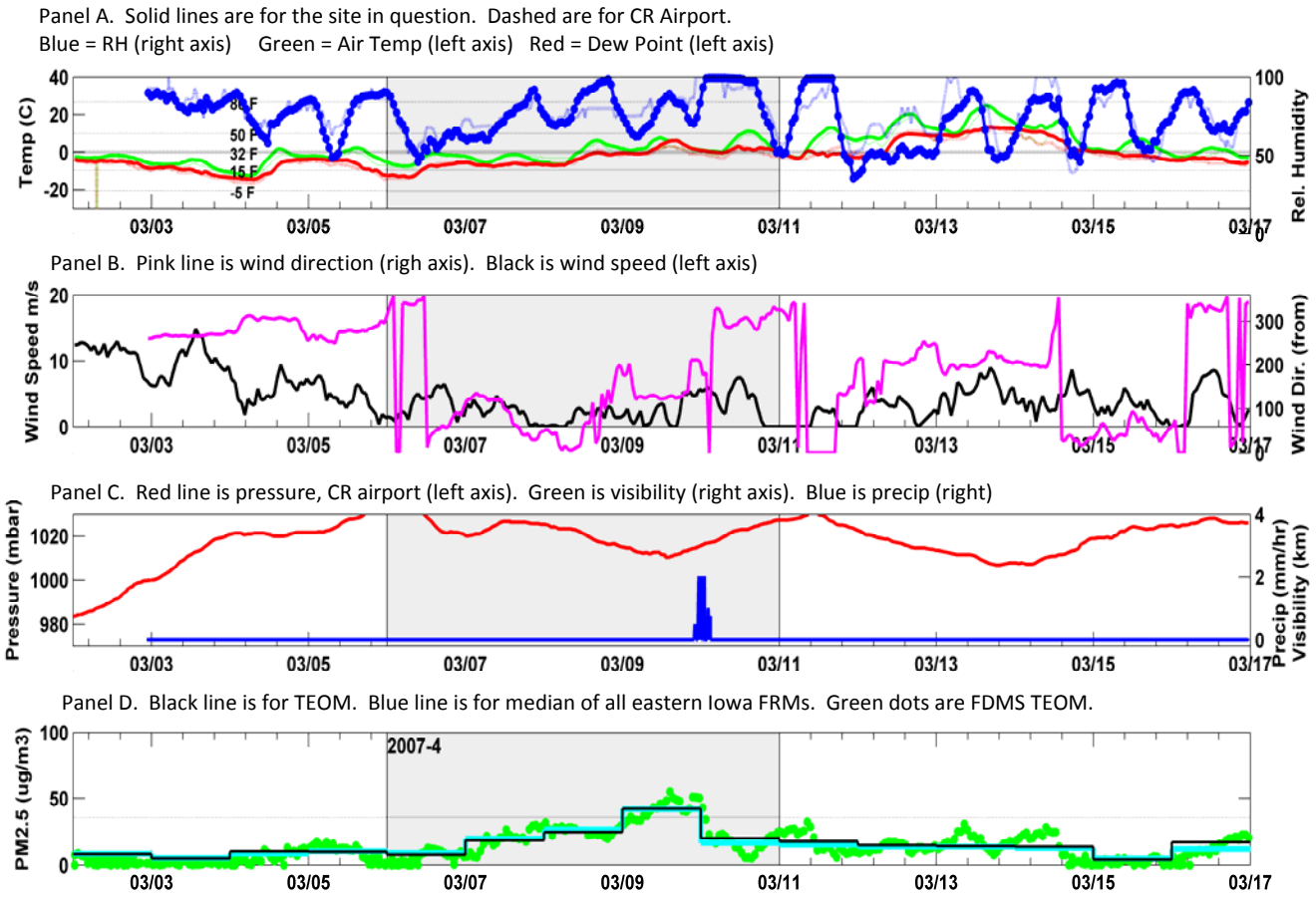


Figure 6-3. Example of signature meteorology of cold weather episodes. (See episode 2007-4 from 3/6/2007 – 3/9/2007).

Figure 6-4 is the afternoon synoptic weather map for episode 2007-4 on March 9, 2007. Synoptic conditions for Eastern Iowa during this event are typical during the passage of a low-pressure system. Eastern Iowa is dominated by a maritime tropical air mass that precedes an approaching cold front and proceeds a warm front. Maritime tropical air masses are characterized by relatively high moisture and temperatures as well as light, easterly wind.

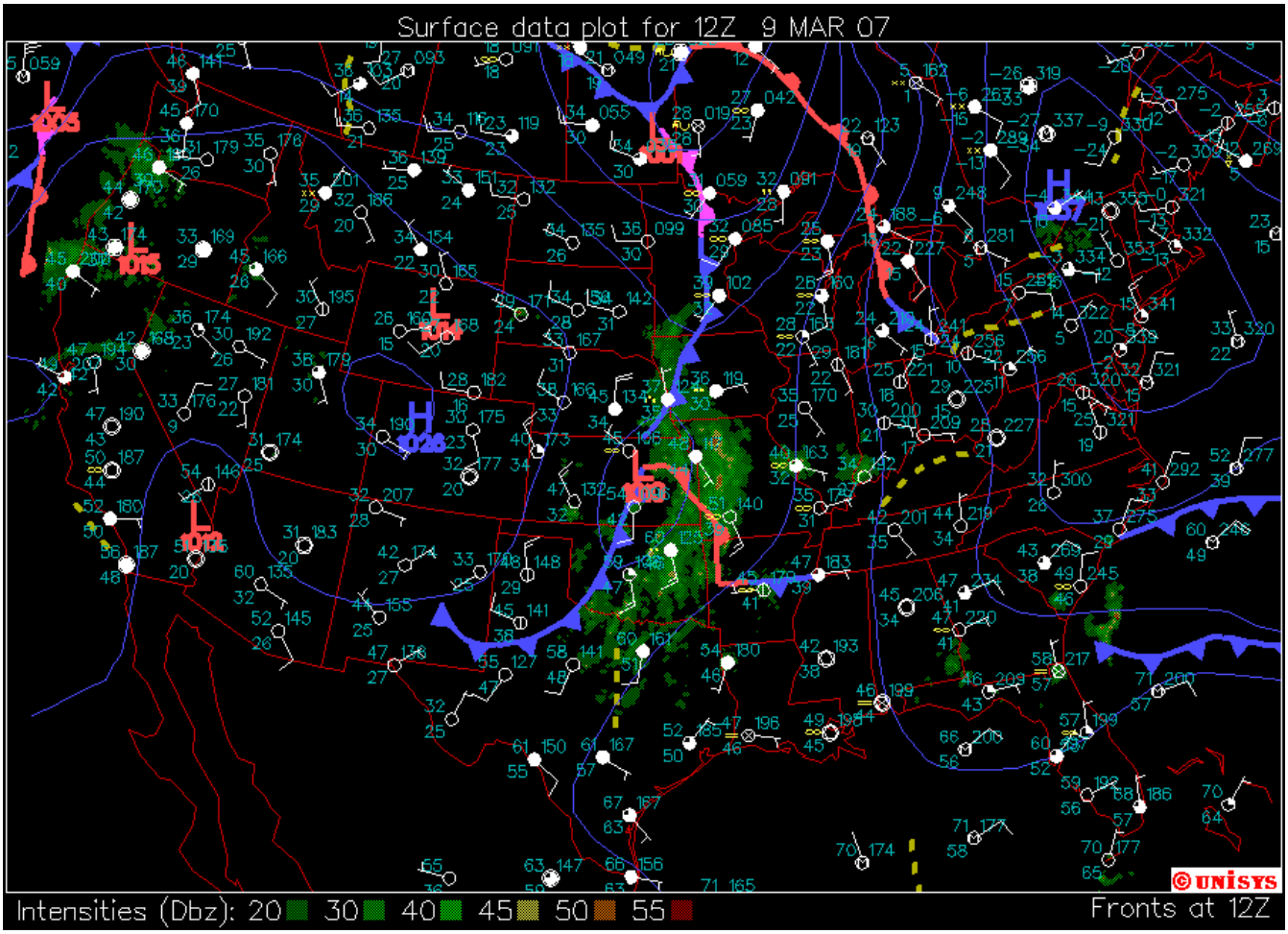


Figure 6-4. Weather map during episode 2007-4

Table 6-1 lists all regional $PM_{2.5}$ episodes that occurred during the winter months (November through March). Values that are bold occurred under the synoptic conditions described earlier. Those events that are not bold occurred during the less frequently observed high pressure case. An example of such a case is illustrated in Figure 6-5, the afternoon surface weather map for December 17, 2007 (episode 2007-20).

Table 6-1. Classification of cold-weather regional episodes by meteorology.

Bold-italic indicates the episode fits the pattern described above.

Episode Code	Date	Classification	Representative Concentration (PM2.5)	Site of Representative Concentration
2002-1	6-Feb-02	2R	29.7	Cedar Rapids - Wenig Rd Ne
2002-1	***8-Feb-02***	***2R***	***30.8***	***Davenport - 10th & Vine***
2002-4	***6-Mar-02***	***2R***	***36***	***Cedar Rapids - Wenig Rd Ne***
2002-5	***19-Mar-02***	***2R***	***32.7***	***Des Moines - NE 3rd St - Saylor Twp***
2002-12	***13-Dec-02***	***2R***	***29.4***	***Clinton - Roosevelt St.***
2002-12	16-Dec-02	2R	33.8	Muscatine
2002-13	***28-Dec-02***	***2R***	***29.9***	***Davenport - Adams Elemntary - N Division St.***
2003-1	***2-Feb-03***	***2R***	***35.5***	***Muscatine***
2003-2	***28-Feb-03***	***1R***	***34.6***	***Davenport - 10th & Vine***
	1-Mar-03	***1R***	***39.7***	***Davenport - 10th & Vine***
2003-3	***12-Mar-03***	***2R***	***37.3***	***Cedar Rapids - Wenig Rd Ne***
	15-Mar-03	***2R***	***37.2***	***Cedar Rapids - Wenig Rd Ne***
	16-Mar-03	***2R***	***34.7***	***Cedar Rapids - Wenig Rd Ne***
	18-Mar-03	***1R***	***48.7***	***Cedar Rapids - Wenig Rd Ne***
2004-1	10-Jan-04	2R	34.5	Des Moines Iowa - Carpenter
2004-2	***18-Feb-04***	***1R***	***42.3***	***Mason City***
	19-Feb-04	***2R***	***33***	***Cedar Rapids - Wenig Rd Ne***
2004-7	***29-Dec-04***	***1R***	***42.3***	***Clinton - Roosevelt St.***
2005-2	***10-Jan-05***	***2R***	***32.7***	***Cedar Rapids - Wenig Rd Ne***
	11-Jan-05	***2R***	***37.7***	***Des Moines Iowa - Carpenter***
2005-4	25-Jan-05	2N	32.2	Clinton - Roosevelt St.
2005-5	***29-Jan-05***	***2R***	***32.3***	***Van Buren County - Lacey Trail***
	30-Jan-05	***1R***	***42.9***	***Des Moines Iowa - Carpenter***
	31-Jan-05	***1R***	***53.2***	***Waterloo***
	1-Feb-05	***1R***	***48.3***	***Cedar Rapids - Wenig Rd Ne***
	2-Feb-05	***1R***	***44***	***Des Moines Iowa - Carpenter***
	3-Feb-05	***1R***	***41.2***	***Clinton - Roosevelt St.***
2005-10	***21-Dec-05***	***1R***	***39.7***	***Clinton - Roosevelt St.***
	24-Dec-05	1R	36.8	Davenport - Adams Elemntary - N Division St.
2006-2	***16-Jun-06***	***2R***	***33.2***	***Davenport - Blackhawk Foundary Monitor - Wellman St.***
2006-6	***7-Nov-06***	***2R***	***36.5***	***Clinton - Roosevelt St.***
2006-7	***25-Nov-06***	***1R***	***50.9***	***Clinton - 23rd & Camanche***
2007-4	***7-Mar-07***	***2R***	***37.7***	***Council Bluffs***
	9-Mar-07	***1R***	***44.2***	***Davenport - Blackhawk Foundary Monitor - Wellman St.***
2007-18	***19-Nov-07***	***1R***	***39.1***	***Davenport - Blackhawk Foundary Monitor - Wellman St.***
	20-Nov-07	***1R***	***38.3***	***Davenport - Blackhawk Foundary Monitor - Wellman St.***
2007-19	***12-Dec-07***	***2R***	***33.5***	***Van Buren County - Lacey Trail***
2007-20	17-Dec-07	1R	38.2	Davenport - Blackhawk Foundary Monitor - Wellman St.
	19-Dec-07	1R	54.8	Iowa City
	19-Dec-07	1R	57.2	Davenport - 10th & Vine
	20-Dec-07	1R	63	Waterloo
2008-2	***11-Jan-08***	***2R***	***34.2***	***Muscatine***
2008-3	***27-Jan-08***	***1R***	***36.3***	***Clinton - 23rd & Camanche***
2008-4	3-Feb-08	1R	37.6	Sioux City
2008-5	***22-Feb-08***	***1R***	***35.1***	***Des Moines Iowa - Carpenter***
	23-Feb-08	***1R***	***50.5***	***Clinton - Roosevelt St.***
	24-Feb-08	***1R***	***49.3***	***Clinton - 23rd & Camanche***
2008-6	11-Mar-08	2R	45.8	Davenport - Blackhawk Foundary Monitor - Wellman St.

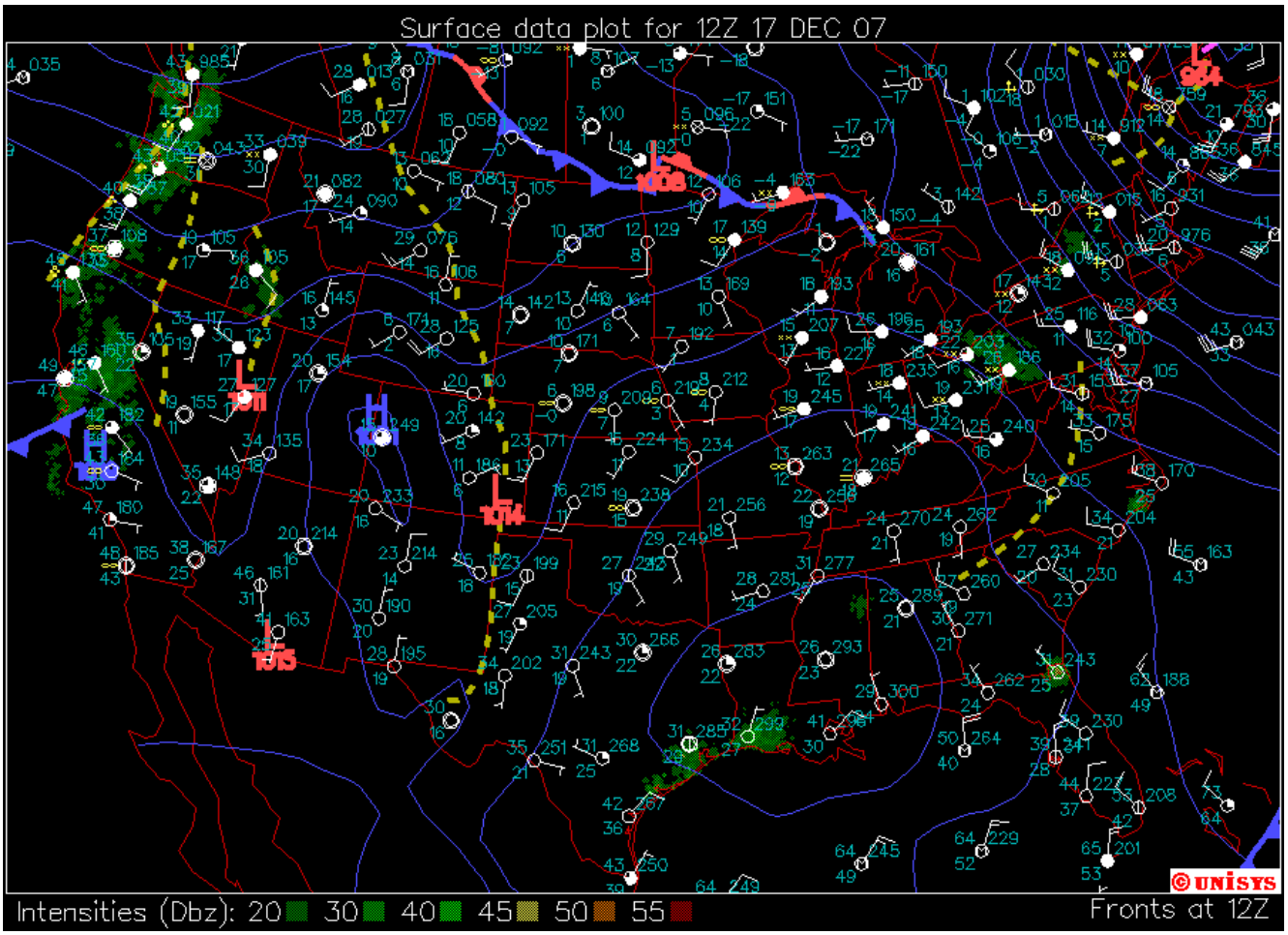


Figure 6-5. Weather map during episode 2007-20

7.0 RELATIONSHIPS BETWEEN $PM_{2.5}$, WIND DIRECTION, AND KNOWN SOURCE LOCATIONS

Based on the boxplots of 98th percentile concentrations (section 4.2), the following sites were identified for further analysis of wind direction versus PM level. The reason for this was a high 98th percentile, or multiple outliers showing occasionally high PM levels. The Montgomery County site was added to the list as a control. Because it is a clean site, no local impact was anticipated.

Site ID	Name	Status
191630019	Davenport (Wellman St.)	complete
190450019	Clinton (23rd and Camanche)	complete
191390015	Muscatine	complete
190450021	Clinton (Roosevelt)	complete
191630015	Davenport (10th and Vine)	complete
191630018	Davenport(Adams Elementary)	complete
191032001	Iowa City	insufficient met data
190130008	Waterloo	insufficient met data
191370002	Montgomery County	complete

7.1 Methods

Our analyses can be broken into three categories: (1) determination **if** there is a direction-specific impact, sites with 1-hour PM; (2) determination **if** there is a direction-specific impact, sites with daily $PM_{2.5}$ only; and (3) once a direction-specific impact is identified, estimation of what the 98th percentile $PM_{2.5}$ value would be if the PM associated with the directional impact was removed, presumably through controls at a local source.

Analyses (1) and (2) are fairly straightforward, and are done by examining (using computer code) PM levels versus wind direction. Analysis (3) is more difficult, and the results here should be considered preliminary.

For analysis (1), our method is simple and routinely practiced in air quality engineering. Wind rose, pollution rose, and conditional probability function plots are developed for the site (these are described in section 2, methods). These are developed based on a list of simultaneous hourly values of (a) wind speed; (b) wind direction; and (c) pollution level. All hours with wind speeds reported as zero, or with wind velocity less than 0.2 m/s, are excluded.

For analysis (2) (only daily pollution levels available), the process is somewhat different. An hourly wind rose can still be created. But the pollution rose and conditional probability

function are problematic. One must either average the wind direction, which can be problematic since it is a vector quantity, or one must assume the pollution was the same during every hour, even in cases where a "medium" 24-hr value is caused by a mixture of high concentration air (possibly from a nearby source) and low concentration air from a different direction. Therefore, a daily exposure score for each of 32 wind directions is calculated. The score can range from 0 to 24, where 24 means that the wind blew from the direction in question for 24 hours continuously. Linear regression is then used to determine the relationship between daily $PM_{2.5}$ and each of the 32 exposure scores. Specifically, the regression is based not on total $PM_{2.5}$, but rather on the local increment of $PM_{2.5}$, which is defined as the difference between the source in question and the daily *median* $PM_{2.5}$ concentration for Eastern Iowa [defined as all FRM samples east of Des Moines (not including Des Moines)]. By subtracting the median FRM value from the FRM value at a given site, an estimate of an incremental $PM_{2.5}$ is calculated. If this increment reliably (in a statistical sense) goes up every time there is a strong exposure (via wind) from a particular direction, that is evidence of a local contribution.

Both the conditional probability method and the regression method have the advantage that statistical confidence limits can be developed.

These methods rely on direction only, and are thus only sensitive to strong local sources. Furthermore, it is not possible to separate sources that may be along the same wind vector relative to the site. Much more sensitive techniques are available; these use detailed aerosol "fingerprints" from each source, and require additional sampling and special analysis methods.

Our method for analysis (3) is described later in the section.

7.2 Davenport Results

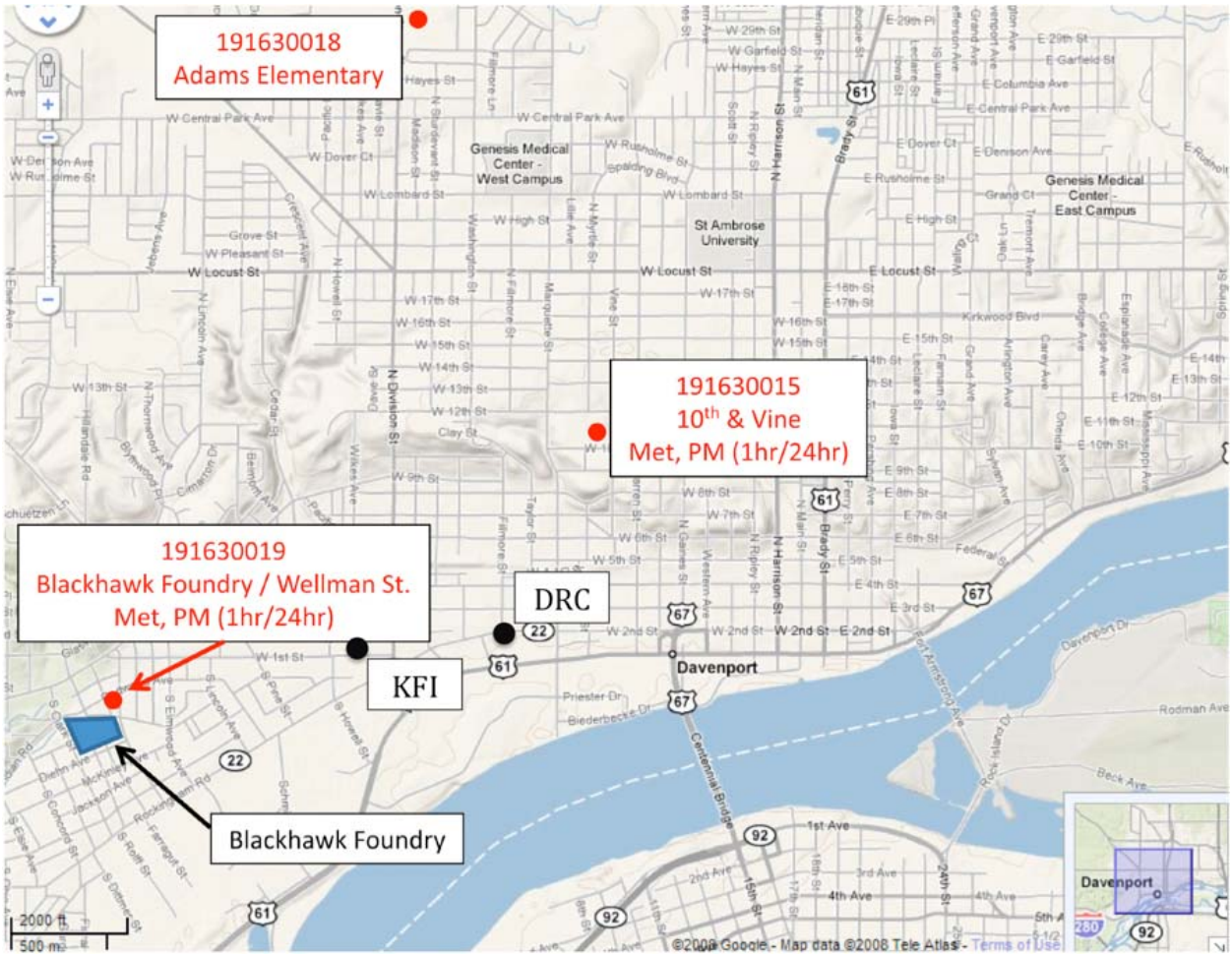


Figure 7-1. Davenport Map

DAVENPORT (WELLMAN ST.) MONITOR

The Davenport Wellman St. monitor is located on the property of Blackhawk Foundry and Machine Company. Its wind rose (figure 7-2), pollution rose (figure 7-3), conditional probability function (figure 7-4), and regression-based $PM_{2.5}$ increment vs. direction (figure 7-5) can be found below. The wind rose and pollution rose use hourly data only. The pollution rose gives the first indication of a directional impact, with the increase in the size of the yellow (50-75 $\mu g\ m^{-3}$) and maroon (75+ $\mu g\ m^{-3}$) stripes for directions to the southwest.

The conditional probability plot quantifies this directional impact; it includes the probability (fraction of samples that meet the threshold) for thresholds of 10, 20, 30 and 40 $\mu g\ m^{-3}$ over the regional median $PM_{2.5}$ value.

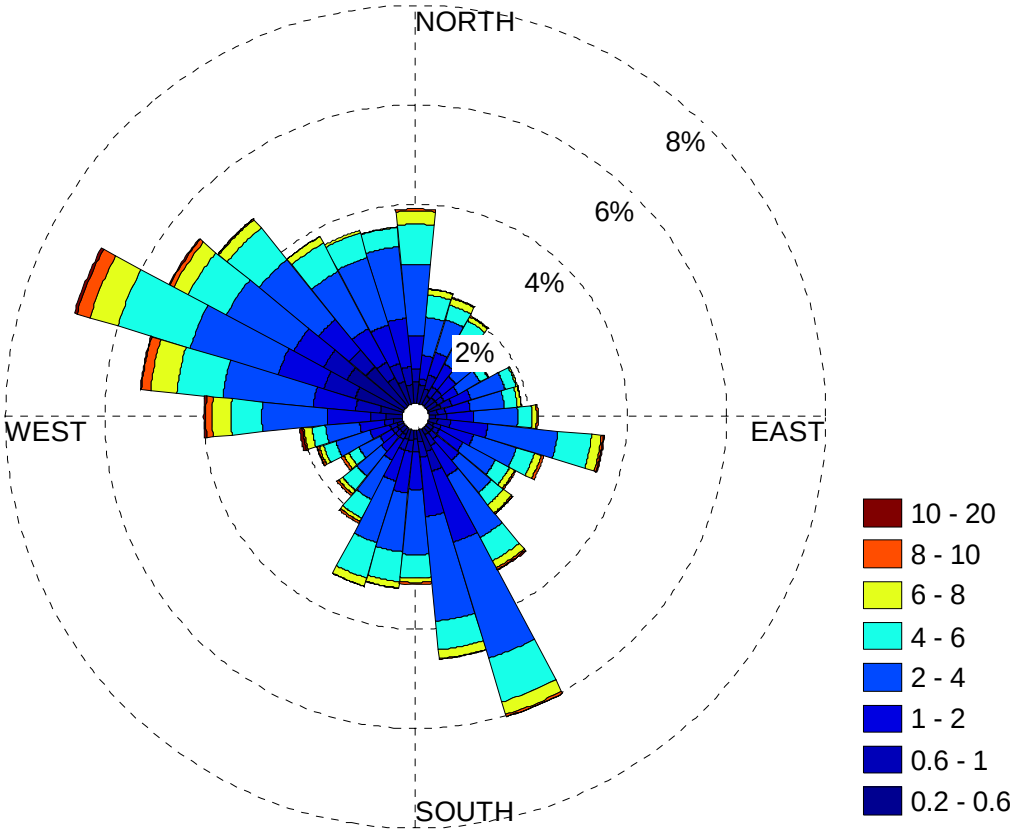


Figure 7-2 Davenport Wellman St. 2007 Wind Rose
Colors refer to wind velocity in m/s. Dominant wind directions are from the northwest, south, and east.

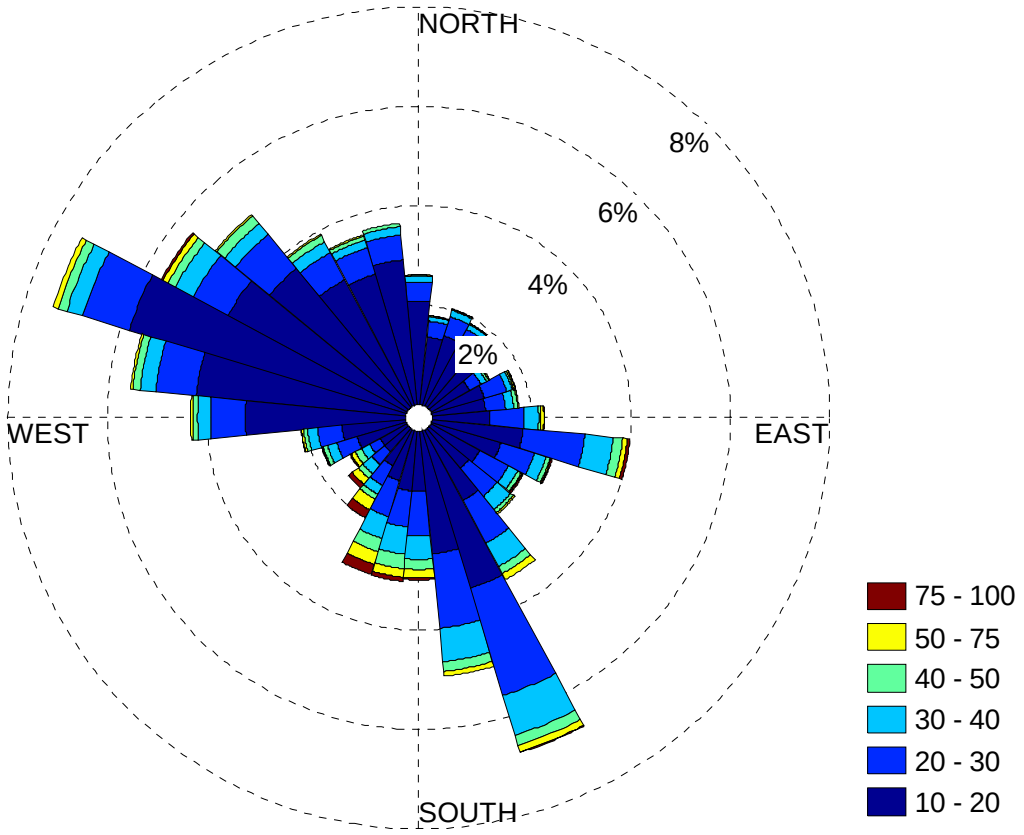


Figure 7-3 Davenport (Wellman St.) 2007 Pollution Rose.
Colors refer to hourly $PM_{2.5}$ as measured by FDMS TEOM. Most dominant wind direction is wind coming from northwest. Highest concentration flows come from the south-southwest.

The regression-based $PM_{2.5}$ increment vs. direction quantifies the directional impact in a different way (and using completely independent $PM_{2.5}$ measurements). The regression-based $PM_{2.5}$ increment can be interpreted that, on average, the Davenport (Wellman St.) monitor will read 10 μg m^{-3} over the regional median value if the wind blows from the direction of peak impact (220°). The large error bars are consistent with significant variability in emissions (and in dilution based on wind speed and atmospheric stability).

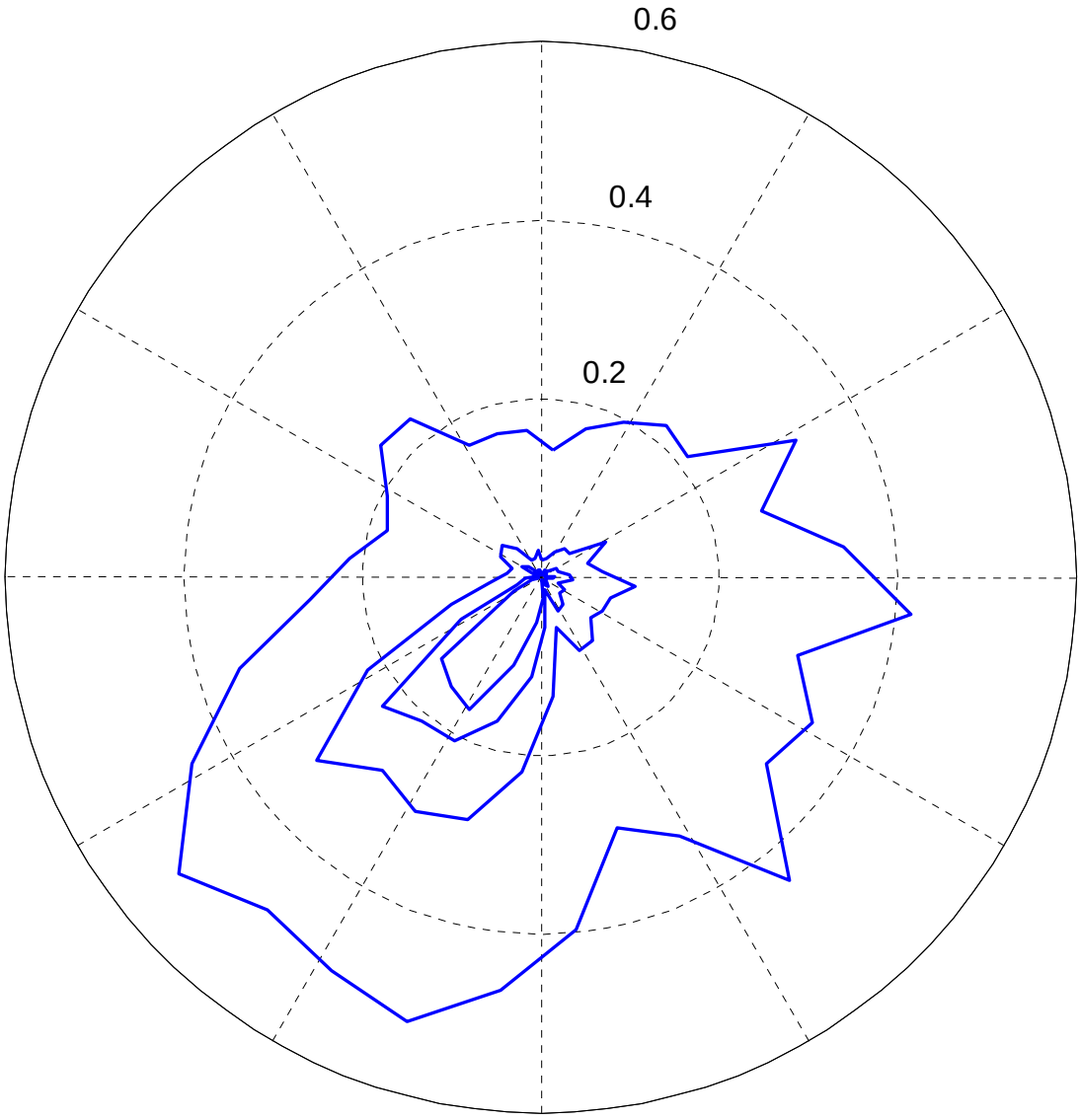


Figure 7-4 Davenport (Wellman St.) Conditional Probability Function (2006-2008)
Outermost ring denotes a 60% probability of exceeding the threshold, which is the increment of hourly PM over the eastern Iowa median PM level. The outermost threshold is 10 μg m^{-3}, followed by 20, 30 and 40 μg m^{-3}. At 40 μg m^{-3} the CPF has highest probability at a heading of 210° and the CPF magnitude at that heading is 16%.

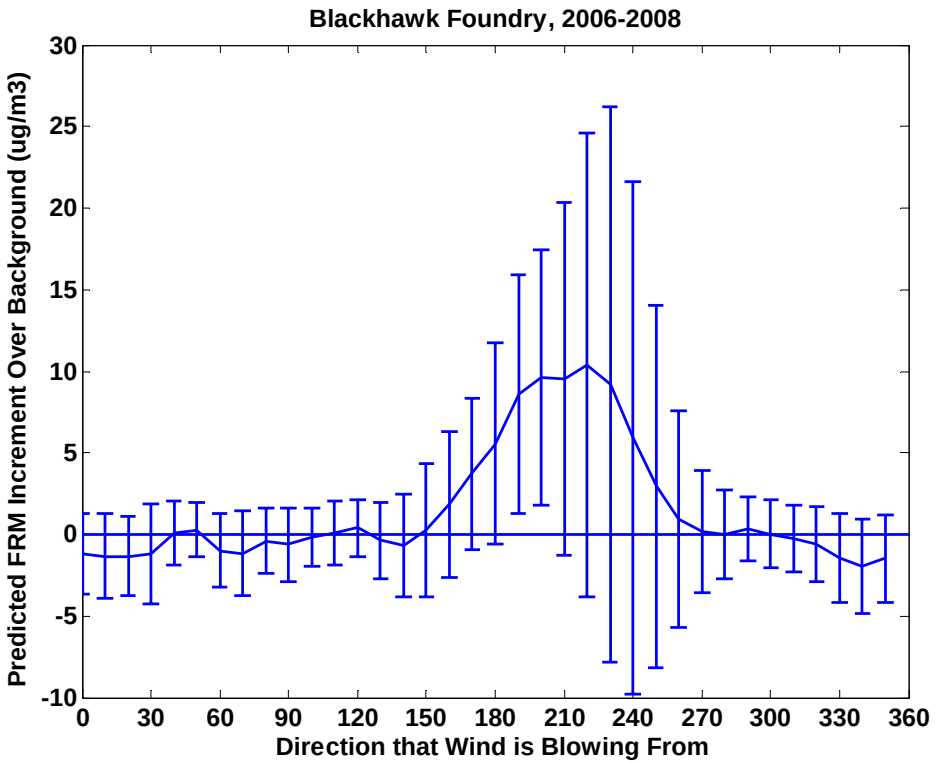


Figure 7-5 Davenport (Wellman St.) Foundry 2006-2008 Regression of Wind Direction as Predictor of Incremental PM2.5 on 24 FRM Samples
Peak is from 200 to 230° Error bars are 95% confidence intervals on the linear regression mean.

10th AND VINE

The analyses done for the Wellman St. monitor were repeated for the monitor at 10th and Vine. There was some evidence of directional impact, but it was much more difficult to interpret than for the previous site. The CPF for Wellman St. had a roughly 30% chance of an impact 20 μg m^{-3} above backround levels (and this impact was focused over a small number of directions). In comparison, at 10th and Vine, the probability of an impact of similar magnitude peaked at 5%, and was not in a distinct direction. While there probably are quantifiable local/directional impacts at 10th and Vine, they would need to be isolated using more sensitive source receptor techniques.

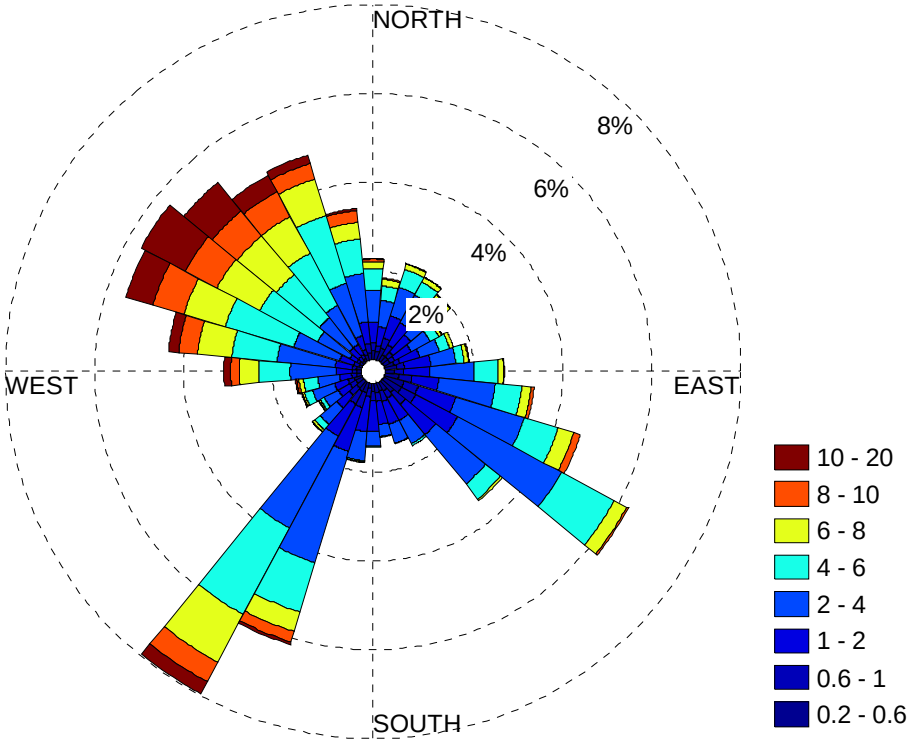


Figure 7-6 Davenport 10th and Vine 2006-2008 Wind Rose

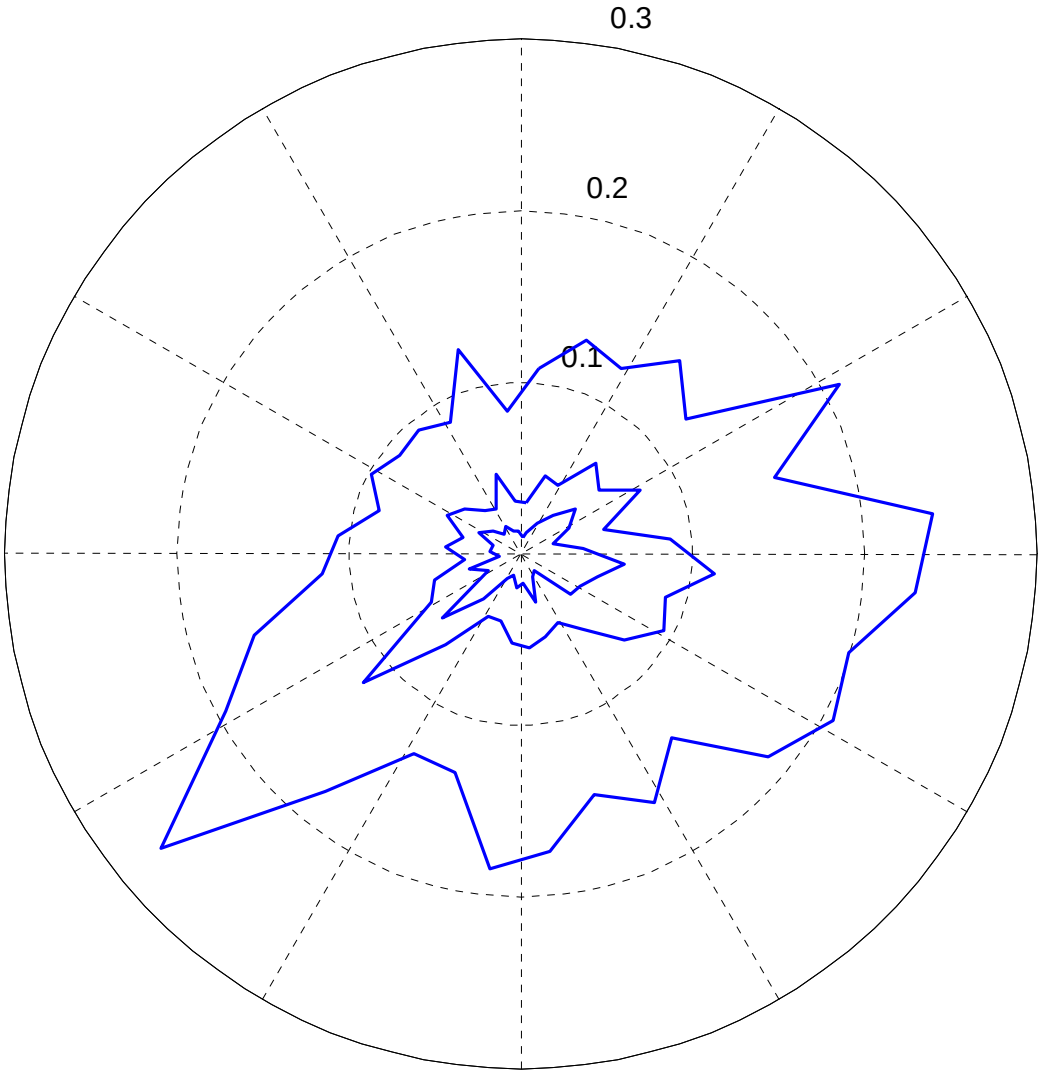


Figure 7-7 Davenport 10th and Vine 2006-2008 Conditional Probability Function
Outermost ring denotes a 30% probability of exceeding the threshold, which is the increment of hourly PM over the eastern Iowa median PM level. The outermost threshold is 10 μg m^{-3}, followed by 15 and 20 μg m^{-3}. The broad shape indicates that there are no dominant local sources. There is a suggestion of a local source at 230° and possibly a source or source grouping to the east of the site. These may be related to topography near the site as well.

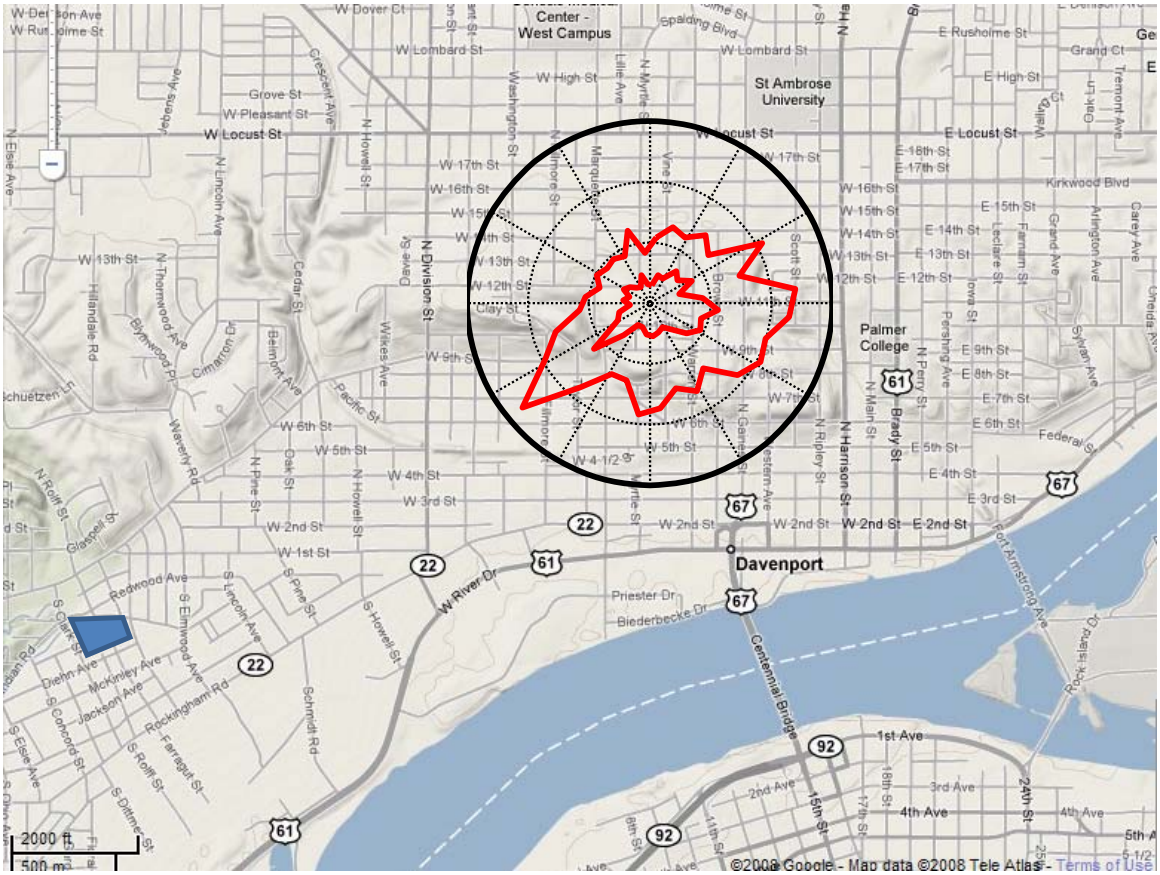


Figure 7-8 Map overlay of 10th and Vine CPF

ADAMS ELEMENTARY

Adams elementary does not have hourly measurements (making it different from the other two Davenport sites) and it does not have collocated meteorology. However, the regression technique was run for Adams Elementary with meteorological data from 10th and Vine. The result is shown below. For comparison purposes, the other two regression-type plots for Davenport are shown.

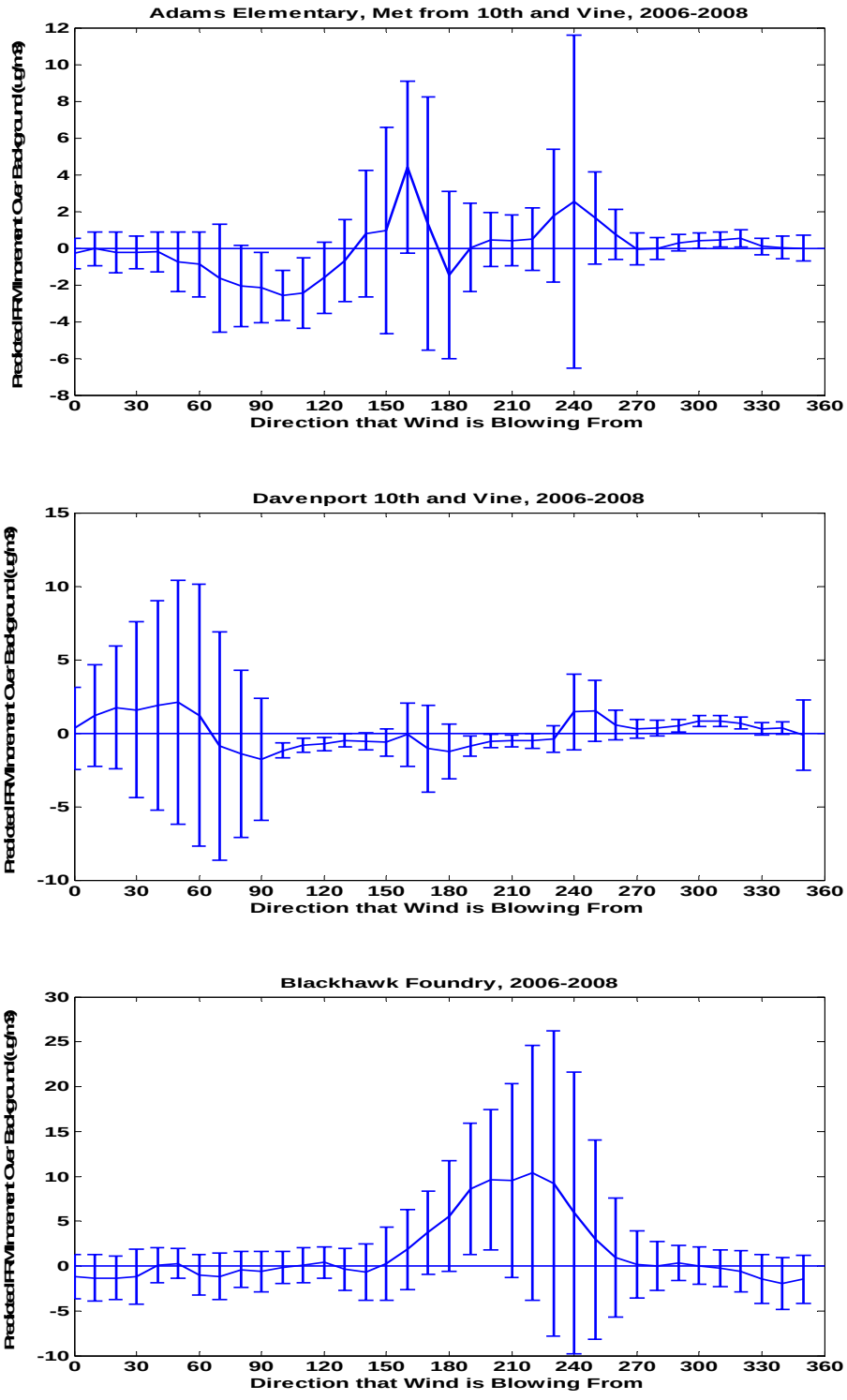


Figure 7-9. Comparison of regression-based estimates of incremental $PM_{2.5}$ as a function of direction. Note change in scale from graph to graph.

7.3 Muscatine Results

The Muscatine monitor does not have an hourly sampler or collocated meteorology. However, meteorology from the other Muscatine sites was examined and it was felt that site 191390020 was the best meteorological station for the $PM_{2.5}$ sampler in Garfield School. Wind roses for met stations at stations 16, 17 and 20 can be found in Appendix G.

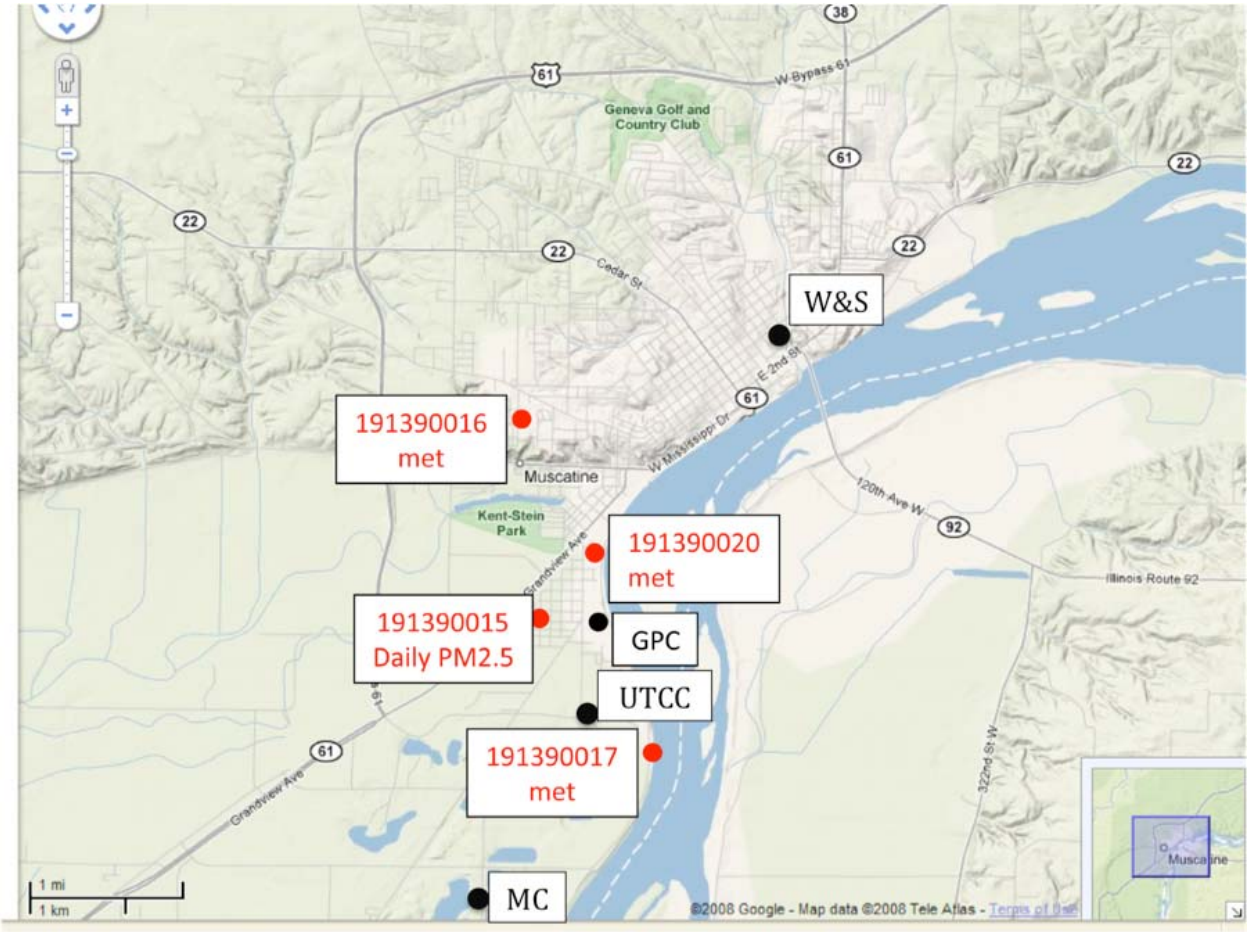


Figure 7-10. Muscatine map with met and $PM_{2.5}$ samplers noted.

Since hourly samples were not available, analysis was limited to the regression technique, and the result is shown in figure 7-11.

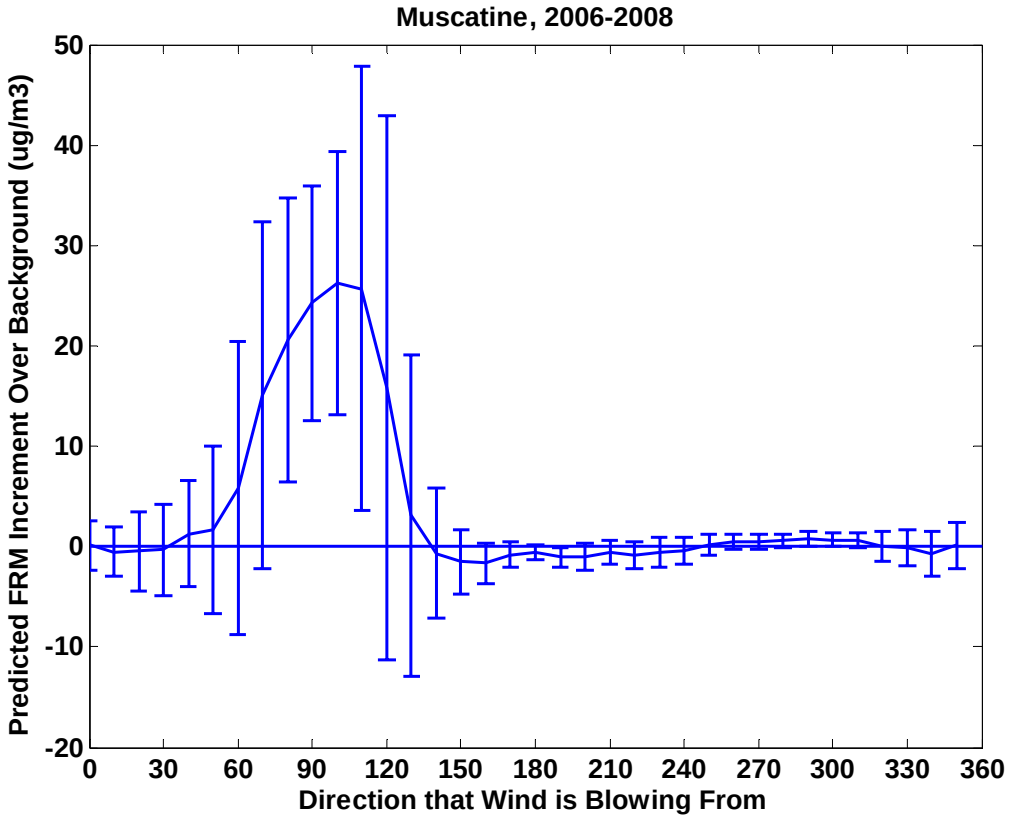


Figure 7-11. Regression-based estimates of incremental $PM_{2.5}$ as a function of direction.

7.4 Other locations

The regression based method was run for Clinton (23rd and Camanche), for Clinton (Roosevelt), and for Viking Lake (Montgomery County). The last site was selected as a control. The regression estimate for Viking lake was not statistically different from zero for any wind direction. The Clinton (23rd and Camanche) sampler showed a broad feature to the south (from 150° to about 230°), which peaked at 20 μg m^{-3} (estimated increment over background for wind from that direction all day) and was statistically different from zero. This is shown in figure 7-12.

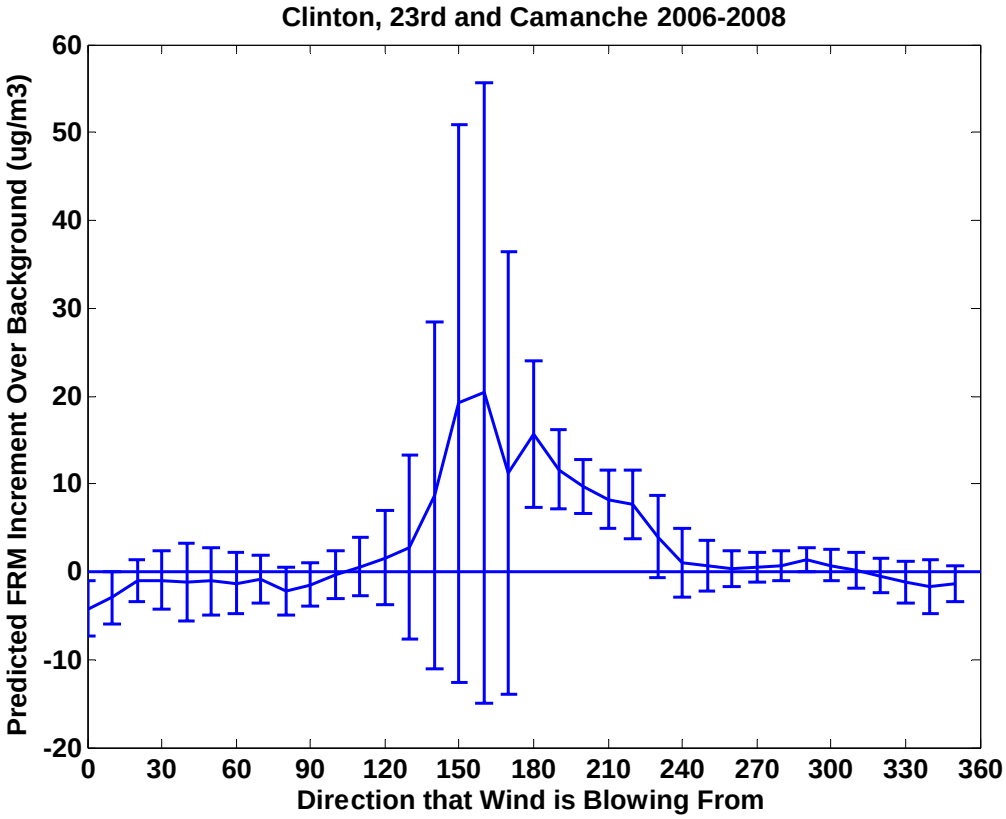


Figure 7-12. Clinton (23rd and Camanche monitor) regression-based estimates of incremental $PM_{2.5}$ as a function of direction.

The CPF method was run for Clinton (Roosevelt), Viking Lake, and Cedar Rapids (Wenig Rd). Cedar Rapids showed a modest local impact to the south (CPF was 20% for a 10 μg m^{-3} increment over background). The other sites showed no features indicative of a local impact.

7.5 Map overlays of directional functions

By overlaying the PM vs. direction functions (either CPF or the regression result), one can determine if the results "line up" with known sources. This is done for the Wellman St. monitor (figures 7-13 and 7-14), the Muscatine monitor (figure 7-15), and the Clinton (23rd and Camanche) monitor (figure 7-16). It should be noted that the regression and CPF analyses were done before any maps or aerial photographs were analyzed. In the case of the Clinton monitor, the University of Iowa team was not aware of the industrial facility to the south of the monitor until after the source locations were investigated as followup to the directional impact results.

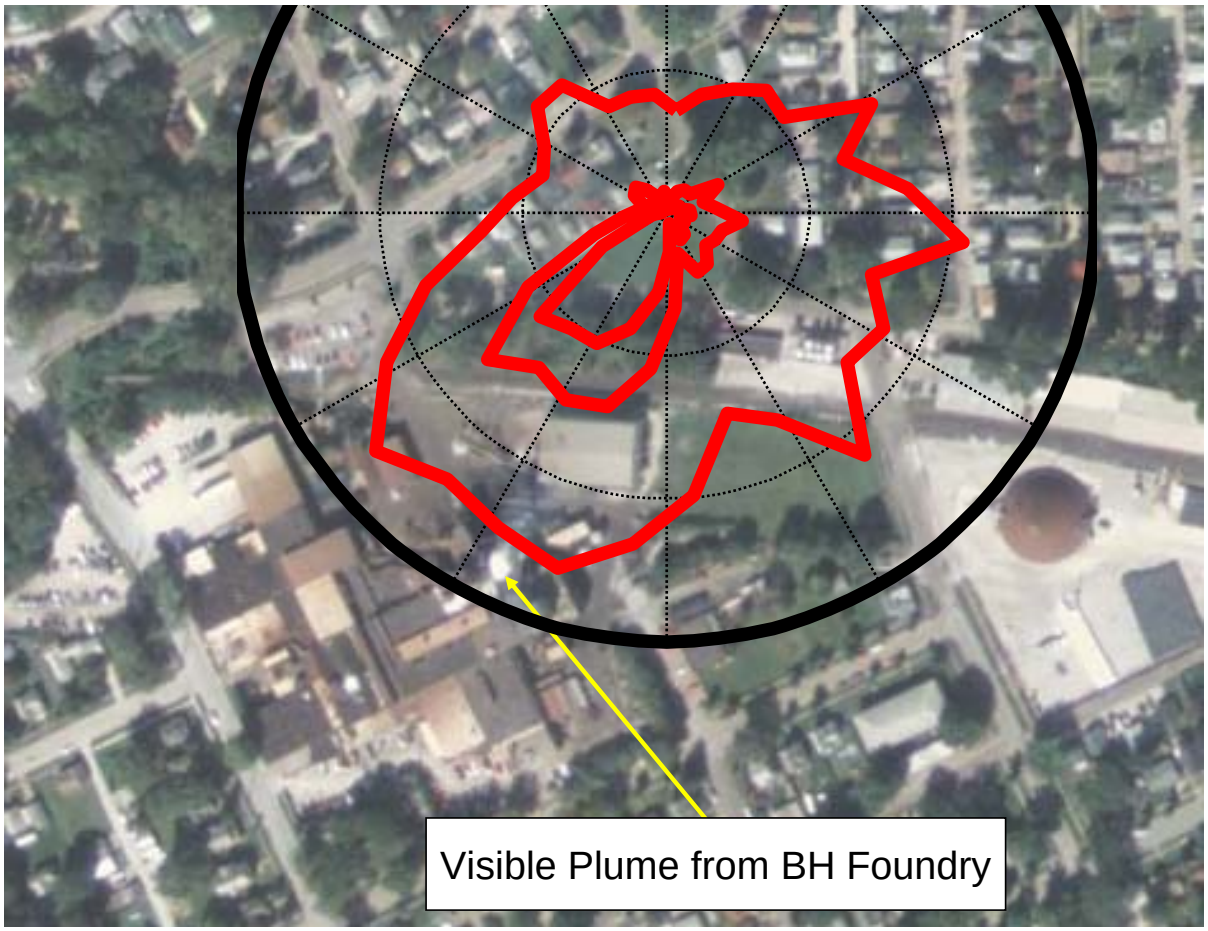


Figure 7-13. Overlay of the conditional probability function from figure 7-4 on aerial photograph of Davenport. The polar plot of the CPF is centered on the monitoring location.

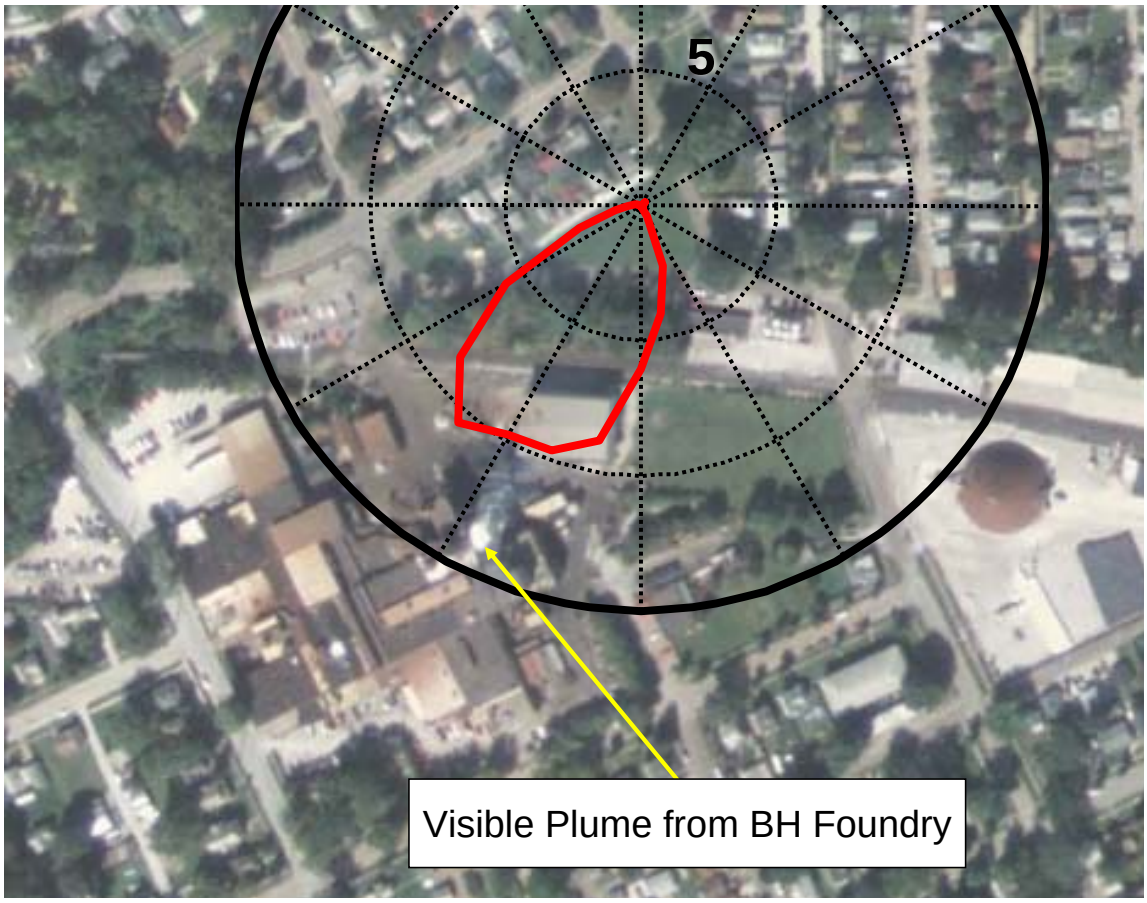


Figure 7-14. Overlay of the regression-based $PM_{2.5}$ increment vs. direction from figure 7-5 on aerial photograph of Davenport. The polar plot is centered on the monitoring location. The rings refer to increments of 5, 10, and 15 μg m^{-3} on FRM measurements (over the regional median level). These values are equivalent to the best prediction of the extra mass on the FRM filter for a constant 24-hr wind direction.

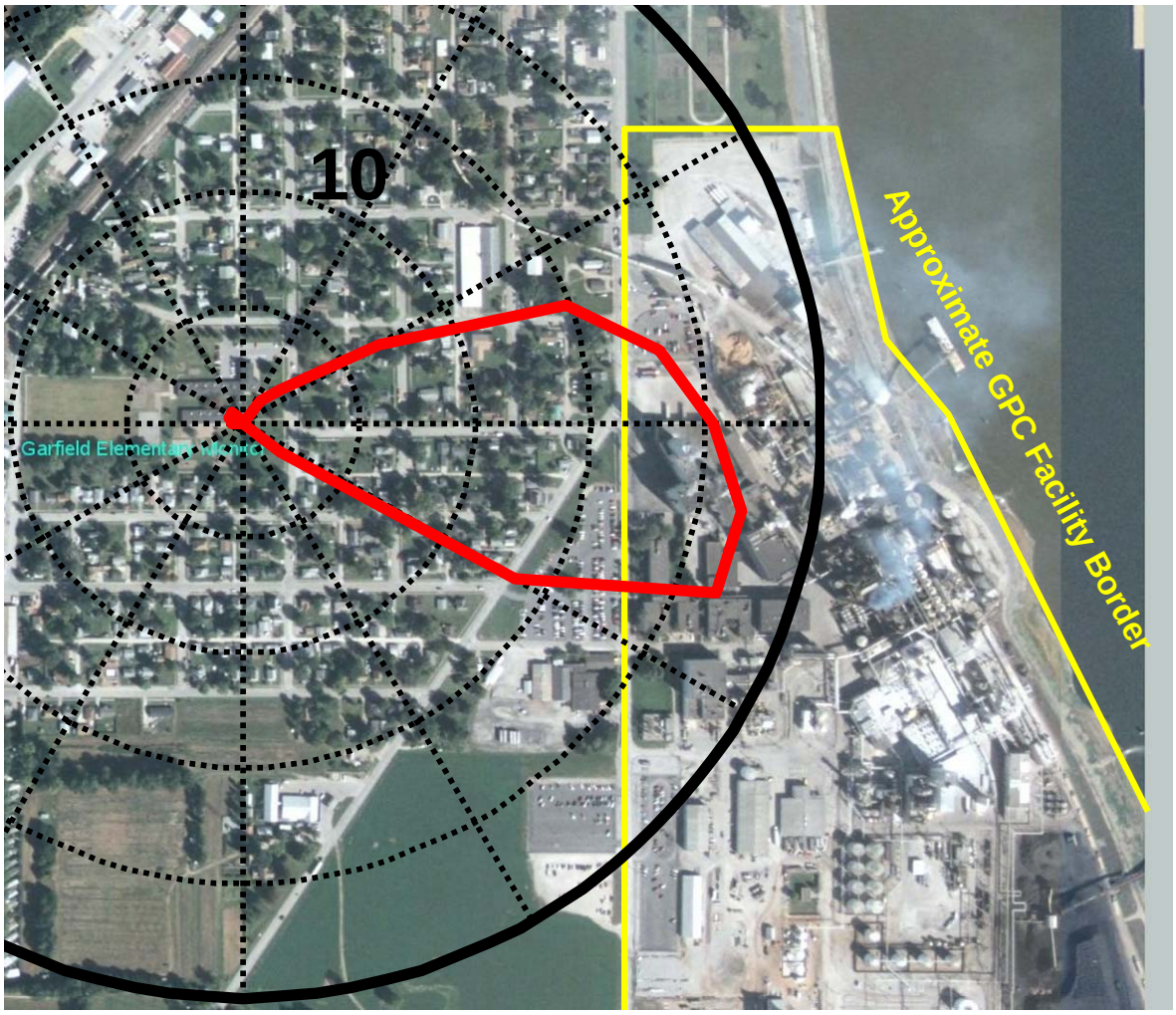


Figure 7-15. Overlay of the regression-based $PM_{2.5}$ increment vs. direction from figure 7-11 on aerial photograph of Muscatine. The polar plot is centered on the monitoring location. The rings refer to increments of 5, 10, 15, 20, and 25 μg m^{-3} on FRM measurements (over the regional median level). These values are equivalent to the best prediction of the extra mass on the FRM filter for a constant 24-hr wind direction.

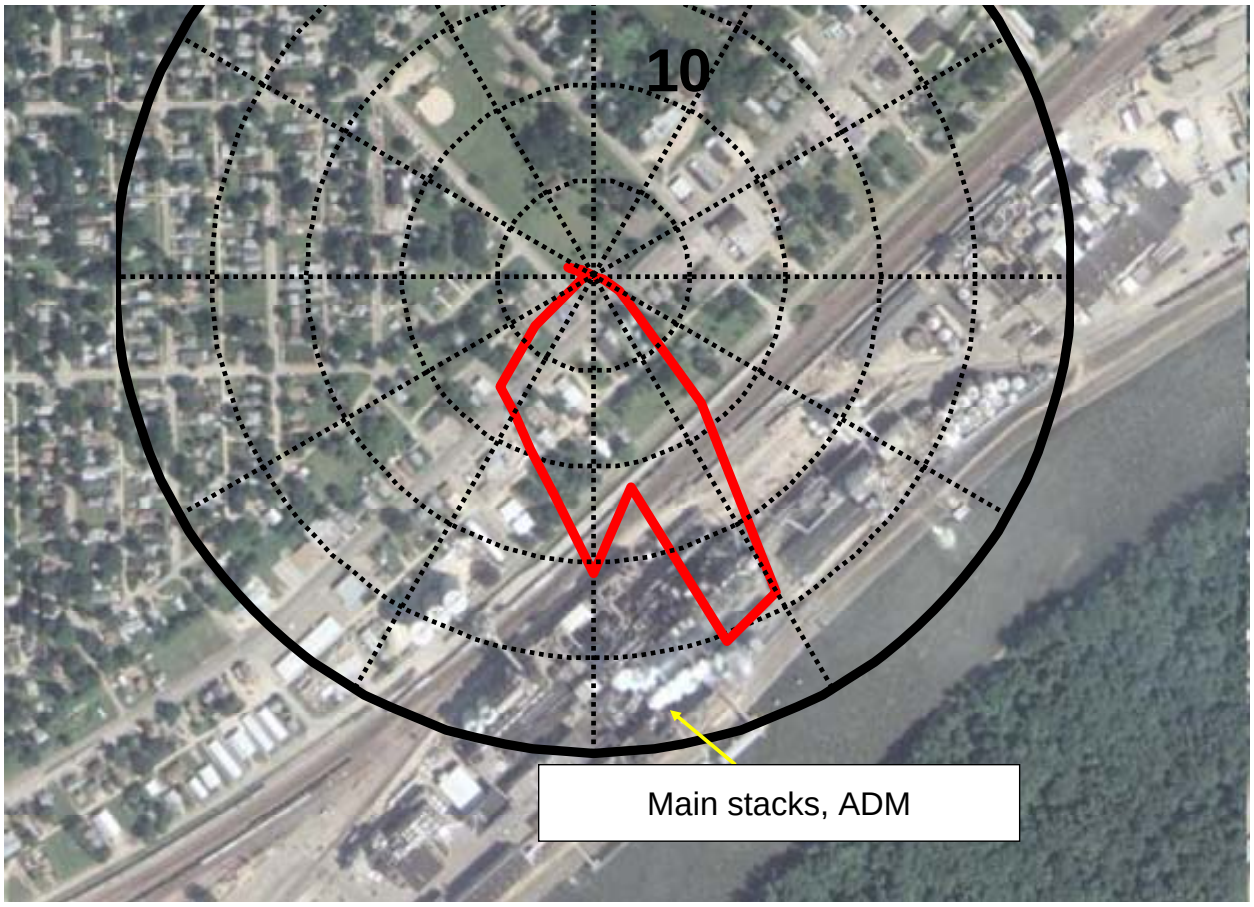


Figure 7-16. Overlay of the regression-based $PM_{2.5}$ increment vs. direction from figure 7-12 on aerial photograph of Clinton. The polar plot is centered on the monitoring location. The rings refer to increments of 5, 10, 15, 20, and 25 μg m^{-3} on FRM measurements (over the regional median level). These values are equivalent to the best prediction of the extra mass on the FRM filter for a constant 24-hr wind direction.

7.6 Probability Analysis of Attainment Assuming Source Controls

As noted in section 7.1, the third type of analysis is to estimate what the 98th percentile $PM_{2.5}$ value would be if the directional enhancement was removed, presumably through source controls. This is a difficult question, and requires a piece of unkown information – what PM is left from a given direction once the source (or a source complex) is controlled, but while other (probably more distant) sources remain along the same wind vector?

Anything more than a preliminary estimate of this question is beyond the scope of this work. Some applicable methods are listed below:

Table 7-1. List of methods that could be used to predict $PM_{2.5}$ 98th percentile after source controls. Underlined methods 1 and 6 used in this work.

Number	Description
1	Assume PM levels will come down to those of a nearby monitor, or of some average of nearby monitors. Assumes all local impacts (except for the one to be controlled) are entirely negligible.
2	Use information about facility operations to determine the PM levels present when the local source is not operating. For facilities only operating ~40 hours a week, this may be an option. But for continuous operations, this is not an option, even with 10% per year of downtime.
3	Use information from nearby existing monitors to fill in for PM levels during wind directions when the source impact is strong.
4	Dispersion modeling to estimate the impact of the source, and subtract that from the monitor value.
5	Dispersion modeling to estimate the impact of all remaining sources in the area, followed by addition to an estimate of the background PM level.
6	Plot the 98th percentile concentration against the *expected* level of directionally-specific PM (from a regression model or dispersion model). Add points to the plot by Monte Carlo sampling of individual days. Use this to extrapolate to the 98th percentile concentration when the directionally-specific PM is zero.
7	Advanced source-receptor tools to quantify multiple sources by chemical composition of their emissions.
8	Deploy a dense network of $PM_{2.5}$ samplers to identify and quantify multiple local plumes.

Of these, method #7 is probably the most accurate, but would require a long time period to collect a statistically significant number of samples. For the Davenport and Muscatine cases, some combination of dispersion modeling (methods 4 or 5), careful inventory of known sources within 5 km of the monitor, and regression techniques (e.g. 6 and 2) would be sufficient.

In this work, only methods 1 and 6 are used, and 100% control efficiency of all directionally-specific PM is assumed. This is not feasible for a complex operation with a variety of emission points; however, the limit on what can be achieved by source controls is a necessary piece of information in considering partial controls.

Method 1 is very simple. In table 4-5, attainment probabilities are given for a number of monitors around the state. In Davenport, the attainment probability at the Wellman St. monitor is 25%, but at 10th and Vine and Adams Elementary, the probabilities are 100% and 99%, respectively. These values are only applicable under assumptions of similar local source impacts at the three monitors (with the exception of the foundry emissions).

For Muscatine, there is no nearby monitor to compare to, so comparison must be to 10th and Vine in Davenport, Adams Elementary in Davenport, the Roosevelt monitor in Clinton, and to Iowa City. There may also be suitable monitors in Illinois to compare to. The attainment probability under the status quo in Muscatine is 42%. At all the other monitors it is between 96 and 100%.

For Clinton, the comparison would be between the 23rd and Camanche sampler (near ADM) with attainment probability of 51%, and the Roosevelt monitor with attainment probability of 100%.

This analysis does not consider actual source controls that may be in the implementation or planning stages at these facilities. Some discussion of controls is included in the regulatory background documentation in Appendix K.

7.6.1 Application of Statistical Sampling of 98th Percentile to the Wellman St. Monitor

These values above probably are high end estimates of the attainment probability. Method 6 (from the list above) can give a lower bound estimate on the attainment probability. It is a Monte Carlo statistical technique. The point of the Monte Carlo technique is to simulate many hypothetical years, and evaluate the 98th percentile concentration in each of the many simulated years. The years are built up by sampling 365 random days – and using the actual wind direction and Eastern Iowa PM background values. Figures below are made for 1000 years of simulation.

The procedure for making figure 7-17 is as follows.

1. Load daily Eastern Iowa background $PM_{2.5}$ values for the same period
2. Load Wellman St. FRM $PM_{2.5}$ values for the same period
3. Randomly select a day in the period 2005-2008
4. Repeat #3 for a total of 365 times (with replacement). Calculate the 98th percentile and graph.

The conclusion from figure 7-17 is that the 98th percentile at the Wellman St. monitor is always above the eastern Iowa background, by about 5±3 μg m^{-3}. The 1000 years of simulation generate 998 3-year averages of the 98th percentile. This is the value that determines compliance with the 24 hour standard. Looking at how many of the 998 3-year averages are above or below 35.5 μg m^{-3}, shows that in the regional background case, ~98% of them are below. Looking at the Wellman St. simulations, only 25% of the cases are below 35.5. The certainty of this prediction is moderately high, and is limited mainly by the short record of data used to train the model.

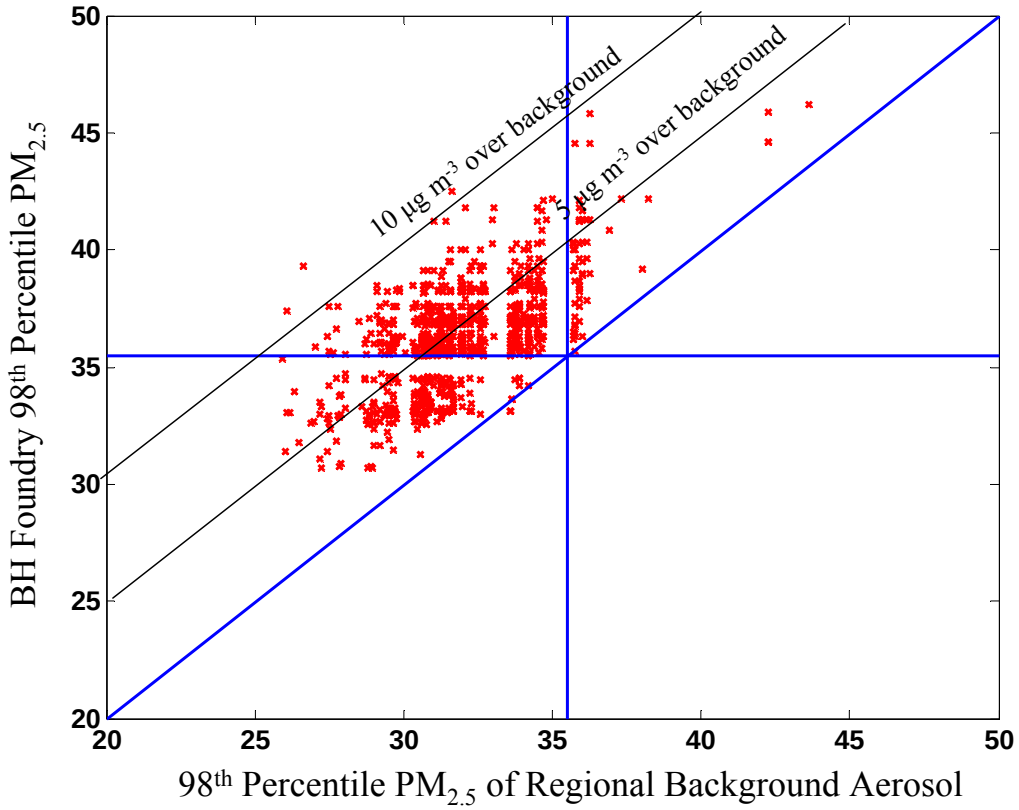


Figure 7-17. 98th Percentile of the Eastern Iowa Background, versus 98th Percentile at Wellman St. monitor. Each x represents a hypothetical one year period developed from Monte Carlo sampling of 2005-2008 daily data. In this simulation, 98% of the background aerosol cases are in attainment, while only 25% of the Wellman St. monitor years are in attainment.

Controls at Blackhawk Foundry would very likely lower the 98th percentile value at the monitor. But by how much would they lower it? To get at this, an additional plot of the same data that are shown in figure 7-17 is constructed. This time, however, the wind direction is used to predict (using the regression results from figure 7-5) the increment over background. For each year of the simulation, this predicted source impact changes, and the variability is used to get some additional insight into how the 98th percentile will change if a source is controlled.

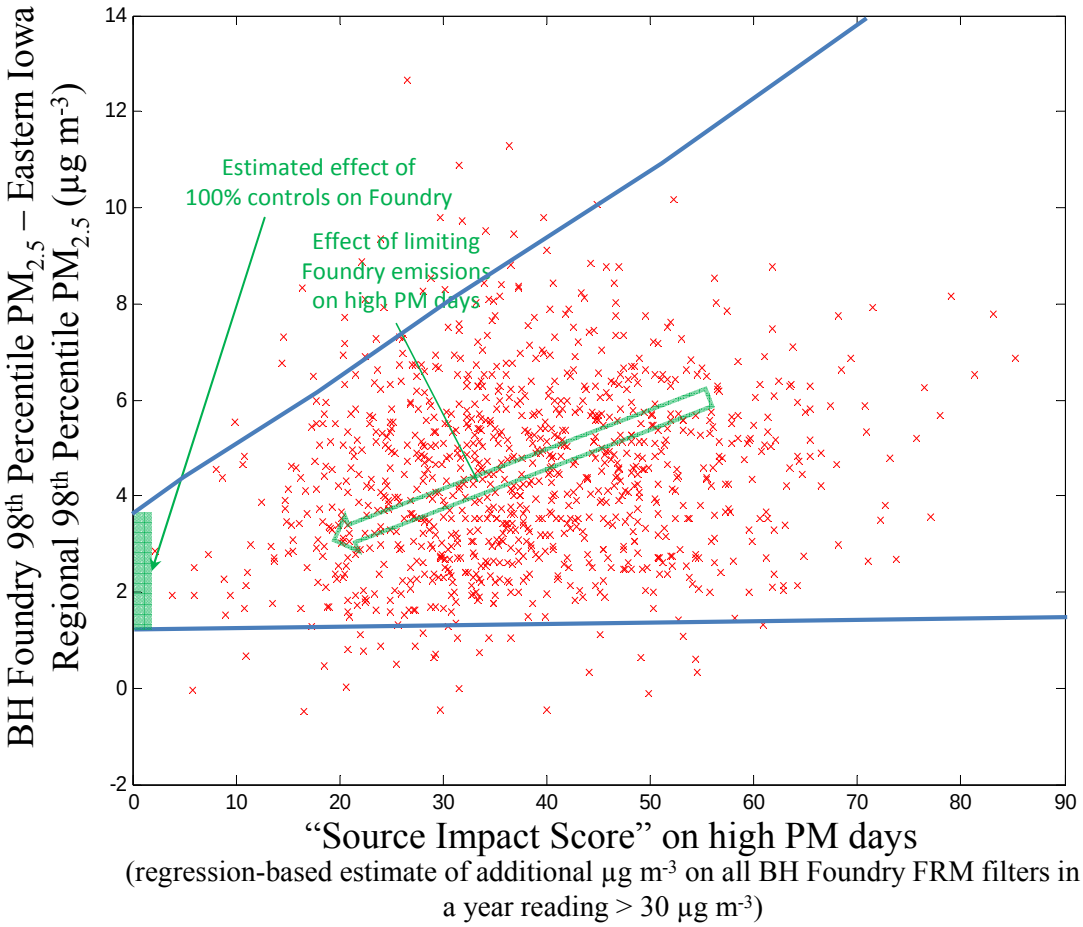


Figure 7-18. Year to year variability in the impact of the source to the southwest of the Davenport (Wellman St) monitor. Each x is a simulation of a hypothetical year (1000 in total). By extrapolating to the left side of the graph, an estimate of the 98th percentile PM values that could be expected with the source controlled is possible. The monitor is tentatively placed at 1.5 – 3.7 µg m^{-3} above the Eastern Iowa background value under 100% controls, compared to the current values of about 2-8 µg m^{-3} above.

Because source controls will effect the 98th percentile only high PM days, the plot is restricted to days with FRM filter values of 30 µg m^{-3} or more.

The extrapolation to "0" for the source impact score on figure 7-18 gives an estimate of the impact of 100% controls on the sources that impact the Davenport (Wellman St.) monitor when the wind blows from 160-260° (presumed to be the foundry emissions). This should be considered a low confidence estimate which could be improved by additional work by the University of Iowa. This analysis places the monitor at 1.5 – 3.7 µg m^{-3} above the Eastern Iowa background value under 100% controls, compared to the current values of about 2-8 µg m^{-3} above.

If the "1.5 – 3.7 μg m^{-3} above the Eastern Iowa background value" condition could be achieved, then the attainment fraction changes from the current value of 25% to a new value of 81%. Thus, under 100% control of the incremental PM coming from the direction 160-260° (presumed to be the foundry emissions), the expected attainment of the 24-hour standard is bracketed between 81% (based on analysis above) and 99-100% (based on other Davenport monitors). These values are predicated on the samples from 2005-2008 being representative of future air quality.

7.6.2 Application of Statistical Sampling of 98th Percentile to Muscatine

An analysis identical to that of 7.6.1 was performed for Muscatine. The results for Muscatine are more definitive and are shown in figures 7-19 and 7-20. The continuous operations at GPC probably improve the robustness of this method.

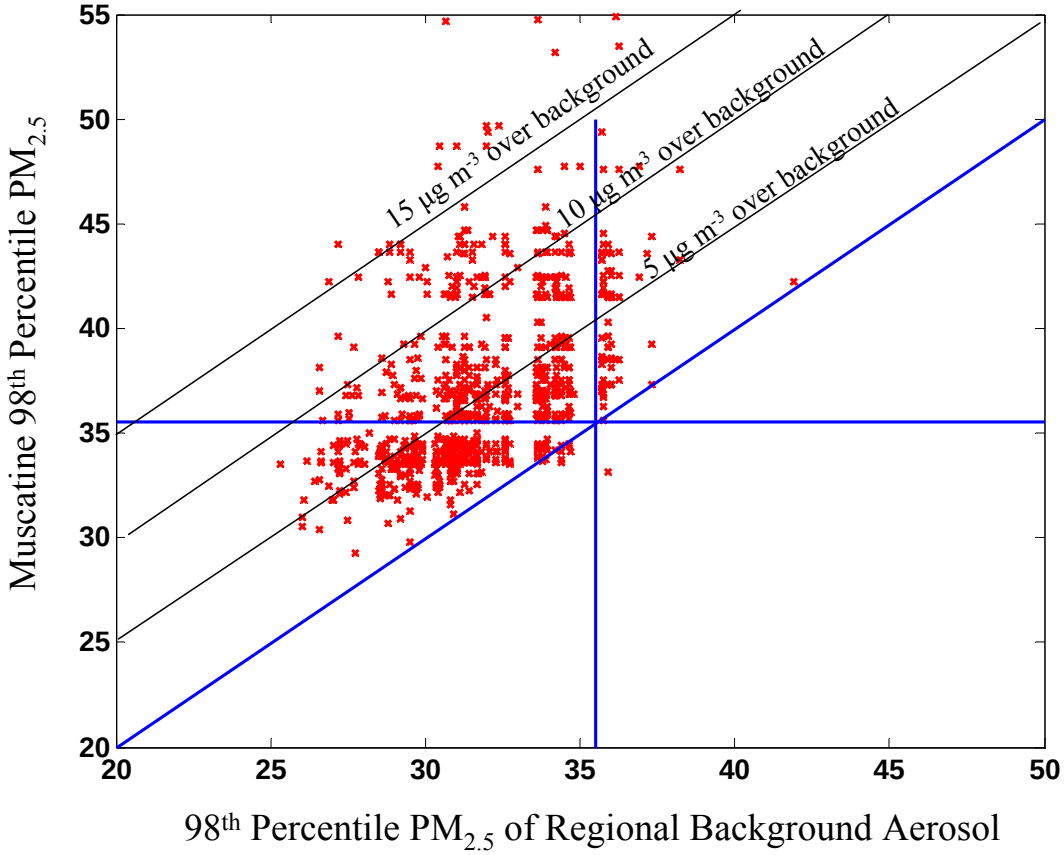
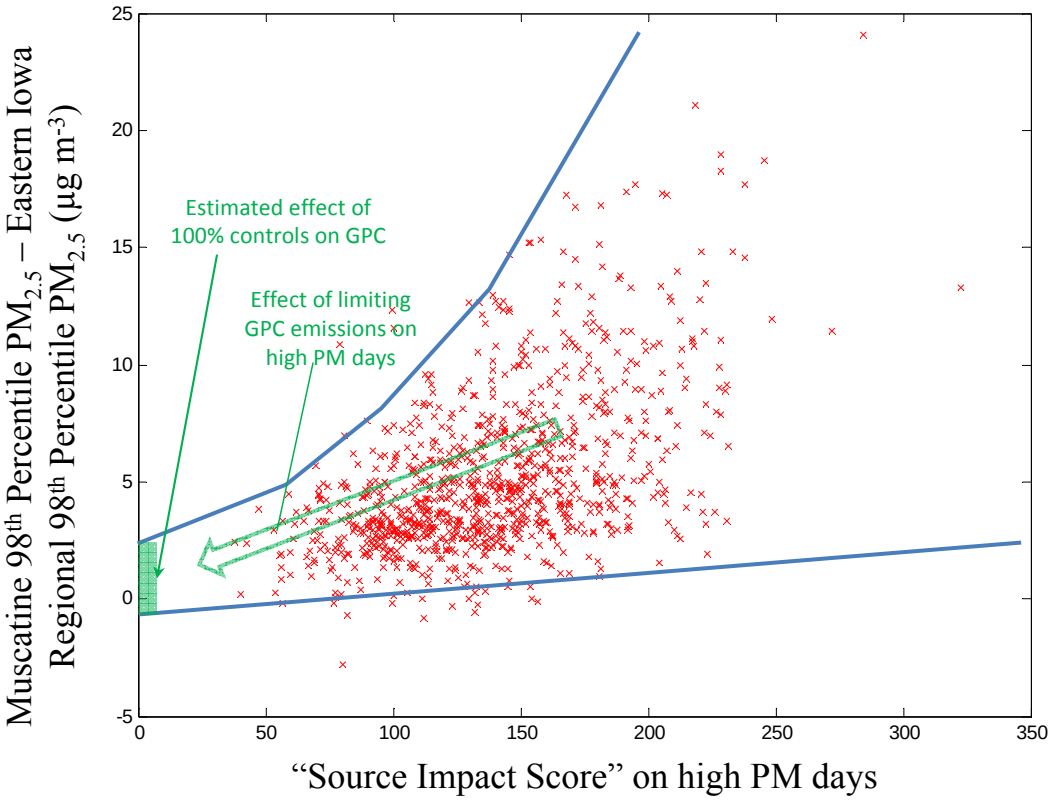


Figure 7-19. 98th Percentile of the Eastern Iowa Background, versus 98th Percentile at Muscatine monitor. Each x represents a hypothetical one year period developed from Monte Carlo sampling of 2005-2008 daily data. In this simulation, 98% of the background aerosol cases are in attainment, while only 43% of the Muscatine monitor years are in attainment.



(regression-based estimate of additional µg m^{-3} on all Muscatine FRM filters in a year reading > 30 µg m^{-3})

Figure 7-20. Year to year variability in the impact of the source to the east of Muscatine monitor. Each x is a simulation of a hypothetical year (1000 in total). By extrapolating to the left side of the graph, an estimate of the 98th percentile PM values that could be expected with the source controlled is possible. The monitor is tentatively placed at -0.5 to 2 µg m^{-3} above the Eastern Iowa background value under 100% controls, compared to the current values of about 2-11 µg m^{-3} above.

The extrapolation to "0" for the source impact score on figure 7-20 gives an estimate of the impact of 100% controls on the sources that impact the Muscatine monitor when the wind blows from 60-130° (presumed to be GPC emissions). This should be considered a low confidence estimate; this could be improved by additional work by the University of Iowa. This analysis places the monitor at -0.5 to 2 µg m^{-3} above the Eastern Iowa background value under 100% controls, compared to the current values of about 2-11 µg m^{-3} above.

If the "-0.5 to 2.0 µg m^{-3} above the Eastern Iowa background value" condition could be achieved, then the attainment fraction changes from the current value of 43% to a new value of 98%. Thus, under 100% control of the incremental PM coming from the direction 60-130°

(presumed to be the GPC), the expected attainment of the 24-hour standard is bracketed between 98% (based on analysis above) and 96-100% (based on other Southeast Iowa monitors), for a range of 96-100%. These values are predicated on the samples from 2005-2008 being representative of future air quality.

7.7 Conclusions

Analysis of wind direction vs. $PM_{2.5}$ levels confirmed previous analysis (e.g. 9-Factor Studies by DNR) of local impacts from wind directions consistent with Blackhawk Foundry and GPC. Quantitative estimates of the directional/local impact (and uncertainty bounds) were calculated.

In addition to local impacts in Muscatine and at the Wellman St. samplers, some possible local source impacts were identified for the 10^{th} and Vine site. A fairly strong local impact was identified originating to the south of one of the Clinton samplers.

Much more powerful source receptor tools (see Literature Review) are available, and have been used to sort out multiple industrial impacts in dense areas such as East St. Louis and Detroit.

Preliminary estimate of the "what if" scenario should substantial decreases be made on the local impact at these sites were completed (see section 7.6). This analysis does not consider actual source controls that may be in the implementation or planning stages at these facilities. Some discussion of controls is included in the regulatory background documentation in Appendix K.

8 DO AIR QUALITY MODELS REPRODUCE IOWA'S PM EPISODES?

The ability of models to reproduce air quality concentrations is very well studied, and a number of the relevant studies were included in the literature review. However, many of these studies focus on the ability of the models to reproduce long term average PM levels. Skill at reproducing long term averages is important. In fact, it is critical for development of implementation plans to bring large sections of the country into compliance with the annual average 15 μg m^{-3} standard. Because of this important application, many air quality models have been optimized to correctly reproduce long term averages of $PM_{2.5}$ and $PM_{2.5}$ composition.

Simulation of episodes, especially wintertime episodes, is a much less studied topic. However, in order to fill the gap in knowledge, 2002 model runs were obtained from Scott Spak (now at University of Iowa) and Tracey Holloway at the University of Wisconsin (Spak and Holloway, 2008). Spak and Holloway evaluated CMAQ predictions over the Great Lakes for a 2002 model year run. Nitrate prediction skill is classified as "Good" in winter and fall, and ammonium prediction is classified as "Good" for all seasons. "Good" is defined as fractional bias less than ±30% and fractional error less than 50%. Nitrate prediction is classified as problematic in spring and summer, although the absolute magnitudes of these errors are small. January mean bias (nitrate) reported by Spak is -0.01 (1% low) for STN and +0.14 (14% high) for IMPROVE samples.

To extend those results, model results during two cold weather episodes from 2002 are examined. These are episode 2002-1 (Feb 6-8) and 2002-12 (Dec 10-16). From the data, these episodes are characterized by $PM_{2.5}$ levels in Iowa in the range of 20-35 μg m^{-3}. Though these are not severe episodes such as the 2007-20 episode, they are the strongest cold weather episodes in 2002 (the year for which model data is available).

8.1 Episode 2002-1

From the standpoint of data, here is how those episodes look.

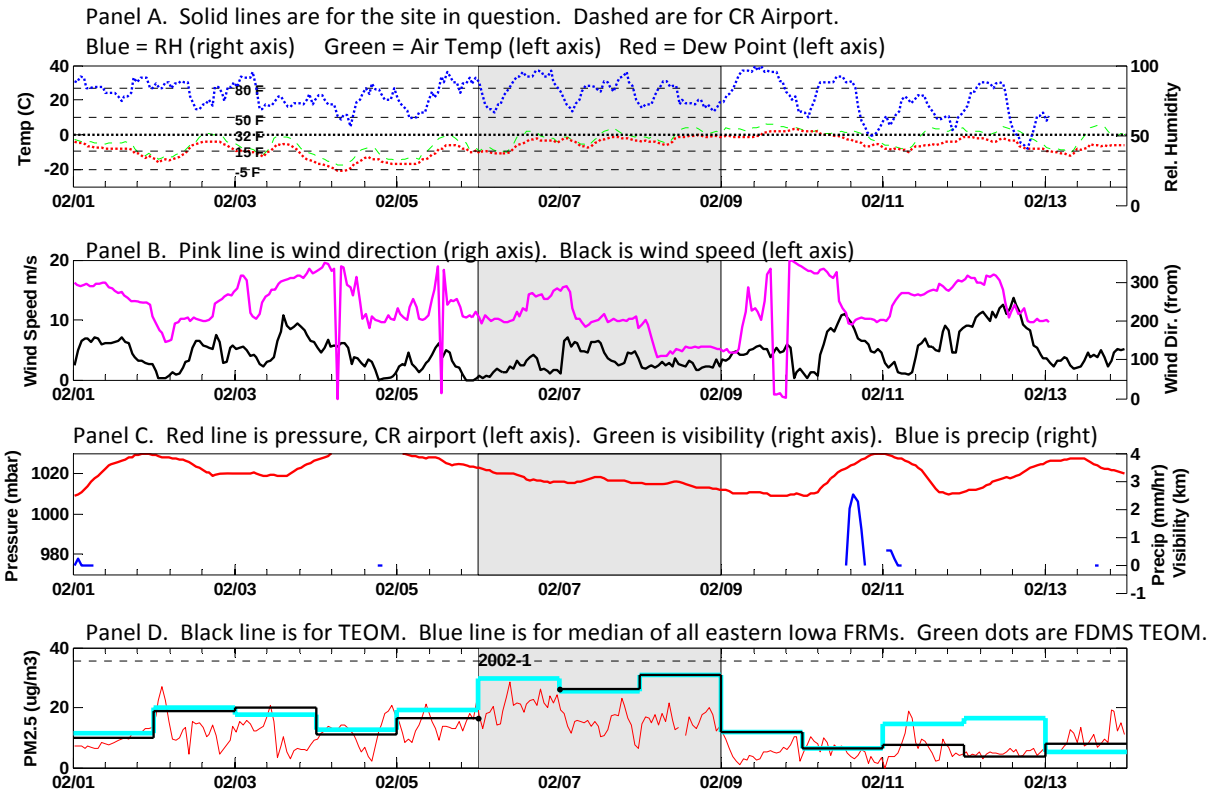


Figure 8-1. Time series of 2 weeks during February 2002 at Davenport, IA, including episode 2002-1 (Gray box)

As shown in Figure 8-1, this episode fits the "standard pattern" of temperatures just below freezing at the beginning of the episode, rising to above freezing at the end. Low wind speeds and high RH are also evident. Southwesterly wind gives way to easterly flow at end of episode. The heated TEOM misses significant mass during episode, suggesting significant nitrate component to aerosol.

Figure 8-2 shows the spatial pattern of $PM_{2.5}$. The spatial pattern of the episode shows a persistent area of elevated PM centered first on Wisconsin, then on Chicago. Differences in the spatial smoothness of figure 8-2A are in part due to the different number of data points (white circles), caused by monitor schedules that do not have a sample every day. With fewer samples on the 6th and 8th, kriging makes a smoother surface. The model places high and low concentration features correctly on each day. More detailed hourly time series are shown in Figure 8-3. Except for over-prediction in Cedar Rapids on the 12th, the magnitude and timing of the event are well predicted.

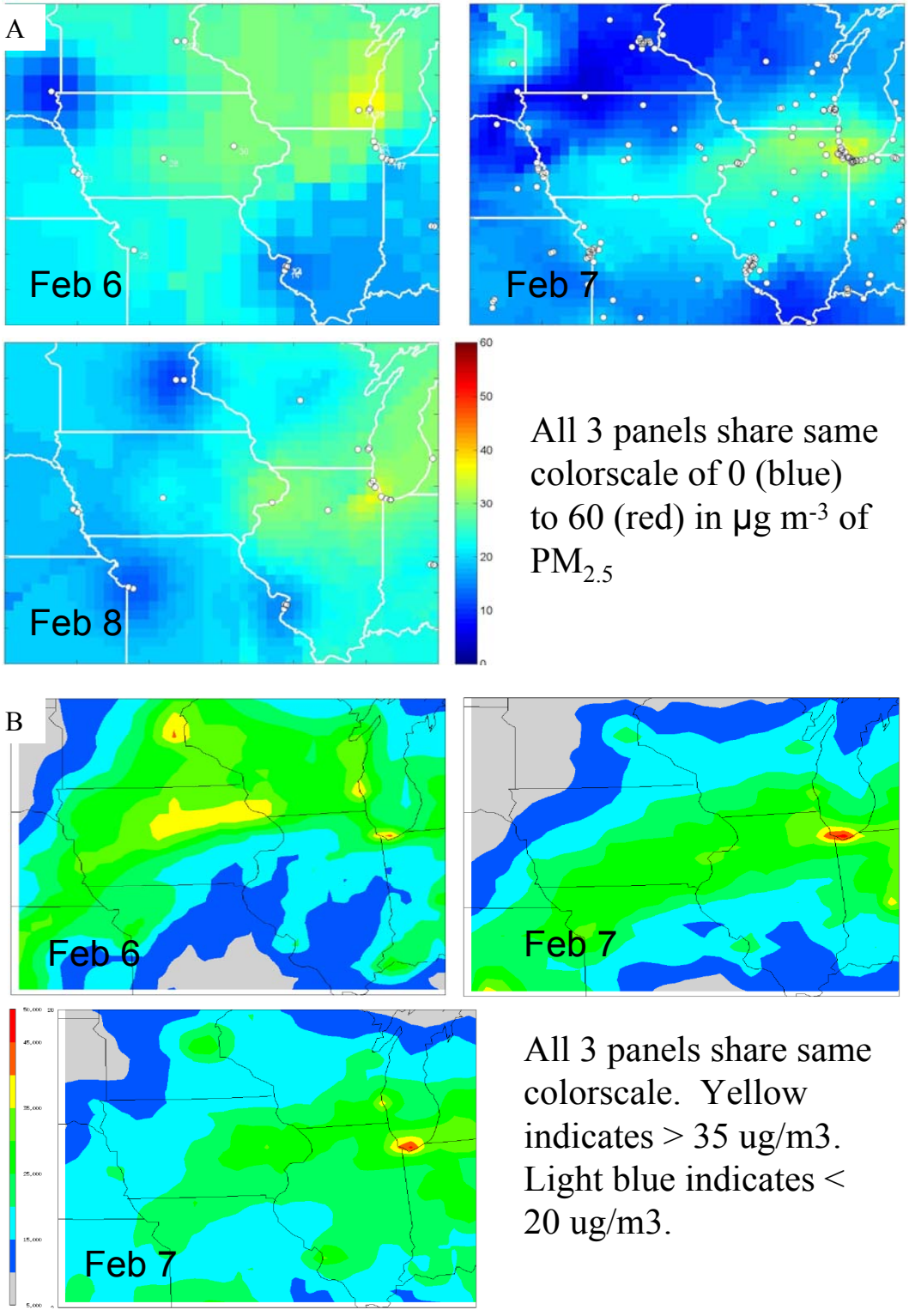


Figure 8-2. Daily average PM2.5 spatial patterns for Feb 6, 7 and 8 2002 A) from FRM data B) from CMAQ simulation

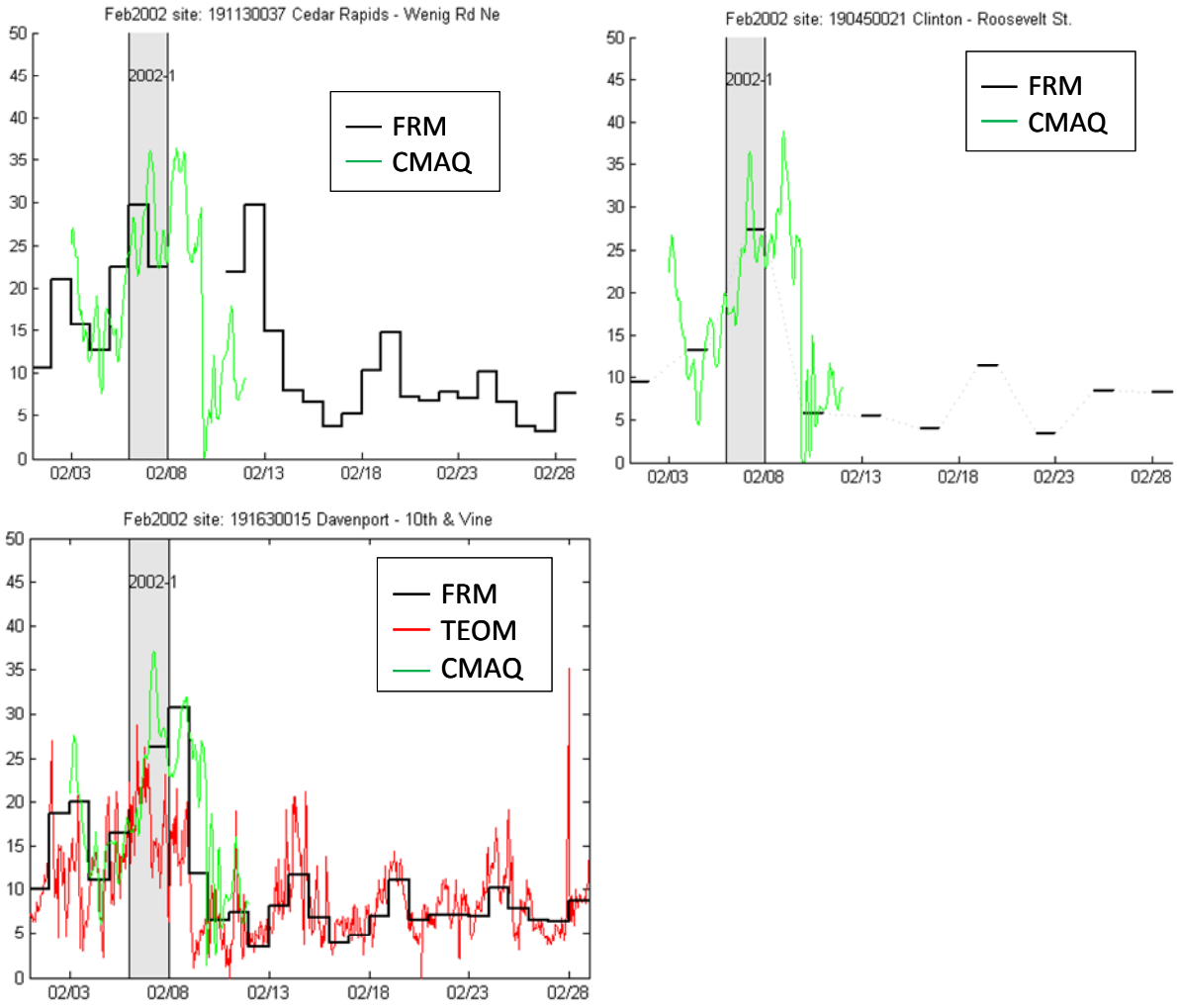


Figure 8-3. Month of February 2002 $PM_{2.5}$ time series for Cedar Rapids, Clinton, and Davenport. FRM (black), heated TEOM (red), and CMAQ prediction (green).

8.2 Episode 2002-12

As shown in Figure 8-4, the second episode (2002-12, December 2002) has two phases – a build up phase from 10th until the 14th, and then a cleanout phase on the 15th and 16th. RH drops from 70-100% during the first phase to 40-70% during the second phase. Wind speed picks up at the end of the episode as well.

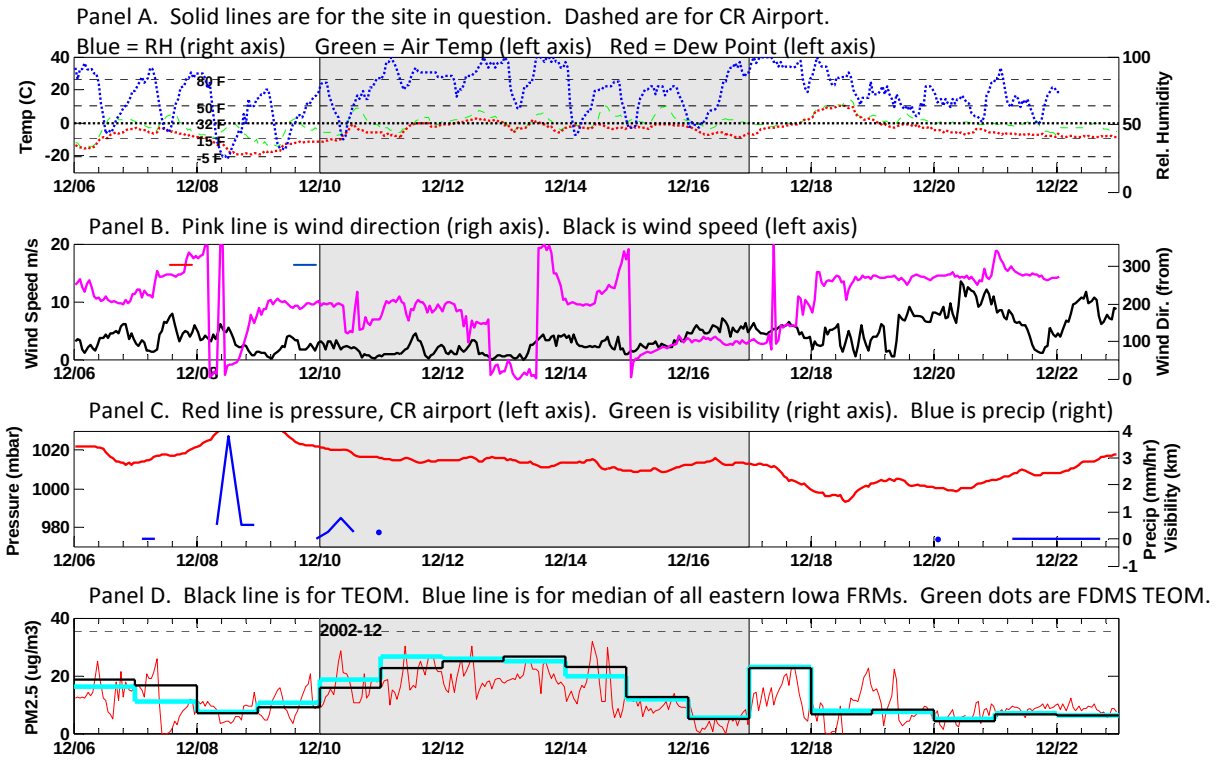


Figure 8-4. Time series for two weeks in December 2002 at Davenport, IA, including episode 2002-12 (Grey box).

The spatial pattern is more complicated in this episode, with strong concentration gradients present on the 10th and 13th (~30 µg m^{-3} to 15 µg m^{-3} over a few hundred km). Actual concentrations in eastern Iowa peak on the 11th in the low 30s and then falls into the 20s. The model has concentrations peaking later (on the 12th) in the mid 30s. General spatial features are again reproduced by the model as shown in Figure 8-5.

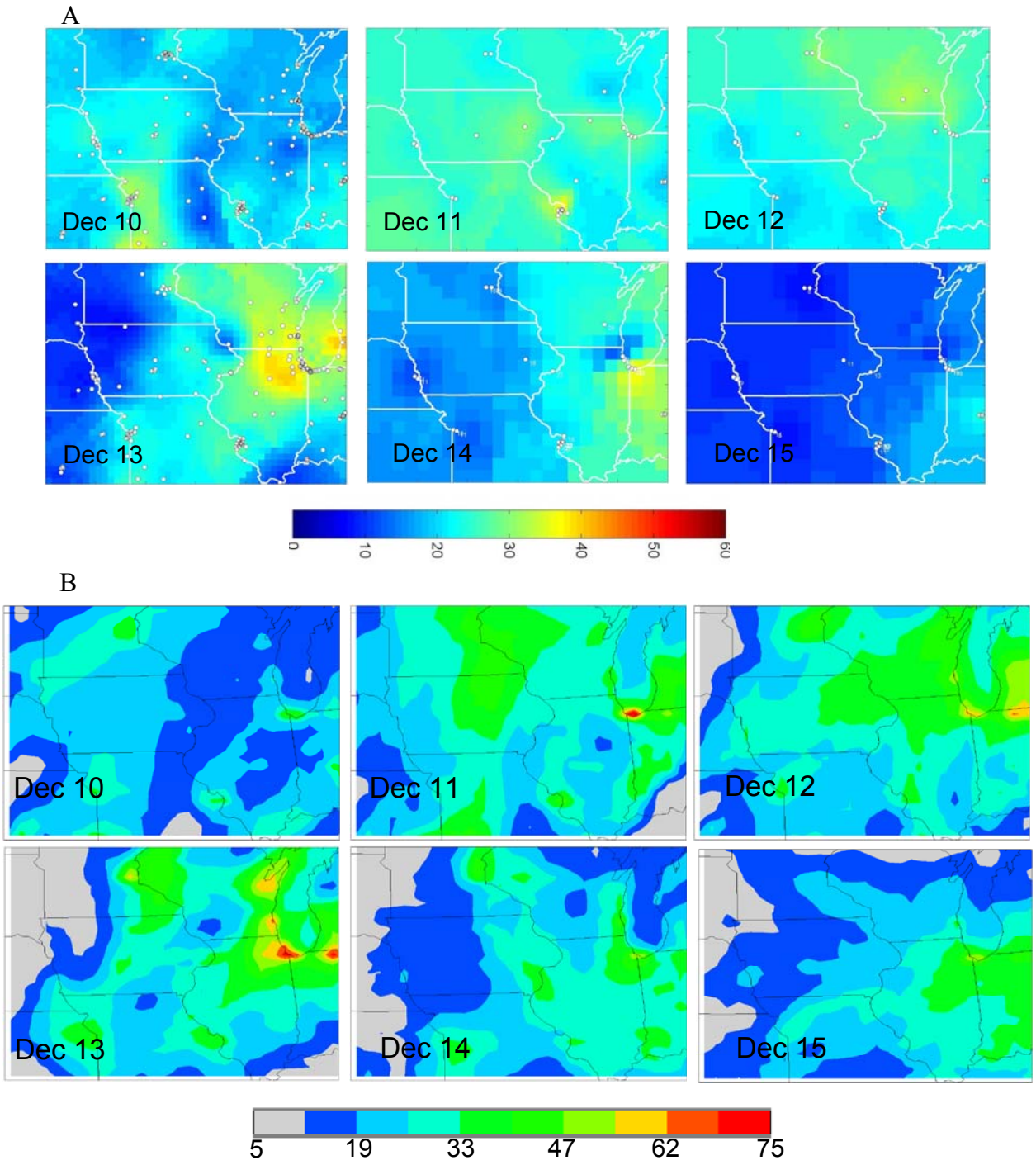


Figure 8-5. Spatial patterns of daily PM2.5 in A) FRM and B) CMAQ during episode 2002-12.

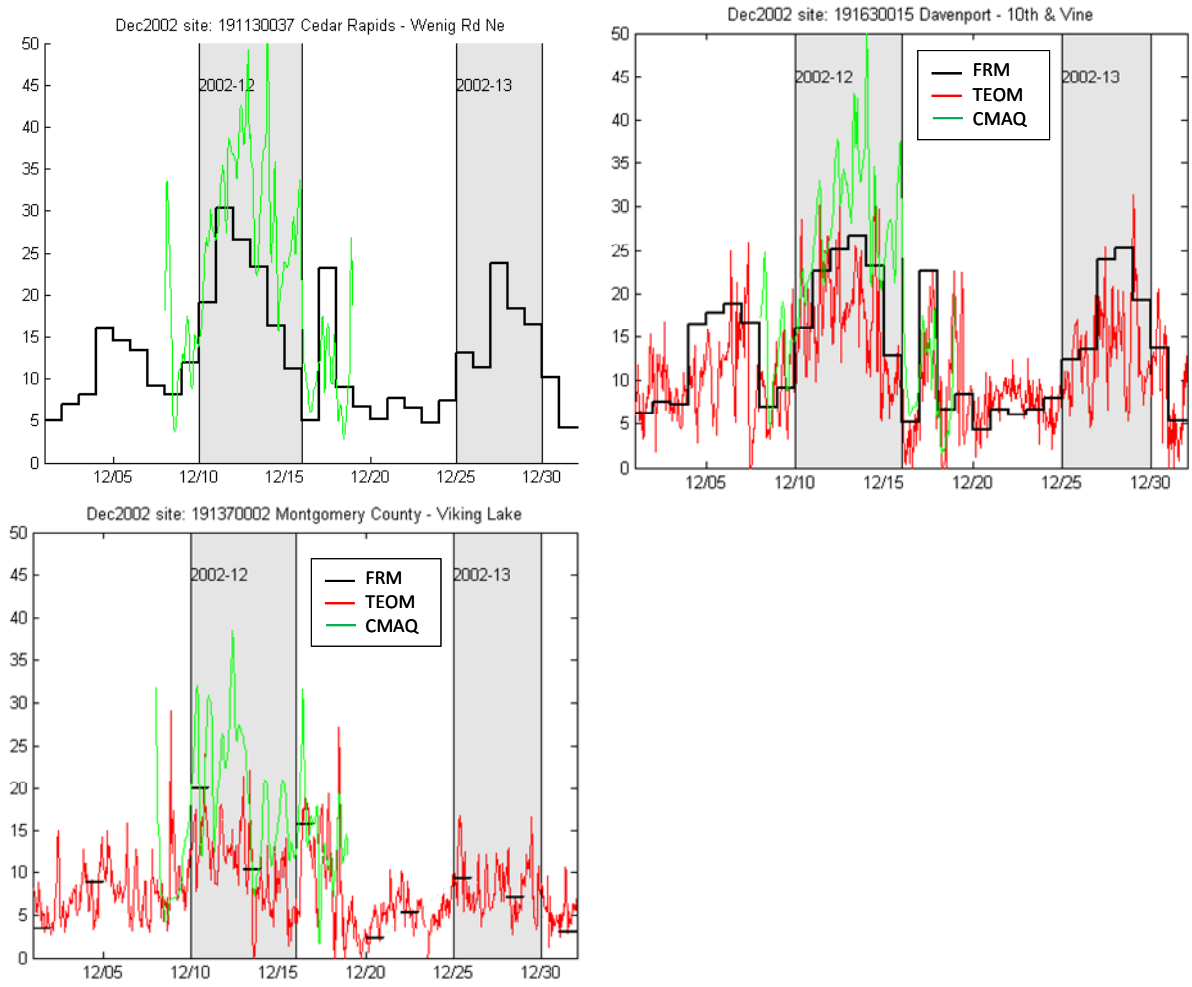
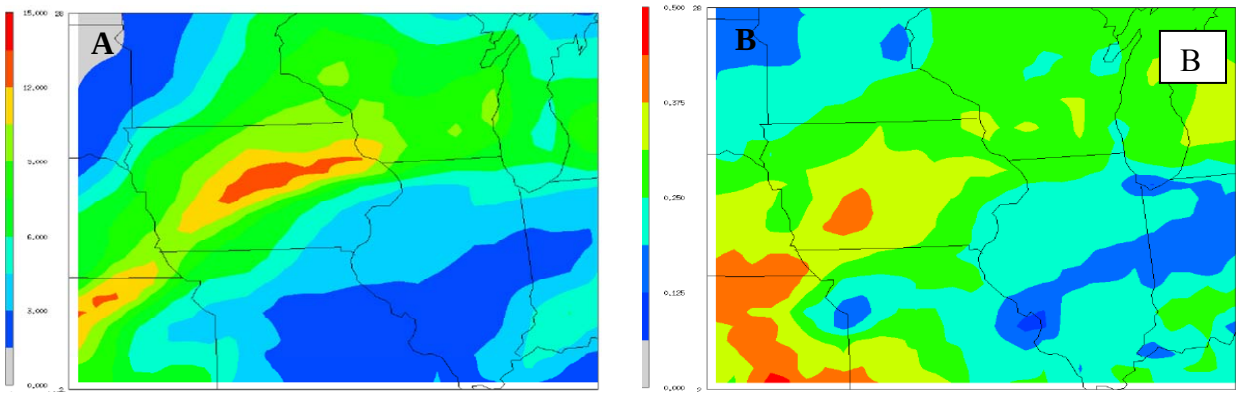
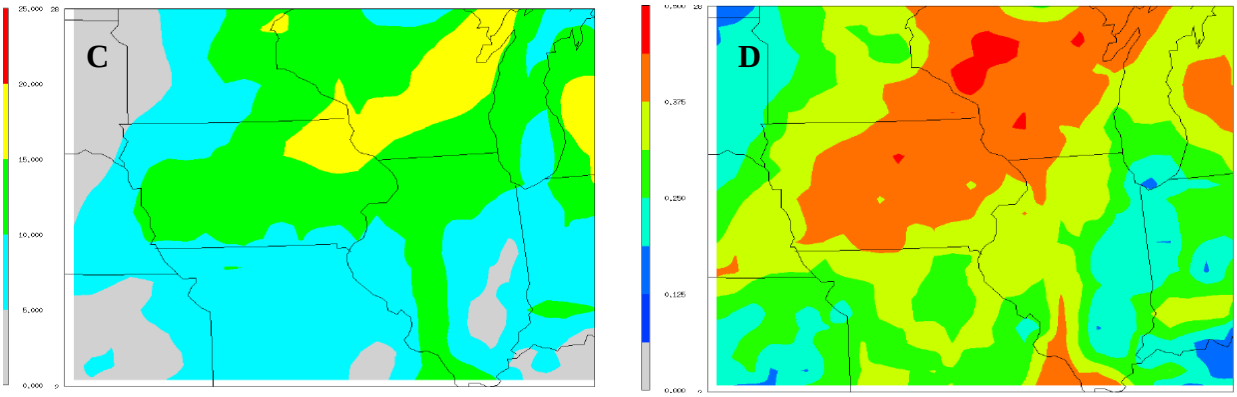


Figure 8-6. Month of December 2002 $PM_{2.5}$ time series for Cedar Rapids, Davenport, and Viking Lake. FRM (black), heated TEOM (red), and CMAQ prediction (green).

Some successes can be seen in the model-data comparison such as the good agreement with FRM in Viking Lake and the matching of the short peak in Davenport on the 17th. Some problems are also evident – the peak of episode is actually measured at around 30 μg/m^3, while the model predicts a peak in the 40s. Some of this may be negative measurement artifact, but model over-prediction is probably more likely.



Feb 6 – nitrate reaching 14 ug/m3
Nitrate fraction reaching 0.4



Dec 12 – nitrate reaching 15-20 ug/m3
Nitrate fraction reaching 0.4

Figure 8-7. Modeled daily average fine aerosol nitrate (A,C) and modeled nitrate fraction in $PM_{2.5}$ (B,D) at the peak of each of the episodes. Data to compare against is very sparse during this period, but the nitrate fractions compare favorably to those from section 5.

8.3 Monthly correlation of model to measurement

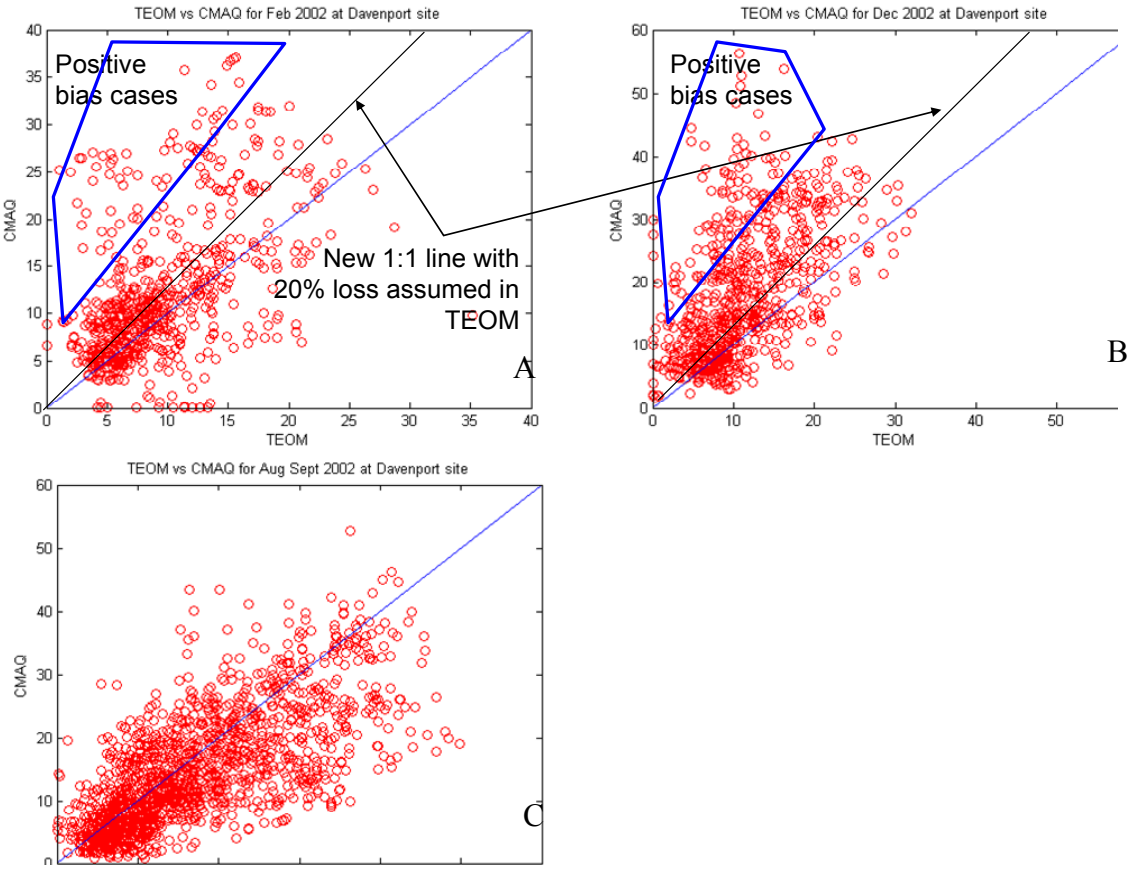


Figure 8-8. Scatterplot of hourly TEOM concentrations versus CMAQ for 3 periods at Davenport, IA site in 2002.
A) Feb B) December C) August and September 2002.

Figure 8-8 shows TEOM versus CMAQ for 3 periods in 2002. Focusing on the winter periods, the known positive bias of the model can be seen. This is commonly observed, as described in the literature review. Agreement with the TEOM is not expected because of known wintertime losses in that instrument. A 20% loss is assumed in the TEOM in drawing the black lines of model-measurement agreement.

8.4 Discussion

While this has been confined to largely qualitative comparison, the behavior of this model at simulating individual episodes can be classified as acceptable to good. And these are predictions by a model that was not designed for the purpose of urban scale prediction (it was run for regional scale prediction). The resolution is coarse (36km x 36km) compared to what is possible, and an important plume-in-grid algorithm that can help with concentrated point sources was not activated in the Spak and Holloway run.

The ability of the model to get reasonable spatial gradients, reasonable nitrate fractions, and its ability to track the temporal rise and fall of the episodes in a realistic way is promising. Finally, it should be stated that for air quality planning purposes individual episodes do not have to be simulated. It is sufficient to reproduce the correct types of episodes on average, with some episodes a bit too strong, and others a bit too weak. Not discussed in this chapter (but considered in the literature review) is the fact that it is critical for air quality planning to have the sensitivities in the model correct. In other words, is the simulated effect of a specific emissions reduction realistic?

Further work would be required to show this for CMAQ or any other model implementation. The limitations in model sensitivities can be overcome somewhat by supplementing the forward model with source-receptor, observational-based considerations, and box models.

9. DISCUSSION & CONCLUSIONS

Although final action by EPA is not complete, the favorable 2008 $PM_{2.5}$ monitoring values from Davenport (Wellman St.) and from Muscatine will most likely result in Iowa having no $PM_{2.5}$ nonattainment areas based on 2006-2008 monitoring data (Fitzsimmons 2009).

The information in this report is valid irrespective of the attainment status of any location. This report explains why concentrations are the way they are, and forecasts the range of these concentrations in the future under various scenarios.

The information in the report should be of high value in (a) keeping Iowa and the Quad Cities in attainment status; (b) understand the likelihood of future nonattainment under various scenarios; and (c) plan for possible future decreases in either the 15 $\mu g\ m^{-3}$ annual standard, or the 24-hour 35 $\mu g\ m^{-3}$ standard. It should be noted that the Clean Air Scientific Advisory Committee (CASAC), which advised the EPA on the setting of the $PM_{2.5}$ standard, recommended values of 13-14 and 30-35 $\mu g\ m^{-3}$, respectively, for the annual and 24-hour standards. The EPA adopted a less stringent annual standard, and chose the high end of the CASAC range for the 24-hour standard. It is reasonable to assume that at some point in the future, these limits will be reconsidered, and that the scientific and public health communities will advise lower limits.

9.1 Discussion of the limiting reagent in wintertime and during episodes

While many authors have looked in general at the sensitivity of PM levels to total nitric acid and ammonia, most analyses have not been directly applicable to wintertime episodes in the Midwest. Instead, they have been focused on longer averaging times, on nitrate replacement of sulfate, and on PM in the Eastern U.S.

Authors who have looked at the wintertime Midwest have some disagreement on nitric acid vs. ammonia sensitivity. Dennis et al. (2008) have in their model that the Midwest in winter (Jan 2002) has an adjusted gas ratio in the range of ~1.1 to 1.7, and thus ammonia is somewhat in excess. Chu et al. (2004) found that ammonia was present in excess in areas west of the Ohio river during the Feb 6-8, 2002 episode.

More detailed analyses shows that the Lake Sugema, IA site is, on average, in balance in terms of ammonia and nitric acid sensitivity in winter (Blanchard 2008). Sensitivity to reductions in either total nitric acid or total ammonia are approximately equal. In winter at

Bondville, IL, the PM appears on average to be more sensitive to ammonia reductions. While in Mayville, WI, average winter levels are such that the system is nitric acid limited. This fits the general pattern of increasing ammonia availability as one moves northwest from Southern Illinois (possibly slight ammonia deficit) to the Illinois-Iowa border (ammonia and nitric acid in balance) to Wisconsin and Minnesota (free ammonia in excess). Blanchard also investigated a high PM episode (Feb 2005) and found that Lake Sugema was balanced in terms of ammonia and nitric acid limitation during the episode.

Lee and Hopke (2006), imply that high nitrate events in St. Louis are ammonia-driven because they have back trajectories that come from the ammonia rich upper Midwest. However, it is difficult to apply this study to Iowa because St. Louis is in general more ammonia limited than Iowa, and the source-receptor technique is less direct and less reliable at determining the limiting reagent than the chemical box models such as that used by Blanchard (2008).

Synthesizing these results, one would have to say that (a) the most common conclusion regarding rural sensitivity on long (monthly timescales) is that Eastern Iowa is either balanced in sensitivity to nitric acid and ammonia, or slightly with ammonia in excess; (b) that said, there is not a solid consensus on the issue of sensitivity, even at monthly averaging timescales and in rural locations; (c) the picture becomes less clear when moving to episodic timescales and urban locations; and (d) there is some evidence that eastern Iowa is on a transition line between ammonia excess (to the northwest) and ammonia limitation (to the southeast). Thus, sensitivity may change from event to event depending on season and meteorology. While it is tempting to focus on intense NOx sources along the Mississippi river valley and decide that nitric acid should be in excess, there are two problems with this: first, it takes time (~days) for the NOx to react to nitric acid; and second, some recent aircraft studies in the Eastern U.S. found the most intense ammonia plumes downwind of cities, and not (as perhaps expected) downwind of agricultural locations (Nowak, Neuman et al. 2007).

These issues of the ammonia-nitric acid balance, and the regions and sources of influence, could be addressed by the University of Iowa or by other researchers using a box-model + measurement + 3D modeling approach [e.g. Pinder et al. (2008)]. Such an analysis could possibly use existing NH_3 and nitrate measurements from Davenport. This would be necessary to further constrain the sensitivity question in eastern Iowa's towns and cities.

9.2 Discussion of control strategies

In general, there is a question on whether to control particulate matter by reducing primary particle emissions, or by reducing the gases that are precursors to secondary aerosols (in this case, NO_x and ammonia). If the decision is to target secondary emissions, then there is a choice on whether to control local NOx, distant NOx, local ammonia, or distant ammonia. In other words, which of the pathways should be limited in the conceptual model figure (repeated here from figure 3.1)?

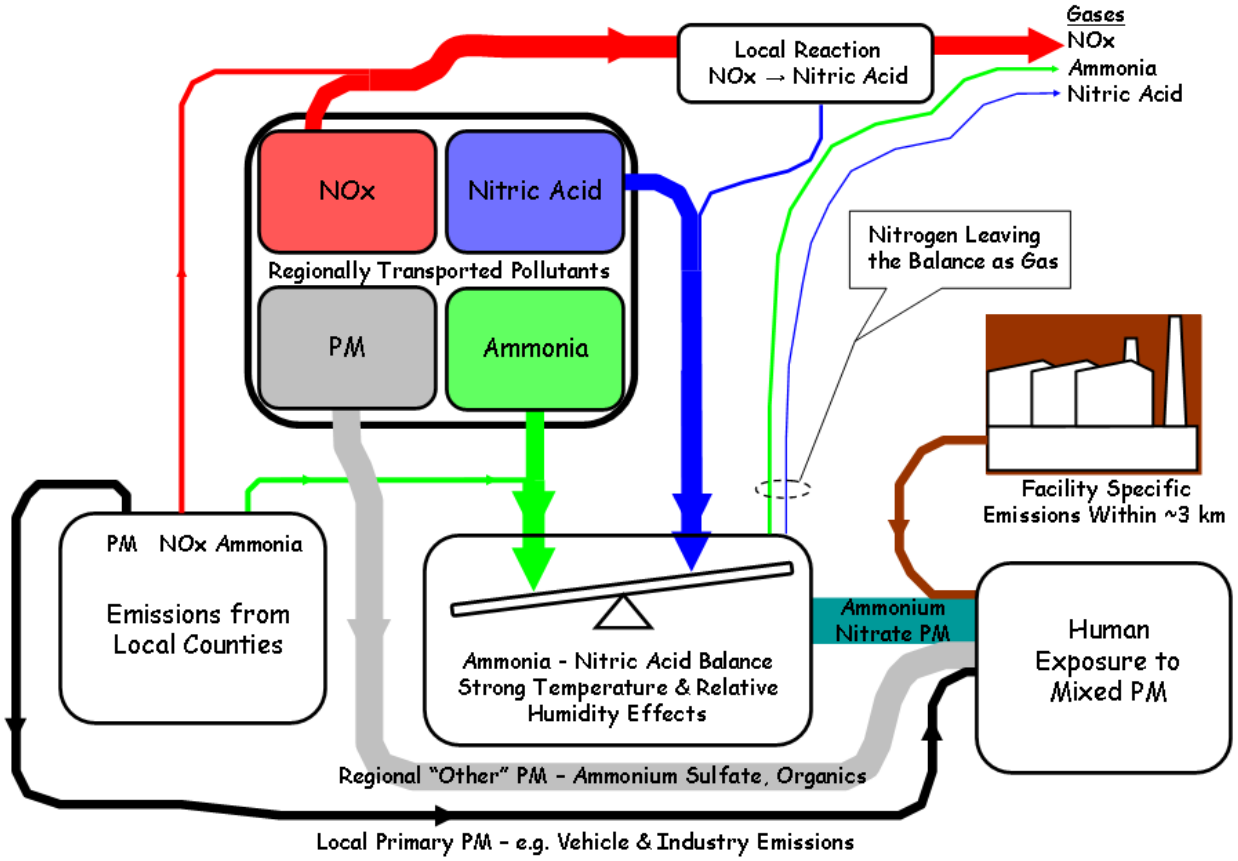


Figure 9-1 (repeat of figure 3-1). Conceptual model for particulate matter formation and concentrations in Iowa.

Since no reaction time is necessary for ammonia to participate in PM formation, ammonia control should be sought wherever they are (a) possible and (b) have an upwind influence on the receptor of interest. Air quality models could be used to determine locations with upwind influence on total ammonia in the affected areas. Detailed analysis of the continuous ammonia monitor data from Lake Sugema and from Davenport could also shed light on this, as could the winter 2008-2009 LADCO study focusing on nitrate episodes in Wisconsin.

Since NOx emissions do require reaction to form nitrate, the issue is more complicated, but also more widely studied. If NOx reacted very slowly, then there would not be an urban increase in nitrate aerosols, as all the NOx would leave the urban area before reacting. A combination of modeling studies and detailed review of existing "local-regional split" studies is recommended prior to targeting local or regional NOx in Iowa.

Based on the speciation results from chapter 5, and the local-regional split values reviewed in chapter 3, the following items seem clear: During cold weather regional episodes, the largest controllable form of PM is ammonium nitrate, of either regional or local origin. Control of either of these could lead to reductions in average and peak $PM_{2.5}$ levels. Ammonium nitrate of local origin is not insignificant, perhaps ~13% of the total during episodes.[1] The decision on what sources to control and where would need to be supported by extensive model-based study, including technical feasibility and cost analysis.

9.3 Potential problems of focusing on source-monitor pairs

This report is focused on the IDNR $PM_{2.5}$ monitoring network, and especially in a few monitor-source pairs with high $PM_{2.5}$ levels. For example, aggressive control of sources to the east of the Muscatine monitor (presumably GPC) and control of sources to the south-southwest of the Wellman St. monitor (presumably Blackhawk Foundry) have the possibility to bring those monitors definitively into compliance with the 35 $\mu g\ m^{-3}$ standard.

It should be realized by all the stakeholders considering air quality in Iowa, that there is more to air quality than just achieving suitable concentrations at the monitors mentioned above. The community needs to think beyond the monitoring network, and make sure that hotspots in terms of $PM_{2.5}$ are identified, evaluated, and mitigated if necessary. One can imagine scenarios where monitors show attainment, but public health concerns were not equitably addressed. As the figures on source locations (Appendix I) show, GPC and Blackhawk Foundry are not the largest PM or NOx sources in Eastern Iowa. And there are multiple industrial sites performing similar operations (corn processing, and industrial metal production and processing, respectively). Fine resolution air quality simulations can help in identifying hotspots, especially if plume-in-grid treatments are used.

[1] Based on 50% ammonium nitrate, and 25% of ammonium nitrate as local in orgin.

9.4 Possible future work

Options for future work can be developed in more detail in response to the discussions engendered by this report. But options can be summarized using the following table:

Table 9-1. Overview of possible future research directions

Knowledge Gap	Solution
Nitric acid or ammonia limiting (whether to reduce NOx or ammonia)	I. Reanalysis of existing Iowa nitrogen data and newer studies; Analysis of LADCO winter 08-09 Wisconsin Study II. Intensive nitrogen sampling winter 2009-2010
Is there a trend in regional episode occurrence? Is this related to shifts in ammonia, NO_x, and SO_2 emissions?	III.Regional modeling and additional data analysis
Control NO_x/NH_3 in the affected county, in Iowa, or on a more broad regional scale?	III. Regional modeling
Local fraction of PM during episodes (3-25% ?) but with very high uncertainty, balance of primary and secondary, and source categories with most leverage	III. Regional modeling IV. Source apportionment study

The solutions fall into four categories:

I. Additional data analysis of speciated $PM_{2.5}$ data from the Midwest ammonia monitoring project and other sampling data would be warranted. This would be done in concert with thermodynamic partitioning computer modeling in use at the University of Iowa, to determine whether nitric acid or ammonia is limiting during episodes. This is a low cost, and low risk exercise.

II. Intensive nitrogen sampling in winter 2009-2010. This would be done only after I, if additional data was needed. The value would be confirmation of the sensitivity to NOx and ammonia determined from other datasets.

III. A modest program of regional air quality modeling is warranted to investigate the spatial scales for effective control of SO_2, NOx and ammonia. Special focus would be given to the relative impacts of county-specific emissions, as compared to more broad Iowa/Illinois Mississippi river corridor emissions, and to emissions from more distant locations. This could be done with the IDNR tools discussed in the literature review, or with unique "inverse modeling" University of Iowa tools. In either case, more extensive evaluation of model performance during episodes is required.

IV. The State of Iowa, and the stakeholders for air quality in Iowa and the Quad Cities, should take a proactive stance toward further understanding the relative contributions of various

air pollution sources to episodes both from a geographical standpoint (where would source controls be effective at reducing episodes), and from a source apportionment standpoint (what source categories should be controlled). A three part effort is recommended: (a) pilot study source apportionment in winter 2010; (b) program of collection and storage of filters for later analysis of episode PM chemistry; and (c) if needed for future air quality management decisions, analysis of the archived filters from b during baseline or episode periods. This would be a cost effective and proactive stance which would be especially important should the EPA lower the annual $PM_{2.5}$ standard to less than 15 $\mu g\ m^{-3}$, or lower the 24-hour standard below 35 $\mu g\ m^{-3}$.

Other research foci that may be useful are:

- Extension of this analysis to other upper Midwest states, thus building a truly regional picture of the episodes. This could include calculations of the episode size (by species, e.g. for nitrate, for sulfate, etc.).
- Detailed analysis and or new sampling to constrain nitric acid formation kinetics (e.g. N_2O_5 reactions). This would be coupled with further analysis of gas phase concentrations (mainly NOx and O_3) to complete the current picture of cold weather episode development. Could be combined with regression analysis of what factors can predict the relative severity of regional episodes on a site-by-site basis. Candidates for analysis include RH, temperature, local point source strength, local mobile source strength, topography, snow cover, fog, ammonia availability.
- Dispersion modeling and high resolution modeling to further identify hotspots and/or source-monitor pairs.

9.5 Conclusions

An analysis of the available peer-reviewed literature on the topics of Midwestern particulate matter formation, and an analysis of 7 years of Iowa and Midwestern meteorological and particulate matter monitoring data, gives a reasonably clear picture of what is going on in Iowa's high PM episodes. High PM events occur over large spatial scales during both warm and cold seasons. For the period 2002-2008, the cold weather episodes have a small edge in both number and severity.

Cold season episodes occur during periods of low wind speed and poor pollutant removal. Depending on the surrounding land use, population density, and level of industrialization, each Iowa monitor is additionally impacted by locally emitted primary particulate matter. At the Muscatine and Davenport (Wellman St.) locations, the local impacts are well above background levels – they can be quantified using analyses based on wind direction and $PM_{2.5}$ measurements.

A list of 44 regional PM episodes (with $PM_{2.5}$ elevated for at least 3 Iowa monitors) was created for the years 2002 – July 2008. A companion list of non-regional episodes for the same

period was created. Detailed time series of pollution levels and meteorological variables were created and are available in online appendices. A time series of daily $PM_{2.5}$ values for the period 2002 – July 2008 was created from the median of Eastern Iowa monitors. This serves as a useful "background" PM from which to gage local impacts.

An attempt to forecast future attainment probabilities at Iowa sites was conducted. This used Monte Carlo sampling of random sets of $PM_{2.5}$ values. The result was that, for sites without significant source impacts, a high probability of future attainment. In other words, regional episodes in excess of 35 $\mu g\ m^{-3}$ are not frequent enough (based on their occurrence rates in 2002-2008) to put Eastern Iowa into non-attainment status. The accuracy of this conclusion is predicated on the assumption that the period 2002-2008 (with 30 episodes exceeding 35 $\mu g\ m^{-3}$) is representative of future conditions. If each year were to have 2 more episodes, then multiple eastern Iowa locations would probably fall into nonattainment.

Our preliminary work with wind direction versus $PM_{2.5}$ levels at Muscatine and Davenport (Wellman St.) show that the state of Iowa has collected a sufficient quality and quantity of data at these locations to establish the direction and magnitude of the source impacts. It should be feasible to gauge compliance with air quality standards in the event of future controls at these sources, and a preliminary estimate of this is included in chapter 7.

Analysis of speciated $PM_{2.5}$ data during episode and non-episode periods confirms a major role for ammonium nitrate during wintertime episodes, with nitrate rising to ~45% by mass of the total $PM_{2.5}$. During episodes, concentrations of all species increase, but the increase is strongest for ammonium nitrate.

There is insufficient evidence to definitely mark either nitric acid or ammonia as limiting during wintertime episodes. The most comprehensive studies to date show balanced influence between ammonia and nitric acid in their leverage on ammonium nitrate concentrations.

But there is disagreement among available studies. Furthermore, there is likely variability from place-to-place within Iowa and from episode-to-episode on which compound is more limiting to aerosol formation.

Nitric acid from NO_3 and N_2O_5 are likely to be important in Iowa in winter. The kinetics of this process are uncertain, and this uncertainty is reflected in a wide range of performance statistics for air quality models applied to wintertime nitrate. Fog processing of aerosols was found (in one source) to probably not be an important reaction mechanism for nitrate formation.

Snowmelt conditions, biological activity or atypical biogenic emissions during snowmelt conditions, and high actinic flux associated with reflective snow surfaces were not investigated, and these remain as open issues for the future.

Two episodes in 2002 were compared to their corresponding model predictions from a regional implementation of the CMAQ air quality model. Even though this model was not set up for urban scale predictions, the model reproduced the episodes fairly well. Spatial patterns of total $PM_{2.5}$ and nitrate, as well as temporal patterns agree fairly well. The model does exhibit some high bias (predicting too high a concentration), sometimes predicting > 40 μg m^{-3} on an hourly basis when less than 10 μg m^{-3} is registered by the monitor. However, the agreement is sufficient to explore control scenarios for reducing average and peak daily concentrations. If combined with observations of inorganic aerosol speciation, accurate scenarios for reducing PM through NOx and or ammonia controls could be developed.

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