



ANALYSIS OF RECENT REGIONAL HAZE DATA

Final Report

Submitted to

Mr. Michael Koerber and Ms. Donna Kenski

Lake Michigan Air Directors Consortium

2250 East Devon Avenue

Des Plaines, IL 60018

by

Betty K. Pun, Mark Leidner ⁽¹⁾ and Christian Seigneur

Atmospheric & Environmental Research, Inc.

2682 Bishop Drive, Suite 120

San Ramon, California 94583

Document Number CP180-04-2

August 2004

(1) 131 Hartwell Av., Lexington, MA

TABLE OF CONTENTS

Executive Summary	E-1
1. Introduction.....	1
2. Do All Upper Midwest Class I Areas Share the Same PM Characteristics?	3
2.1 Comparing PM and PM composition at Boundary Waters National Canoe Area, Isle Royal National Park, and Seney National Wilderness	3
2.2 Correlations of PM and PM components for IMPROVE sites in the vicinity of the Midwest RPO	7
3. Organic Compounds	18
3.1 Anthropogenic vs. biogenic OM.....	18
3.2 Primary vs. secondary OM	20
4. Inorganic Aerosols	32
4.1 What are the relationships between the inorganic components, sulfate, nitrate, and ammonium?.....	32
4.2 What are the possible responses of inorganic PM to the availability of sulfate, total (gas + particulate) ammonium, and total nitrate?.....	38
4.3 Can current information provide insights into the formation processes of sulfate and nitric acid?	45
5. What Can Be Inferred from Aloft Data about the Transport and/or Formation of PM? ...	48
5.1 Upper Midwest flights (Regional flight route for the WI aircraft)	48
5.2 Other flights	52
6. Analysis of Transport Pathways	58
6.1 Meteorological analyses by STI.....	58
6.2 Additional analyses.....	60

TABLE OF CONTENTS (CONTINUED)

7. Urban Excess67

8. Updates To Conceptual Model73

 8.1 PM composition73

 8.2 Transport73

 8.3 Formation of ammonium nitrate74

 8.4 Formation of sulfate74

 8.5 Organic compounds74

9. Recommendations for Future Work.....76

 9.1 Top priorities.....76

 9.2 Moderate priorities.....77

 9.3 Low priorities.....78

10. References.....81

Appendix A..... A-1

Appendix B.....B-1

LIST OF TABLES

Table 2-1	Average PM _{2.5} composition at Boundary Waters Canoe Area (BOWA), Isle Royale National Park (ISLE) and Seney Wilderness (SENE) in 2002 under IMPROVE and alternative assumptions	4
Table 2-2	Correlation coefficients of daily PM concentrations between selected IMPROVE sites	10
Table 2-3.	Correlation coefficients of daily sulfate concentrations between selected IMPROVE sites	13
Table 2-4.	Correlation coefficients of daily OM concentrations between selected IMPROVE sites	14
Table 2-5.	Significant correlations of monthly concentrations between selected IMPROVE sites	16
Table 3-1.	Estimated primary vs. secondary organic carbon (microgram/m ³) at speciation and IMPROVE sites using the OC/EC method.	27
Table 4-1.	Total nitrate (HNO ₃ T), free ammonia (NH ₃ F) and gas ratio (GR) representative of days with high PM concentrations from the MARCH-Midwest database.....	40
Table 4-2.	Common responses of total PM to changes in sulfate at low, high or all relative humidity conditions for several locations and seasons	41
Table 4-3.	Responses of total PM to changes in free ammonia (gas + particulate ammonia – 2 x sulfate) at low, high or all relative humidity conditions for several locations and seasons.....	43
Table 4-4.	Responses of total PM to changes in total nitrate (gas + particulate nitrate) at low, high or all relative humidity conditions for several locations and seasons.	44

Table 7-1.	Average differences ($\mu\text{g}/\text{m}^3$) between urban Indianapolis and nearby rural speciation site for summer, winter, and all seasons for several PM components.	68
Table 7-2.	Average differences ($\mu\text{g}/\text{m}^3$) between urban Indianapolis and nearby IMPROVE sites for summer, winter, and all seasons for sulfate, nitrate, and total carbon.....	70

LIST OF FIGURES

Figure 2-1.	Monthly average concentrations of PM and components at BOWA, ISLE, and SENE?	6
Figure 2-2	Quantile-quantile plot of daily concentrations of PM sulfate and OM at BOWA and SENE.....	8
Figure 2-3.	Graphical display of the spatial correlation of daily data.	12
Figure 3-1.	Total terpene emissions on a representative summer day and a representative winter day.....	19
Figure 3-2.	IMPROVE (squares) sites, urban (filled stars), suburban (filled diamonds) and rural (circles) speciation sites included in the OC/EC analysis.	22
Figure 3-3.	Monthly median OC/EC ratios at groups of selected IMPROVE sites.	23
Figure 3-4.	Monthly median OC/EC ratios at groups of speciation sites by latitude and by land use.	24
Figure 3-5.	Summer primary and secondary OC (microgram/m ³) at IMPROVE sites.	29
Figure 4-1.	(Top) Monthly average concentrations of nitrate, sulfate, ammonium, total negative charge, total positive charge and excess negative charge at speciation sites within the Midwest RPO and in surrounding states. (Bottom) Molar ratios of negative charge to sulfate by month.....	33
Figure 4-2.	Monthly average concentrations of nitrate, sulfate, ammonium, and total negative charge at Bondville.....	36
Figure 4-3.	Scatter plot of hourly negative charges vs. ammonium (micromole/m ³) at Bondville during summer 2003	37
Figure 5-1.	Regional flight path (SUP) of the Wisconsin aircraft and surface monitoring sites near the flight path	49
Figure 5-2.	Concentrations of PM components aloft and at ground level at several nearby monitoring sites for the Wisconsin regional flights	50

Figure 5-3.	Sulfate, nitrate and OC concentrations recorded on Wisconsin and Purdue aircraft during 2002 grouped by routes.....	54
Figure 5-4.	Flight paths of the Wisconsin aircraft (top) and the Purdue aircraft (bottom) and concentrations at surrounding surface sites.....	55
Figure 5-5.	Spatial distributions of sulfate (IMPROVE and speciation) and OC (speciation sites only) on June 22	56
Figure 5-6.	Measured concentrations of elemental carbon, nitrate, organic carbon, and sulfate for the Purdue and Wisconsin flights flying regional patterns and related surface concentrations at 4 Class I areas on October 14 and 23, 2003.....	57
Figure 6-1.	Surface analyses for 0000 UTC June 25, 2003 (7:00 p.m. CDT June 24) (top) and 1200 UTC June 25, 2003 (7:00 a.m. June 25, 2003) (bottom).....	61
Figure 6-2.	Upper air charts (850 hPa) for 0000 UTC June 25, 2003 (7:00 p.m. CDT June 24) (top) and 1200 UTC June 25, 2003 (7:00 a.m. June 25, 2003) (bottom).....	63
Figure 6-3.	Surface analyses for 0000 UTC February 28, 2003 (6:00 p.m. CST February 27) (top) and 1200 UTC February 28, 2003 (6:00 a.m. February 28, 2003) (bottom)	64
Figure 6-4.	Upper air charts (850 hPa) for 0000 UTC February 28, 2003 (6:00 p.m. CST February 27) (top) and 1200 UTC February 28, 2003 (6:00 a.m. February 28, 2003) (bottom).....	66
Figure 7-1.	Sulfate gradients around Indianapolis: all data (top), summer data (bottom).....	71
Figure 7-2.	Nitrate gradients around Indianapolis during winter.	72

EXECUTIVE SUMMARY

Recent regional haze data are analyzed to update the “conceptual model” for regional haze and particulate matter (PM) in the Upper Midwest (Pun et al., 2001). The original conceptual model was formulated base on data available prior to 2001. The key finding in the 2001 conceptual model that the two important PM components in the Upper Midwest, sulfate and OM, contribute almost equally to the annual PM at Boundary Waters Canoe Area (BOWA), also holds for Seney National Wilderness (SENE) and Isle Royale National Park (ISLE) in Michigan. In the Upper Midwest, key PM components show different seasonal cycles, with high concentrations of organic matter (OM) and sulfate in the summer and high concentrations of nitrate in the winter. PM shows a stronger summer peak in the Michigan Class I areas than in BOWA, mostly due to a stronger sulfate cycle.

On a daily basis, the Upper Midwest Class I areas, including BOWA, ISLE, SENE, and Voyageurs National Park (VOYA), correlate with one another for PM, sulfate, and OM. They do not correlate to any significant extent to sites South of Lake Michigan. On a monthly basis, the correlations of OM are particularly strong among the Upper Midwest sites. Sulfate correlations are moderate, indicating some differences in the spatial distribution of these components. Of the Upper Midwest sites, SENE shows the most correlations with sites to the South for sulfate and OM.

OM is dominated by biogenic organic aerosols in the summer, according to the Carbon Preference Index calculated from alkane data from SENE. The contribution of anthropogenic aerosols is higher in the winter. The organic-to-elemental carbon (OC/EC) ratios at different monitoring sites suggest a summer peak, especially at northern latitude sites, that is consistent with secondary aerosol production and/or biogenic emissions. The lack of seasonal variations in the OC/EC ratio at some sites may be an indication of different sources of carbonaceous PM in the summer and winter or the loss of volatile organic compounds from the sampling medium. Assuming that the lowest OC/EC ratios are characteristic of primary emissions at a given site, the contributions of primary and secondary organic compounds are estimated. Both primary and secondary compounds are important at the IMPROVE and speciation sites analyzed. Typically

secondary compounds are important in the summer. The contribution of primary compounds peak in the summer or winter at different sites. There are significant uncertainties in the estimates of primary and secondary organic compounds, due to both the uncertainties in measurements and the assumptions in the OC/EC method.

The sulfate-nitrate-ammonium balance at speciation sites indicate that excess negative charges are present when compared to the amount of ammonium and other cations originating from soil. Measurement artifacts due to ammonium volatilization may explain the charge imbalance. The presence of protons (ammonium bisulfate or nitric acid) can also be inferred, especially during summer. The sensitivity of PM to ammonia, nitrate, and sulfate is spatially and seasonally variable in the Upper Midwest. Removal of sulfate mostly results in the reduction of PM during summer, although in several cities, some increase in nitrate may diminish the response at high relative humidity. In winter, the removal of sulfate can cause an increase in PM under some conditions conducive to the formation of PM. The formation of ammonium nitrate can be sensitive to either component under conditions conducive to PM formation.

The observed sulfate in Pittsburgh, PA seems to originate from both gas-phase and aqueous-phase chemistry.

Aloft concentrations are typically not representative of surface concentrations. A South-to-North gradient is observed when the Wisconsin and Purdue aircraft both fly their regional routes, especially for sulfate and OM. This spatial gradient is consistent with surface distributions of these components. The analysis of transport pathways also confirms that areas to the South may be a source of PM for the Upper Midwest. Other conditions conducive to high PM concentrations include stationary fronts and stagnant conditions. However, the slow evolution of weather systems associated with stagnant conditions does not preclude transport of PM from areas farther away.

Indianapolis is used as a case study to illustrate urban production of PM. The “urban excess” for carbonaceous PM and nitrate are significant. Both organic and elemental carbon exhibit significant urban excess throughout the year. The estimated urban excess of total carbon

is between 1.4 and 3.2 $\mu\text{g}/\text{m}^3$, depending on the sites/networks considered. Nitrate excess tends to be more significant during winter than summer. These findings are consistent with LADCO (2004).

LADCO is presently pursuing many of the measurements that would clarify the conceptual model. Among the top priorities are measurements aimed to understand the ammonium-nitrate-sulfate closure. The continuous ion-chromatograph deployed in Bondville and soon to be deployed in Northbrook will soon provide a suitable data set for the analysis of ammonium-nitrate-sulfate closure and the presence of nitrate in an acidic environment. In addition, short time-scale fluctuations of the thermodynamic equilibrium can also be explored to provide further insights.

The contribution of OM to total PM is currently uncertain. Measurements are recommended to determine a suitable conversion factor between organic carbon, the measured quantity, and organic material. Uncertainties in OC measurements, including different methodologies to distinguish between EC and OC, and different sampling protocols between IMPROVE and EPA's speciation sites, should be resolved to allow the most productive use of current data.

Other measurements can be made to help understand the formation of sulfate, nitrate, and ammonium compounds. Sulfate size distribution information is useful for elucidating the relative importance of the aqueous and gaseous chemical pathways. Diurnal profiles of gas plus particulate nitrate can be used to assess the chemical pathways for nitrate. Aloft formation of nitrate is a possibility that should be evaluated if feasible. Sensitivity studies of the ammonium-nitrate-sulfate equilibrium can be pursued using the ion chromatography data set, especially for rural areas. For organic matter, there is a need to understand sources of primary OC as a function of location and season. To that end, Principal Component Analyses using different EC and OC fractions may be used to supplement efforts to identify marker species. Measurements of hydrogen peroxide are recommended as a lower priority, if sensitivities of secondary PM components to oxidants are identified.

Several areas of research will also be useful for addressing current uncertainties. Fundamental research into the emissions and secondary organic aerosol formation from different landscapes will eventually be needed to address the importance of primary and secondary aerosols. The conceptual model of transport and source areas can be confirmed using modeling exercises. A more comprehensive strategy for aircraft and surface sampling, including temporal coverage, equivalency of particle size, will allow more definitive conclusions to be drawn regarding the role of vertical mixing on air quality in the Upper Midwest.

1. INTRODUCTION

In 2000, the Midwest Regional Planning Organization commissioned a “Scoping Study” to assess the state of the science with respect to regional haze and particulate matter (PM) in the Upper Midwest. A “conceptual model” was formulated as a product of that work (Pun et al., 2001) based on the data available at the time. Key findings of the conceptual model include the almost equal (within the uncertainty limits) contributions of the two most important components, sulfate and organic compounds, to PM in Boundary Waters Canoe Area; a non-negligible contribution from nitrate, especially in winter; and the lack of a significant seasonal pattern to the reconstructed extinction coefficient. The spatial gradient of sulfate concentrations between the southern part of the Midwest RPO and Class I areas in the northern part shows the influence of emissions from Midwest RPO states. However, air masses aloft may also originate from the west, e.g., Washington and Colorado.

While an overall picture started to emerge from the scoping study, important questions remain regarding the characteristics of regional PM and processes leading to its formation. Recent PM and regional haze monitoring activities, driven by the needs of the PM_{2.5} and regional haze rules, provide a basis for the refinement of the conceptual framework for PM and regional haze in the Upper Midwest. This report addresses several questions about the observed PM and its composition using data from new Interagency Monitoring of Protected Visual Environments (IMPROVE) stations and EPA’s speciation network (including Speciation Trends Network (STN) and supplemental stations), as well as non-routine measurements from special studies and aircraft measurements. The report is organized as follows:

- (1) The earlier conceptual model was largely formulated based on data from Boundary Waters Canoe Area (BOWA). Do all Upper Midwest Class I areas (including Seney Wilderness and Isle Royale National Park) share the same PM characteristics?
 - Composition on an annual basis?
 - Composition on a monthly basis?
 - Spatial distribution?

- (2) For organic compounds:
 - What is the relative importance of biogenic versus anthropogenic compounds?
 - What are the relative fractions of primary versus secondary compounds?
- (3) For inorganic compounds:
 - What are the relationships between the inorganic components, sulfate, nitrate, and ammonium?
 - What are the possible responses of inorganic PM to the availability of sulfate, total (gas + particulate) ammonium, and total (gas + particulate) nitrate?
 - Can current information provide insights into the formation processes of sulfate and nitrate?
- (4) What can be inferred from aloft data about the transport and/or formation of PM?
- (5) What are possible source areas for PM that can be inferred from an analysis of the transport pathways?
- (6) What are the differences in PM between urban areas and the surrounding rural areas?
 - The so-called urban excess is explored using Indianapolis as an example.
- (7) What new insights are provided by the new measurements to update the conceptual model for regional haze?
- (8) What are the most pressing needs for measurements and analyses?

2. DO ALL UPPER MIDWEST CLASS I AREA SHARE THE SAME PM CHARACTERISTICS?

2.1 Comparing PM and PM composition at Boundary Waters National Canoe Area, Isle Royale National Park, and Seney National Wilderness

Annual. The analysis of MACTEC (2004) shows small differences in the reconstructed fine mass at the three Class I areas and downward concentration gradients from south to north and from east to west in Michigan, Wisconsin, and Minnesota. Reconstructed fine mass is calculated using the following standard assumptions from the IMPROVE protocol: (1) complete neutralization of sulfate and nitrate ions by ammonium, which is not measured at IMPROVE, (2) a factor of 1.4 to convert organic carbon to organic material, and (3) a fixed composition of soil consisting of oxides of aluminum, silicon, calcium, iron, and titanium. Table 2-1 presents the 2002 annual PM_{2.5} composition at these three sites using the IMPROVE assumptions and a set of alternative assumptions.

Using the IMPROVE assumptions, ammonium sulfate represents the most abundant PM_{2.5} species at these three sites. Because of the hygroscopic nature of ammonium sulfate, it is by far the dominant component of ambient light extinction in many parts of the LADCO region (ARS, 2004). The sulfate concentration gradient among these three sites is consistent with the PM gradient. The second most abundant component is organic material (OM). All three sites share very similar concentrations of OM, which account for 26% of PM_{2.5} mass at SENE but closer to 30% at BOWA. The next most important component is ammonium nitrate, which, like ammonium sulfate, shows a gradient consistent with PM_{2.5}. Soil concentrations range from 0.3 to 0.4 µg/m³ and represent between 6 and 8% of total PM. Elemental carbon is a minor component of PM_{2.5}. Other components are estimated as the difference between the measured PM_{2.5} mass and the sum of all measured (sulfate, nitrate, EC) and estimated (ammonium, OM, soil) components. In theory, these other components include water and other primary components such as fly ash and they account for 0.2 µg/m³ (4.1%) of PM_{2.5} at BOWA and 0.6 µg/m³ (13%) at ISLE on an annual average basis. At SENE, the other component is negative, indicating that the measured PM_{2.5} mass is smaller than the sum of the measured and estimated

Table 2-1. Average PM_{2.5} composition at Boundary Waters Canoe Area (BOWA), Isle Royale National Park (ISLE), and Seney Wilderness (SENE) in 2002 under IMPROVE and alternative assumptions.

	Mass concentrations ($\mu\text{g}/\text{m}^3$) (% of PM _{2.5})		
	BOWA	ISLE	SENE
PM _{2.5} ⁽¹⁾	4.4	4.9	5.2
(NH ₄) ₂ SO ₄ ⁽²⁾	1.9 (42)	1.9 (40)	2.5 (49)
H ₂ SO ₄ ⁽³⁾	1.4 (32)	1.4 (29)	1.9 (36)
Organic material = OC x 1.4 ⁽²⁾	1.3 (30)	1.3 (26)	1.4 (25)
Organic material = OC x 2.1 ⁽⁴⁾	2.0 (44)	1.9 (40)	2.0 (39)
NH ₄ NO ₃ ⁽²⁾	0.6 (13)	0.6 (12)	1.0 (18)
Soil ⁽²⁾	0.3 (8)	0.3 (6)	0.3 (5)
Soil (including MgO) ⁽⁵⁾	0.3 (8)	0.3 (6)	0.4 (7)
Elemental Carbon (EC) ⁽²⁾	0.2 (4)	0.2 (4)	0.2 (4)
Other (IMPROVE assumptions)	0.2 (4)	0.6 (13)	-0.1 ⁽⁶⁾ (-2)
Other maximum (H ₂ SO ₄)	0.6 (15)	1.1 (23)	0.6 (11)
Other minimum (2.1 x OC and Mg in soil)	-0.5 (-11)	-0.0 (-0.4)	-0.8 (-16)

(1) Measured PM_{2.5}, likely underestimated due to volatilization from Teflon filter.

(2) IMPROVE protocol assumes ammonium sulfate; ammonium nitrate; EC = EC1+EC2+EC3-OP (pyrolyzed carbon); OC (organic carbon) = OC1+OC2+OC3+OC4+OP and organic material = OC x 1.4; and soil composes of oxides of Al (2.20 x Al), Si (2.49 x Si), Ca (1.63 x Ca), Fe (2.42 x Fe), Ti (1.94 x Ti).

(3) Low bound of sulfate: sulfate assumed to be in the form of H₂SO₄.

(4) Best estimate for organic material = OC x 2.1 (Turpin and Lim, 2001).

(5) High bound for soil = IMPROVE soil + MgO (1.67 x Mg).

(6) Negative numbers mean that the sum of components exceeds PM_{2.5} mass (see note no. 1 above).

components. The negative other concentration may be due to negative measurement artifacts of $PM_{2.5}$ on teflon filters (due to volatilization of components such as nitrate and organics) or errors in the estimation of individual components such as ammonium and soil.

If highly oxidized OM is assumed at these remote Class I locations, a factor of 2.1 can be used to convert measured organic carbon to OM (Turpin and Lim, 2001). A factor of 2.0 has previously been applied in the calculation of extinction coefficients (ARS, 2004) and was shown to provide better agreement with the measured extinction than the IMPROVE equation, which uses a factor of 1.4 for the OC-to-OM conversion. When a factor of 2.1 is used, the contribution of OM to $PM_{2.5}$ becomes comparable to ammonium sulfate at BOWA and ISLE, but is still lower than ammonium sulfate at SENE. With no change in the estimates of ammonium sulfate and ammonium nitrate, the estimate of the other component decreases when the estimate of OM increases. In these cases, the minimum estimates of other PM are negative at all three sites. As discussed before, negative concentrations may be caused by an underestimation of $PM_{2.5}$ mass and not necessarily a result of overestimation of individual components.

The degree of neutralization of sulfate is not determined in the IMPROVE data. If there is insufficient ammonium to neutralize all sulfate, sites with higher sulfate may exhibit a lesser degree of neutralization. Limited data from a co-located monitor at SENE (ARS, 2004) seem to support this hypothesis. Therefore, OM contribution (estimated using a 2.1 conversion factor between OC and OM) at SENE may also be comparable to sulfate on an annual basis. The assumption that sulfate is not completely neutralized will result in lower estimates of ammonium sulfate and more mass being allocated to the other component. The key finding in the 2000 conceptual model that the two most important PM components, sulfate and OM, contribute almost equally to the annual PM at BOWA, also holds for the most part for ISLE and SENE.

Seasonal. MACTEC (2004) analyzed the time series of PM components by quarter at BOWA and SENE and found that OM controls high $PM_{2.5}$ mass at BOWA during the warm quarters and sulfate drives the summer peak $PM_{2.5}$ concentrations at SENE. Figure 2-1 presents the monthly average concentrations of $PM_{2.5}$ mass and species at BOWA, ISLE, and SENE from

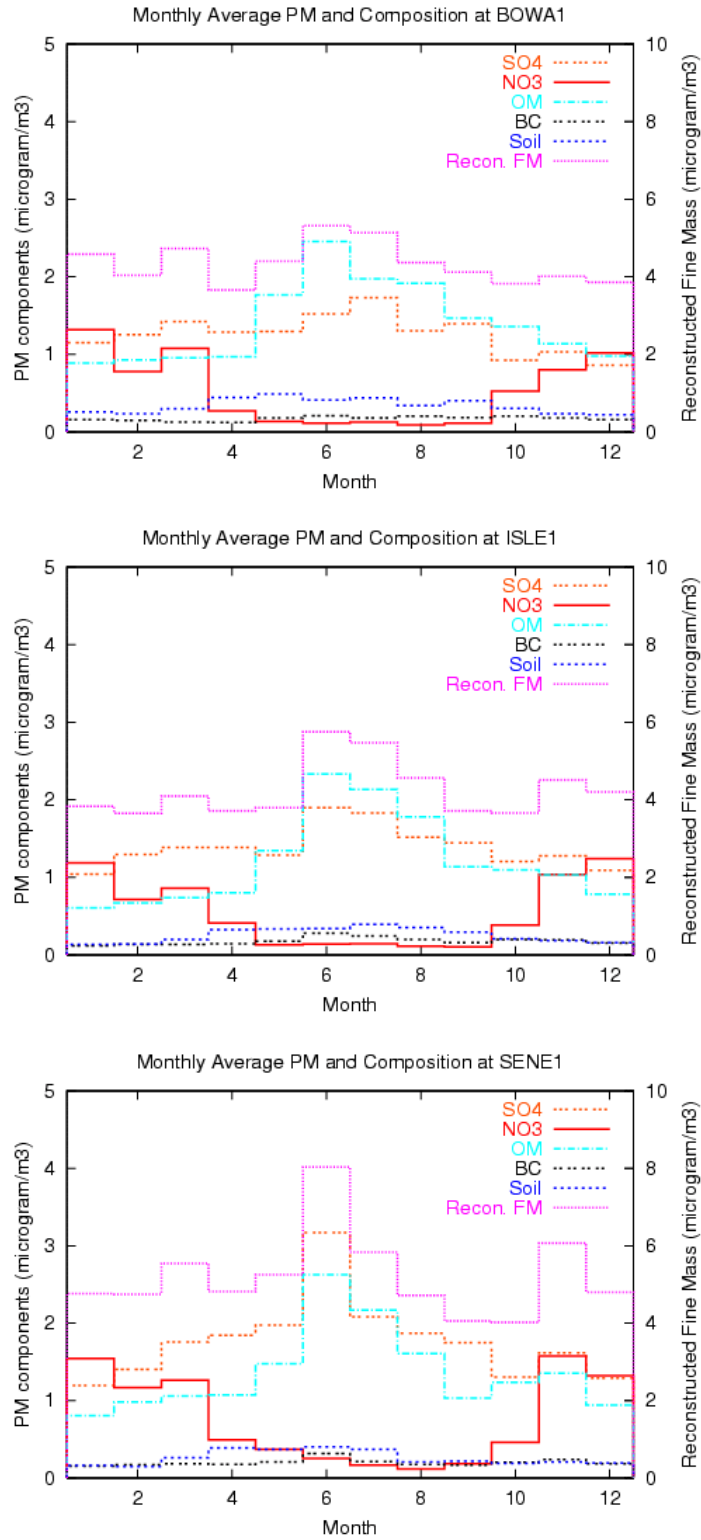


Figure 2-1. Monthly average concentrations of PM and components at BOWA, ISLE, and SENE.

November 1999 to May 2003. At BOWA, $PM_{2.5}$ shows no significant annual cycle. Of the key components, OM shows a propensity for high concentrations in the late spring and summer months (May through August), sulfate is associated with a weak annual cycle that peaks in June and July. On the other hand, nitrate shows a marked winter peak (November through March) and its formation is suppressed from late spring to early fall (April through September). While the same general trends hold for these components at ISLE and SENE, the sulfate and OM peak concentrations in summer are quite a bit more pronounced at the Michigan Class I areas, especially at SENE. The summer peaks of $PM_{2.5}$ are due to fairly strong OM and sulfate seasonal variations at these two locations.

On a monthly basis, SENE and ISLE share some PM characteristics with BOWA. The contributions of sulfate and OM are significant throughout the year, especially in summer. Nitrate compounds represent a solid contributor as well, especially in winter months. Both sulfate and nitrate show some downward concentration gradients from SENE to ISLE to BOWA on a monthly average basis. The two Class I areas in Michigan differ from BOWA in that stronger seasonal cycles of the annual $PM_{2.5}$ are observed, resulting from stronger cycles of sulfate that show peak concentrations in the summer in Michigan. Even though both OM and sulfate show summer peaks, the quantile-quantile plot in Figure 2-2 shows that it is the sulfate cycle, not the OM cycle, that differs more significantly between BOWA and SENE. The difference in the summer sulfate contribution is noteworthy because it may be indicative of different influences from the more industrialized SO_2 source areas where peak sulfate concentrations are frequently observed in summer.

2.2 Correlations of PM and PM components for IMPROVE sites in the vicinity of the Midwest RPO

MACTEC (2004) studied the spatial distribution of PM and PM components in Wisconsin, Minnesota, Michigan and parts of Canada. The following trends are noted: (1) a south to north and east to west downward gradient for $PM_{2.5}$ during 2002, (2) same trends for sulfate in 2001, and (3) a south to north downward gradient for nitrate in 2001. There were

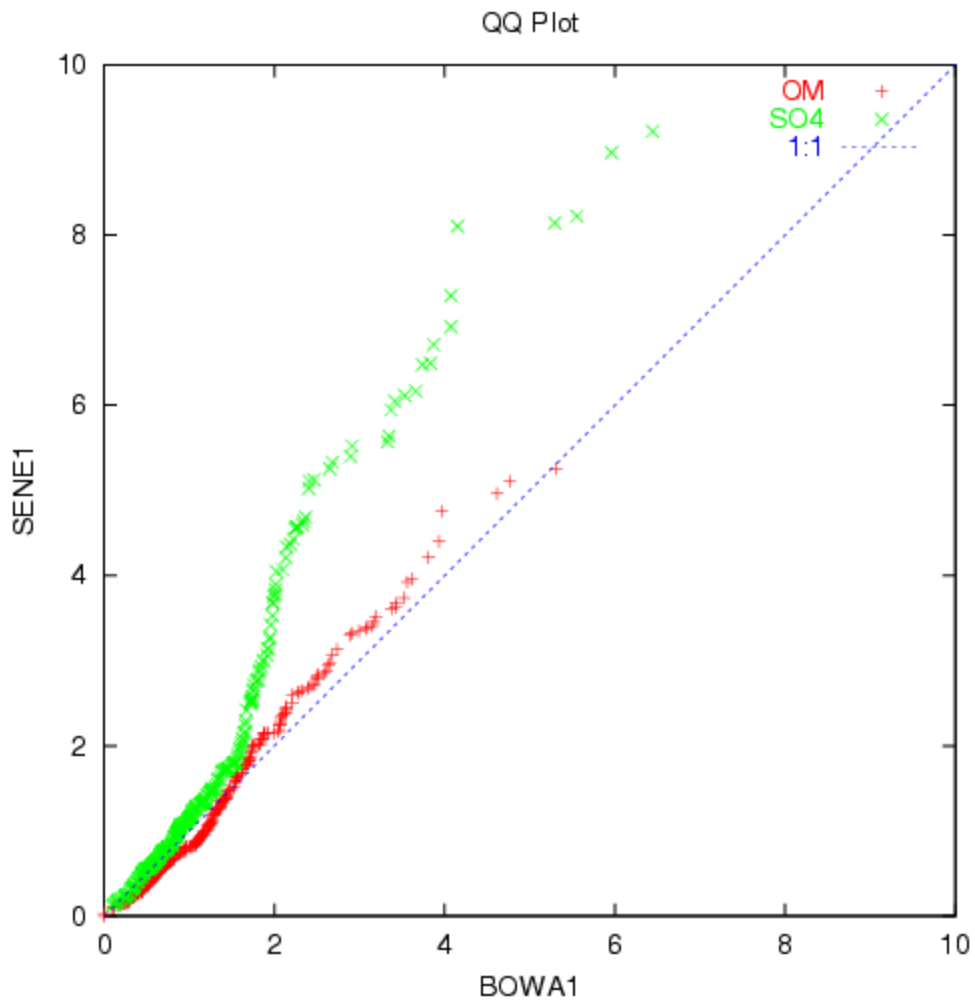


Figure 2-2. Quantile-quantile plot of daily concentrations of PM sulfate and OM at BOWA and SENE.

insufficient OC data to assess spatial trends. We extend the spatial analysis to sites to the south and east by looking at the level of correlation between sites.

Sixteen IMPROVE and IMPROVE protocol sites in operation since November 1999 were selected for this analysis. Many of these sites are located within the Midwest RPO or in surrounding states. A few sites, such as Acadia National Park (ACAD) and Shenandoah National Park (SHEN), were also included for comparison with a previous study (Pun et al., 2001). The higher latitude sites, including BOWA, ISLE, SENE, Voyageurs National Park (VOYA) and ACAD, are by far the least polluted sites on an annual basis. Of the four sites in the upper Midwest, SENE shows higher sulfate and nitrate concentrations ($1.7 \mu\text{g}/\text{m}^3$ and $0.8 \mu\text{g}/\text{m}^3$, respectively) than BOWA, VOYA, and ISLE (1.1 to $1.4 \mu\text{g}/\text{m}^3$ for sulfate and approximately 0.6 for $\mu\text{g}/\text{m}^3$ nitrate). Sulfate is highest around Quaker City (QUCI), OH with a concentration of $4.8 \mu\text{g}/\text{m}^3$. Nitrate is highest in Bondville (BOND), IL with an average concentration of $2.5 \mu\text{g}/\text{m}^3$. Organic materials tend to be high (2.6 to $3.0 \mu\text{g}/\text{m}^3$) at a cluster of sites to the south, including Mingo (MING), Mammoth Cave (MACA), Cadiz (CADI), and Hercules Glades (HEGL).

Table 2-2 shows the correlation coefficients between selected pairs of sites for $\text{PM}_{2.5}$ mass on a daily basis. Correlation coefficients of 0.87 ($r^2 = 0.75$) or higher are considered to be very significant and correlation coefficients between 0.71 ($r^2 = 0.5$) and 0.87 are considered to be moderately significant. Only pairs of sites affected by the same emissions, chemistry, and transport characteristics are expected to share high correlation coefficients. Indeed, ACAD, being geographically separated from the other Class I areas considered in this exercise, does not correlate with the other sites. For $\text{PM}_{2.5}$, Arendtsville (AREN), BOND, and HEGL also share little daily variability with other sites. Neither BOND nor HEGL appears isolated in Figure 2-3, compared to the distances between sites that share correlations. Therefore, factors other than physical distance are at work determining the degree of correlation between sites in the Midwest. M.K. Goddard, PA (MKGO) and QUCI form the only pair of sites that share a significant correlation of $\text{PM}_{2.5}$ on a daily basis. There are some moderate correlations between pairs of nearby sites. Examples of these pairs include SHEN-DOSO (Dolly Sods/Otter Creek Wilderness

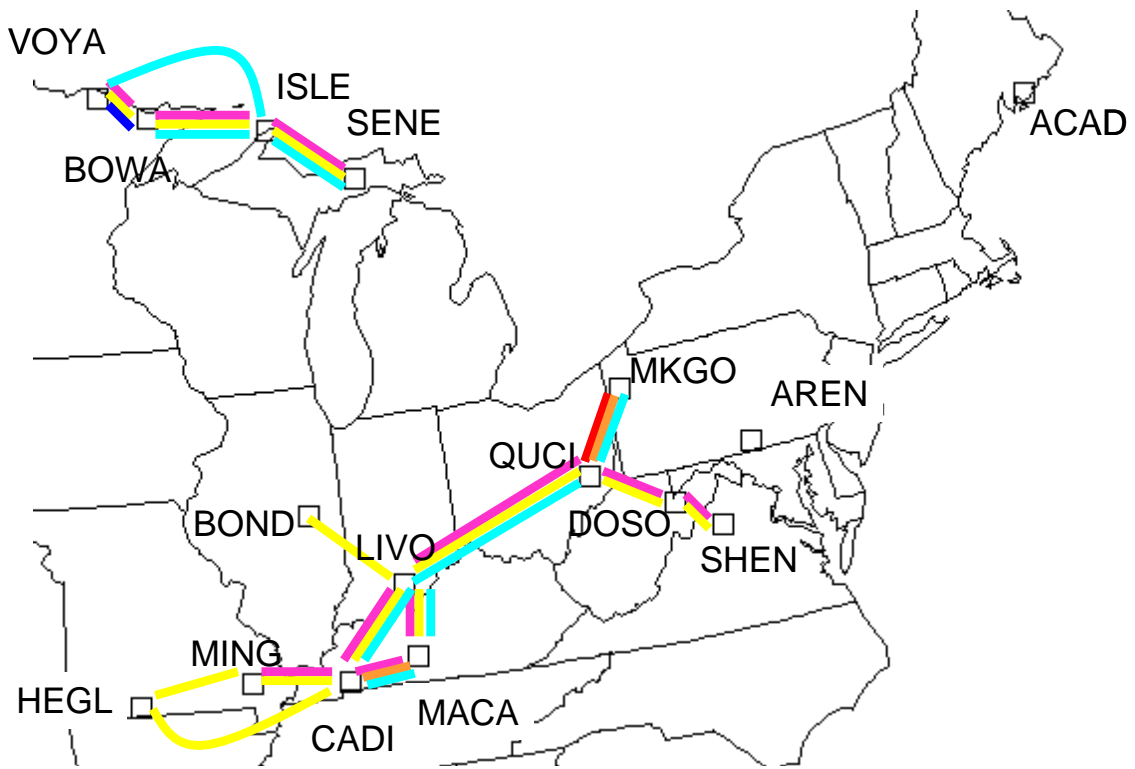
Table 2-2. Correlation coefficients of daily PM concentrations between selected IMPROVE sites ($r = 0.87$ correspond to $r^2 = 0.75$; $r = 0.71$ corresponds to $r^2 = 0.5$).

	ACAD	AREN	BOND	BOWA	CADI	DOSO	HEGL	ISLE	LIVO	MACA	MING	MKGO	QUCI	SENE	SHEN
AREN	0.41														
BOND	0.21	0.36													
BOWA	0.00	0.14	0.35												
CADI	0.27	0.33	0.55	0.35											
DOSO	0.33	0.62	0.34	0.07	0.50										
HEGL	0.22	0.26	0.55	0.32	0.66	0.37									
ISLE	0.08	0.25	0.43	0.72	0.31	0.08	0.31								
LIVO	0.40	0.50	0.63	0.29	0.82	0.56	0.58	0.38							
MACA	0.30	0.44	0.52	0.18	0.84	0.54	0.57	0.26	0.85						
MING	0.23	0.21	0.63	0.22	0.76	0.30	0.70	0.27	0.69	0.60					
MKGO	0.53	0.65	0.46	0.21	0.45	0.66	0.41	0.38	0.69	0.60	0.37				
QUCI	0.45	0.65	0.55	0.28	0.58	0.73	0.46	0.42	0.77	0.68	0.43	0.87			
SENE	0.13	0.32	0.45	0.59	0.32	0.20	0.27	0.80	0.43	0.34	0.26	0.50	0.49		
SHEN	0.25	0.62	0.32	0.10	0.49	0.85	0.35	0.14	0.53	0.52	0.31	0.52	0.63	0.20	
VOYA	-0.07	-0.02	0.30	0.85	0.23	0.00	0.28	0.64	0.22	0.10	0.23	0.05	0.16	0.45	0.02

Area), DOSO-QUCI, QUCI-LIVO (Livonia), LIVO-MACA, LIVO-CADI, CADI-MACA, and CADI-MING from East to West. Sites to the South of the Great Lakes do not share strong daily correlations with any of the Upper Midwest sites. The Upper Midwest sites correlate with their neighbors in PM_{2.5} concentrations (e.g., SENE with ISLE, ISLE with BOWA, BOWA with VOYA). The strength of the correlation deteriorates with distance in the Upper Midwest. For example, the correlation coefficient between SENE and ISLE is 0.8, SENE to BOWA is 0.59, and SENE to VOYA is 0.45. Figure 2-3 depicts the correlations geographically.

The daily correlations of sulfate, a key PM component, at various sites are shown in Table 2-3. As in the case of fine particulate mass, sulfate at each Upper Midwest site correlates with the neighboring sites, and none share any correlation with sites to the South. Among the sites to the South of the Great Lakes, sulfate seems to be more regionally distributed than PM_{2.5} among the sites in KY, IN, IL, and MO, with moderate correlations between BOND and LIVO and between HEGL and MING, and between HEGL and CADI, pairs of sites that show lower PM_{2.5} correlation. Among the sites in OH, WV, PA, and VA, MKGO and DOSO again show the most significant correlation, and other sites correlate moderately with their closest neighbors. As in the case of PM_{2.5}, sulfate at ACAD and AREN does not correlate with any other site on a daily basis.

There are fewer correlations for daily organic mass than for sulfate in general, as shown in Table 2-4. However, the strongest daily correlation is observed between the Upper Midwest sites of VOYA and BOWA. In addition, VOYA also correlates moderately with ISLE for OM, and ISLE correlates with its two neighbors, BOWA and SENE. The distribution of OM in the Upper Midwest seems more homogeneous than those of sulfate and PM_{2.5}. The same cannot be said about OM in the southern sites. The only moderate daily OM correlations were found for the following pairs of sites, CADI-MACA, CADI-LIVO, MACA-LIVO, LIVO-QUCI and QUCI-MKGO. OM at the southeastern sites, including SHEN, and AREN, do not correlate with other sites. BOND, MING and HEGL, whose sulfate concentrations correlate with other sites, do not show any significant correlations on OM. ACAD also shows no correlation with the other IMPROVE sites considered here.



Key:

- PM correlation ≥ 0.87
- PM correlation ≥ 0.71
- Sulfate correlation ≥ 0.87
- Sulfate correlation ≥ 0.71
- OM correlation ≥ 0.87
- OM correlation ≥ 0.71

Figure 2-3. Graphical display of the spatial correlation of daily data.

Table 2-3. Correlation coefficients of daily sulfate concentrations between selected IMPROVE sites ($r = 0.87$ correspond to $r^2 = 0.75$; $r = 0.71$ corresponds to $r^2 = 0.5$).

	ACAD	AREN	BOND	BOWA	CADI	DOSO	HEGL	ISLE	LIVO	MACA	MING	MKGO	QUCI	SENE	SHEN
AREN	0.36														
BOND	0.23	0.35													
BOWA	-0.01	0.15	0.36												
CADI	0.19	0.34	0.64	0.41											
DOSO	0.27	0.70	0.46	0.09	0.46										
HEGL	0.14	0.29	0.64	0.46	0.72	0.35									
ISLE	0.04	0.15	0.47	0.72	0.39	0.13	0.42								
LIVO	0.26	0.46	0.71	0.34	0.79	0.59	0.65	0.43							
MACA	0.21	0.42	0.62	0.21	0.87	0.56	0.59	0.35	0.83						
MING	0.08	0.21	0.62	0.24	0.82	0.22	0.77	0.28	0.66	0.61					
MKGO	0.45	0.62	0.49	0.26	0.40	0.67	0.34	0.40	0.65	0.50	0.26				
QUCI	0.33	0.67	0.61	0.30	0.54	0.73	0.44	0.38	0.73	0.58	0.38	0.87			
SENE	0.09	0.25	0.45	0.56	0.27	0.26	0.27	0.77	0.43	0.31	0.18	0.49	0.47		
SHEN	0.17	0.63	0.42	0.10	0.46	0.84	0.38	0.14	0.52	0.49	0.26	0.50	0.58	0.18	
VOYA	-0.14	-0.02	0.36	0.79	0.20	-0.05	0.32	0.57	0.19	0.14	0.26	0.04	0.16	0.40	0.01

Table 2-4. Correlation coefficients of daily OM concentrations between selected IMPROVE sites ($r = 0.87$ correspond to $r^2 = 0.75$; $r = 0.71$ corresponds to $r^2 = 0.5$).

	ACAD	AREN	BOND	BOWA	CADI	DOSO	HEGL	ISLE	LIVO	MACA	MING	MKGO	QUCI	SENE	SHEN
AREN	0.40														
BOND	0.29	0.35													
BOWA	0.18	0.03	0.36												
CADI	0.25	0.27	0.55	0.31											
DOSO	0.09	0.24	0.26	-0.01	0.42										
HEGL	0.19	0.20	0.48	0.17	0.51	0.22									
ISLE	0.21	0.10	0.32	0.82	0.26	0.00	0.11								
LIVO	0.31	0.41	0.66	0.25	0.72	0.39	0.48	0.25							
MACA	0.24	0.47	0.55	0.17	0.76	0.20	0.45	0.18	0.79						
MING	0.16	0.21	0.47	0.08	0.52	0.31	0.36	0.09	0.50	0.46					
MKGO	0.47	0.57	0.57	0.28	0.43	0.36	0.29	0.37	0.63	0.49	0.34				
QUCI	0.37	0.58	0.51	0.26	0.53	0.46	0.31	0.40	0.73	0.60	0.40	0.78			
SENE	0.26	0.29	0.51	0.70	0.37	0.04	0.18	0.80	0.44	0.37	0.16	0.51	0.46		
SHEN	0.17	0.28	0.23	0.10	0.30	0.31	0.12	0.11	0.32	0.33	0.20	0.32	0.39	0.20	
VOYA	0.24	0.03	0.28	0.89	0.27	0.03	0.14	0.79	0.18	0.13	0.10	0.25	0.22	0.65	0.04

Daily correlations reflect groups of sites affected by the same air mass on a daily basis. The above analysis indicates that the Upper Midwest Class I areas are quite isolated from areas south of the Great Lakes on a day-to-day basis. Upwind-downwind relationships between pairs of sites may result in correlations on a time scale greater than a day. Therefore, monthly correlations are also explored to identify those relationships between sites (Table 2-5).

LIVO, QUCI, and CADI show moderate to significant $PM_{2.5}$ correlations with each other and with many sites in the same latitude band from MO to VA. LIVO and QUCI share the most significant monthly correlation of 0.98 for fine particulate mass on a monthly basis (Table 2-5). The least significant monthly correlation was between M.K. MKGO and VOYA. Of the sites that do not correlate on a daily basis with other sites, some monthly correlations were found (e.g., for ACAD, AREN, and HEGL). Interestingly, the Bondville site (BOND, IL) does not correlate significantly on a monthly basis with any nearby site. Fine particulate mass correlations among the Upper Midwest sites improve over the corresponding daily values.

It is interesting to note that sulfate correlations did not change from daily to monthly at the Upper Midwest sites. However, sulfate at ISLE correlates on a monthly basis with LIVO and CADI, two sites to the south-southeast of ISLE. PM and sulfate at SENE correlate moderately with QUCI and LIVO. Except for the upper Midwest sites and ACAD, sulfate correlations tend to be more numerous and in some cases stronger than $PM_{2.5}$ correlations among the sites considered. The most significant sulfate correlation is 0.97 between Dolly Sods (DOSO) and Shenandoah (SHEN). The least significant correlation is between BOWA and ACAD, not surprisingly. LIVO shows the largest number of significant correlations, with BOND, CADI, DOSO, HEGL, MACA, MKGO, QUCI, and SHEN, indicating that sulfate is quite uniformly distributed in this area on a monthly basis. BOND shows a fair number of moderate to significant correlations with other sites for sulfate, despite a lack of correlations for $PM_{2.5}$ mass.

There are fewer correlations for monthly organic mass than for sulfate in general. However, the upper Midwest Class I areas show somewhat different trends. For OM, all four Upper Midwest sites correlate with one another on a monthly basis. In addition, moderate correlations are also observed between VOYA and CADI and between VOYA and LIVO. ISLE

Table 2-5. Significant correlations of monthly concentrations between selected IMPROVE sites (key: **P** = r(PM) >= 0.87 ; **p** = r(PM) >= 0.71; **S** = r(sulfate) >= 0.87; **s** = r(sulfate) >= 0.71; **O** = r(OM) >= 0.87; **o** = r(OM) >= 0.71).

	ACAD	AREN	BOND	BOWA	CADI	DOSO	HEGL	ISLE	LIVO	MACA	MING	MKGO	QUCI	SENE	SHEN
AREN															
BOND															
BOWA															
CADI	p s		s												
DOSO		s	s		p s										
HEGL		s	s		p S										
ISLE				p s O	S										
LIVO	p	p s	S		P S	P S	p S	s o							
MACA			s		P S o	p s	p S		P S o						
MING			s		p S		p S		p s	p s					
MKGO	p o	p s	S		p s	p S	s		P S o	p s	s				
QUCI	o	P S o	S		p s	P S	P s	O	P S o	P s o	s	P S O			
SENE								P s							
		p	o	p o	o			O	p s o			o	p s o		
SHEN		p s	s		p s	P S	s		p S	p s		p s	P s		
VOYA				P s o	o			p O	o					O	

also shows correlations with LIVO and QUCI. OM at SENE correlates with VOYA and ISLE most significantly, and moderately with a number of sites including BOND, BOWA, CADI, LIVO, NKGO, and QUCI. The general trend that SENE, of the upper Midwest sites, shows the most correlations with sites outside of the Midwest RPO, holds for OM in addition to sulfate. However, VOYA also shows some correlation with sites to the southeast.

OM at DOSO, HEGL, and MING shows very little correlation with other sites. The site with the most correlations for OM is LIVO, which correlates with MACA to the south and VOYA to the north. The most significant OM correlation occurs between BOWA and VOYA. A negative correlation (statistically insignificant based on the number of data points and the magnitude of the correlation coefficient) occurs between HEGL and MING, 2 sites in MO, indicating that these two sites are likely to be affected by different sources of OM.

The upper Midwest Class I areas correlate strongly with one another in terms of monthly average $PM_{2.5}$, especially between the pairs of sites BOWA/VOYA and ISLE/SENE. These correlations are driven by the OM correlations, which are very significant. Sulfate correlations between the upper Midwest Class I areas are moderate. In addition to correlations among VOYA, BOWA, ISLE and SENE, sulfate at ISLE correlates with LIVO and CADI and sulfate at SENE correlates with QUCI and LIVO. OM correlations are significant for the following pairs of upper Midwest sites, BOWA/VOYA, BOWA/ISLE, ISLE/SENE, ISLE/VOYA, SENE/VOYA, and moderate for BOWA/SENE. OM at three out of four upper Midwest sites shows some correlations with sites to the south. Therefore, there are differences between the spatial distributions of sulfate and OM, indicating the possibility of different source areas and/or processes governing the distribution of these species. Of the four upper Midwest Class I areas, $PM_{2.5}$, sulfate, and OM at SENE tends to show more correlations with sites to the South, perhaps indicating greater influence from the more industrialized areas than the other three Class I areas.

3. ORGANIC COMPOUNDS

Organic material is composed of primary and secondary compounds. Both types of compounds can originate from biogenic or anthropogenic sources. Figure 2-1 shows that OM tends to be high in summer and low in winter at the upper Midwest Class I areas. Two hypotheses seem to be consistent with this observation. First, biogenic emissions are more abundant in the summer (see Figure 3-1); therefore, primary and secondary biogenic compounds contribute to the OM observed in the summer. Second, increased photochemical activity during summer months contributes to significant SOA formation from both anthropogenic and biogenic precursors. OC speciation data from Schauer seem to indicate a preponderance of secondary organic compounds in the summer, and variable composition of SOA as a function of source area. On the other hand, OM in the winter is dominated by anthropogenic emissions (e.g., biomass burning) (Sheesley and Schauer, 2004).

3.1 Anthropogenic vs. biogenic OM

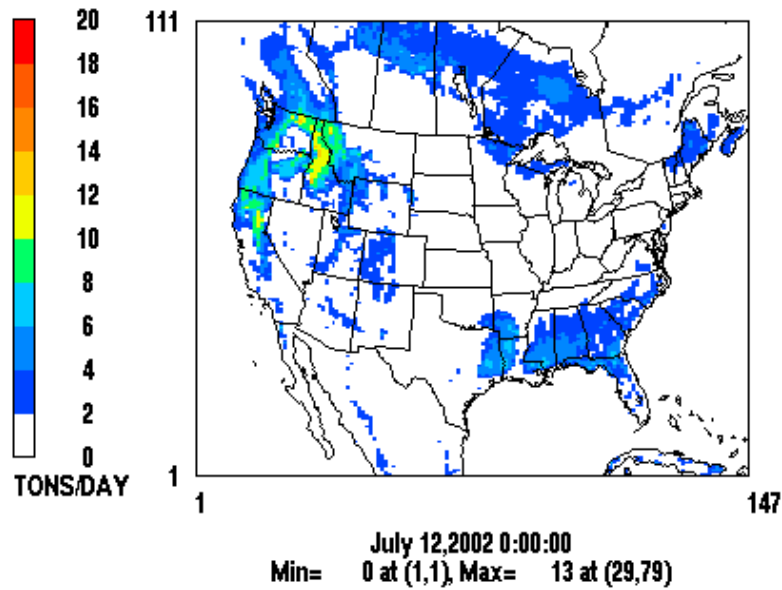
The relative importance of biogenic versus anthropogenic OC can be estimated in first approximation from the relative amounts of odd- versus even-number carbon atoms in the molecular analyses. The identification and quantification of the n-alkane series allows for the determination of the Carbon Preference Index (CPI). The CPI has been used as an indicator of biogenic and anthropogenic contributions to organic aerosol (e.g., Simoneit, 1978, 1989; Didyk et al., 2000). The alkane CPI is defined as the sum of the concentrations of odd carbon number alkanes divided by the sum of the concentrations of the even carbon number alkanes:

$$\text{AlkaneCPI} = \frac{\sum \text{Odd Carbon Number Alkanes}}{\sum \text{Even Carbon Number Alkanes}} \quad (1)$$

Biogenic sources emit odd carbon number alkanes in greater concentrations than even carbon number alkanes, and, therefore, have CPIs greater than 1; anthropogenic emissions evidence no carbon preference and have CPIs of about 1. Urban environments, with large contributions from anthropogenic emissions, generally have CPIs ranging between 1.1 and 2.0,

biog TERSUM : BEIS3

natl 36km 020712
LADCO/MIDWEST RPO



biog TERSUM : BEIS3

natl 36km 020111
LADCO/MIDWEST RPO

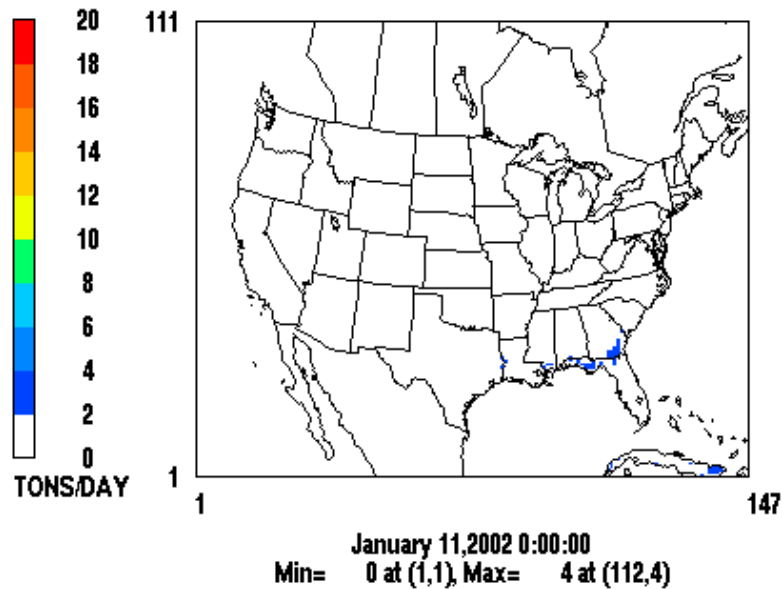


Figure 3-1. Total terpene emissions on a representative summer day and a representative winter day (source: K. Baker, LADCO, personal communication).

while rural environments with more biogenic influence generally have CPIs above 2.0. This type of information was recently used in the BRAVO study at Big Bend National Park to characterize the importance of anthropogenic emissions for OC (Brown et al., 2003). Sheesley and Schauer, 2004) measured 8 straight chain alkanes (C25 to C32) in organic aerosols in Seney National Wilderness. Based on their data, the even carbon number alkanes were below detection limit during July, August, October, November, and December 2002. Alkane CPIs were calculated to be 3.7, 2.2, and 10.6 for May, June, and September 2002, respectively, indicating a significant presence of organic aerosols of biogenic origin. During the earlier part (November 2001 to April 2002) of the measurement period, the alkane CPI ranged from 0.2 to 1.1, indicating lesser biogenic influence. The average OC observed during November 2001 and November 2002 were 1.61 and 0.68 $\mu\text{g}/\text{m}^3$, respectively. Both the difference in OC concentration and alkane CPI indicate that a variety of sources affected Seney National Wilderness Area at this time of the year.

3.2 Primary vs. secondary OM

The relative fractions of primary and secondary organic compounds can be estimated using some empirical approaches. Elemental carbon (EC) is solely primary whereas organic carbon (OC) contains both primary and secondary components. The rationale is that since EC and OC share many common sources in a given area, there is a characteristic OC/EC ratio for the emissions, regardless of transport and dilution processes. As an air parcel ages, SOA is formed and the OC/EC ratio increases. If the source OC/EC ratio can be determined for the area, then an estimate of primary OC can be obtained by multiplying the sample EC by the source OC/EC ratio, and the difference between total OC and the estimated primary OC is attributed to SOA. This method has typically been applied in an urban area setting for episodes of PM pollution. Periods dominated by emissions (e.g., morning traffic) or with minimal photochemical activity are used to estimate the OC/EC ratio when little or no SOA is formed. This ratio is then used to estimate the amount of SOA during periods (e.g., late afternoon) or days of high photochemical activity in the same area. The implicit assumption is that the characteristics of the underlying source mixture, in particular the OC/EC ratio, do not change between samples.

When applied to a more rural setting with one-in-3-day 24-hour samples and over a longer period of time, some limitations need to be considered. First, there are several sources of EC, including diesel exhausts and biomass combustion (Park et al., 2003; Seigneur et al., 2003), and the primary OC/EC ratio is likely to differ among source categories, whose contributions vary with season. Second, in areas removed from urban emissions, samples that have low OC/EC ratios may originate from intermittent (e.g., forest fires) events that are not representative of the primary mixture affecting the area. Third, while many anthropogenic combustion sources emit both OC and EC, the assumption about a consistent OC/EC ratio may not be valid if biogenic sources are significant (e.g., plant waxes).

Figure 3-2 shows the locations of the sites used in the OC/EC analysis. Figure 3-3 shows the annual variability of the OC/EC ratio at three groups of IMPROVE sites in different latitude bands. The OC/EC ratios of individual sites are presented in Appendix A. Figure 3-4 shows the same information for speciation sites grouped by latitude bands and for urban, suburban, and rural EPA speciation sites (as defined in the Air Quality System database). Speciation sites are grouped because much variability is observed with individual sites due to limited data in many cases. Data from IMPROVE and EPA's speciation networks are presented separately because of different sampling and analysis protocols. The analysis protocol for OC and EC used by EPA's speciation network tends to result in higher OC and lower EC than the IMPROVE protocol (Chow et al., 2001; Rice et al., 2004). This difference is reflected in the overall magnitude of the calculated OC/EC ratios for the two networks.

For a given location, we expect a priori some seasonal difference due to the composition of sources (e.g., residential wood burning in the winter, forest fires in the summer, mobile sources throughout the year). In addition, a summer peak in the OC/EC ratio due to SOA production from active photochemistry and/or biogenic emissions is anticipated. Using aromatic and aliphatic poly-acids as tracers for SOA of urban origins, Sheesley and Schauer (2004) concluded that SOA peaks in July and tapers off in fall at Seney National Wilderness. In addition, pinonic acid, a known biogenic SOA, show similar monthly variations. The expected summer peak OC/EC ratio is observed at a few IMPROVE sites, including the Upper Midwest Class I areas and ACAD. There may be a weaker summer signal at several other sites, but no

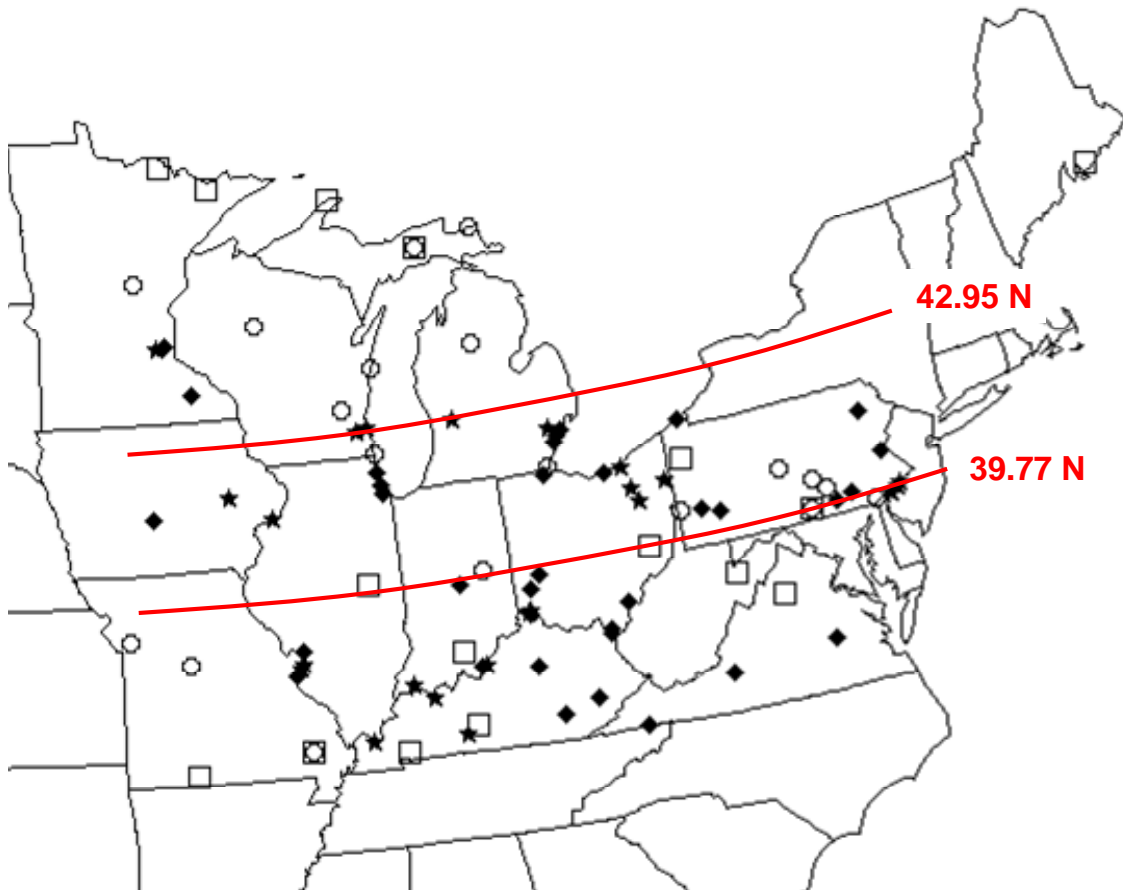


Figure 3-2. IMPROVE (squares) sites, urban (filled stars), suburban (filled diamonds) and rural (circles) speciation sites included in the OC/EC analysis. Red lines represent 39.77 and 42.95 latitude lines.

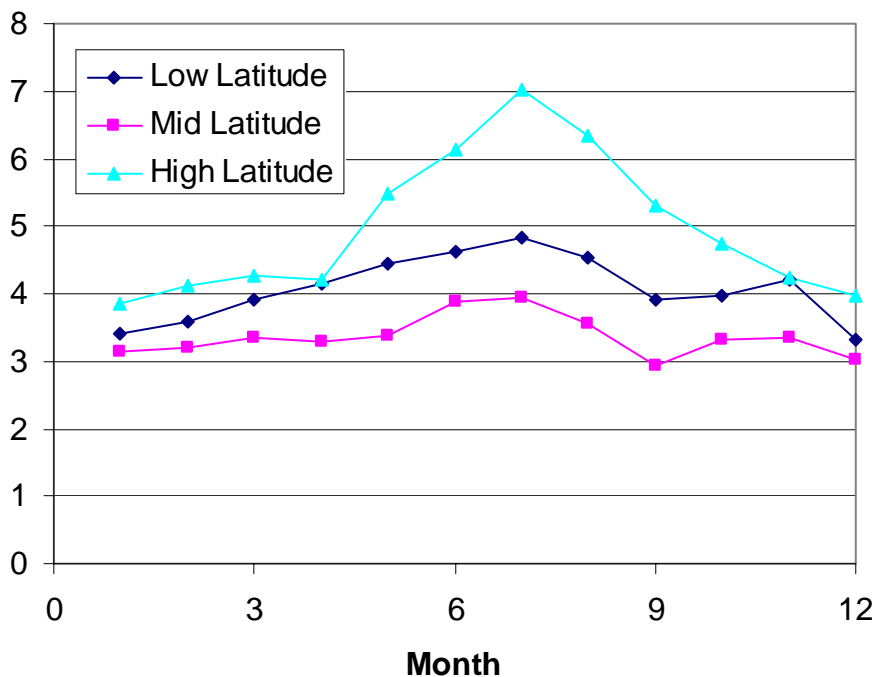


Figure 3-3. Monthly median OC/EC ratios at groups of selected IMPROVE sites. High latitude (≥ 42.95) sites include VOYA, BOWA, ISLE, SENE, and ACAD. Mid latitude ($39.77 \leq \text{latitude} < 42.95$) sites include AREN, BOND, MKGO, and QUCI. Low latitude (< 39.77) sites include CADI, DOSO, HEGL, LIVO, MACA, MING, and SHEN. See Appendix for the OC/EC ratios of individual sites.

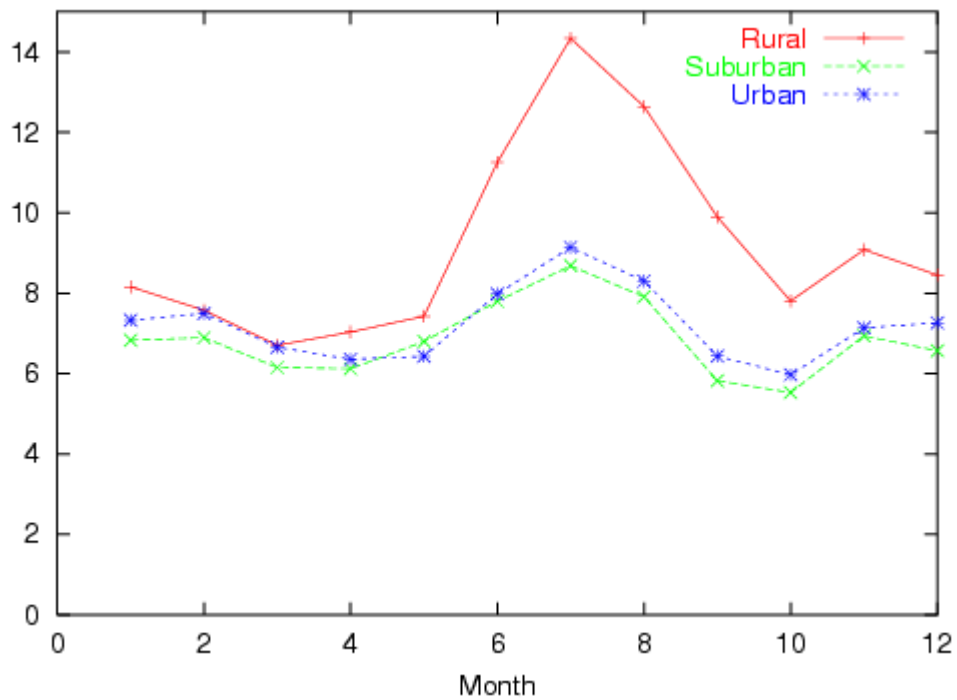
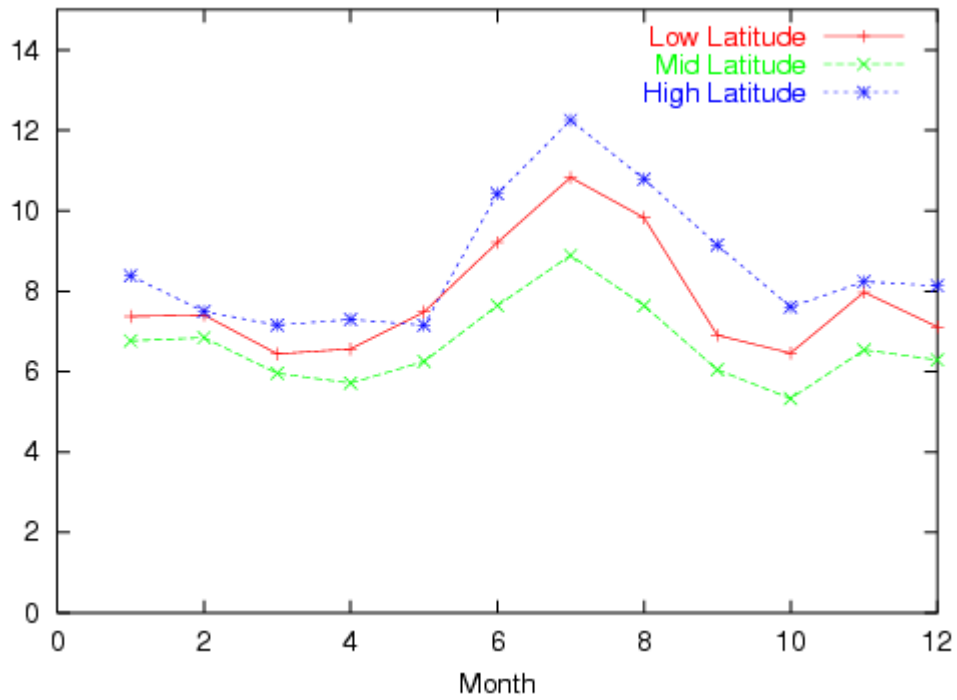


Figure 3-4. Monthly median OC/EC ratios at groups of speciation sites by latitude (North: latitude ≥ 42.95 ; Mid: $39.77 \leq$ latitude < 42.95 ; South: latitude < 39.77) and by land use.

discernable signal at BOND, MKGO, LIVO, DOSO, QUCI, MING. The speciation sites show this summer increase in the OC/EC ratio at sites in all latitude bands, with the most significant increase observed at the rural sites at northern latitudes. Weaker summer signals are also observed at many suburban and urban speciation sites. In addition to the summer peak, many speciation sites show an increase in the OC/EC ratio in the winter months as well. These OC/EC ratios raise very intriguing questions. First, why is there a difference between rural sites located in the northern latitudes and the remaining rural sites (IMPROVE and speciation)? Second, how do we reconcile the differences between the relatively flat monthly OC/EC profile at many IMPROVE sites with the seasonal trends at the speciation sites and what we know about VOC emissions and formation of SOA in the summer?

The most probable explanation of the difference in the OC/EC seasonal behavior at rural sites seems to be a difference in the combination of sources affecting individual sites. If so, the differences in carbonaceous PM sources between the higher latitude rural sites and the lower latitude rural areas will have implications towards the effectiveness of control strategies placed on PM sources on different locations. Figure 3-1 shows significant biogenic emissions at these northern latitudes during summer. One distinct possibility is that boreal forests, which cover northern New England and northern Michigan and Minnesota, have different emission characteristics than temperate forests to the south. Different types of vegetation emit different mixtures of terpenes (current emission inventories do not separate different terpene compounds), and may lead to different amount of condensable products with different thermodynamic properties. The significant OC/EC increase in summer is consistent with biogenic SOA formation due to a combination of factors including high levels of biogenic VOC emissions from boreal forests, high SOA formation potential from the mixture of compounds, and low volatility of organic products. Primary organic compounds (e.g., plant wax) may also be a contributor; little is known at this point about the importance of primary organic aerosols from vegetation.

Given the increased biogenic VOC emissions and the increased photochemical activity in summer, higher SOA formation seems to be a reasonable expectation. In this case, a lack of increase in the OC/EC ratio at some sites implies that other sources of EC increase to balance the increases in SOA in summer. A significant shift in the sources of primary carbonaceous PM in

some areas may explain the negligible increase in the ambient OC/EC ratio in the summer. The speciation data in particular suggest the possibility of a small increase of the OC/EC ratio during winter at many sites. The seasonal differences in carbonaceous PM emissions need to be characterized in better detail.

Another plausible explanation is that semivolatile organic compounds are lost in the samples. The loss of volatile organic compounds has been observed previously (Pang et al., 2002). Such losses depend on the volatility of the partitioning compound as well as on the ambient condition. Lower temperatures in the upper Midwest Class I sites may result in better retention of semivolatile compounds than the IMPROVE sites in the lower latitudes, and contribute to the observed differences in the seasonal OC/EC ratios. Smaller losses at speciation sites in the summer may be a result of the sample handling procedures (speciation samples are transported at reduced temperatures, while IMPROVE samples are transported at ambient temperatures) or backup filter subtraction procedures (an average background is subtracted from IMPROVE samples, while no subtraction is typically conducted for the speciation network). There may be a need to evaluate the collection efficiency and potential losses during transport and analyses and data manipulation procedures for semivolatile organic compounds.

We calculated the minimum OC/EC ratio at each IMPROVE site and each group of speciation sites. With an assumption that the source mixture remains fairly constant within a season, the minimum monthly values are averaged to provide an estimate of the OC/EC ratio characteristic of primary carbonaceous particles within a given season. This ratio is then applied to the average EC value of each month to estimate the average primary OC for that month at that site, secondary OC is calculated as the difference between the observed OC and the estimated primary OC. Estimated primary and secondary OC are presented in Table 3-1 by season for groups of speciation sites and selected IMPROVE sites (shown in Figure 3-5).

Table 3-1. Estimated primary vs. secondary organic carbon (microgram/m³) at speciation and IMPROVE sites using the OC/EC method.

	Spring (March - May)		Summer (June - August)		Fall (September - November)		Winter (December - February)	
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary
Speciation network * (no. of sites)								
L1SU (15)	0.80	2.92	1.79	3.87	1.20	3.51	1.42	3.39
L1UR (9)	1.70	1.75	2.38	2.90	2.37	2.36	2.66	1.81
L1RU (3)	1.00	1.44	1.60	2.05	0.38	2.74	1.87	1.73
L2SU (17)	1.23	2.11	1.67	3.69	1.59	2.36	1.72	2.76
L2UR (10)	0.93	2.44	1.07	4.19	0.51	3.24	0.76	2.95
L2RU (9)	1.09	1.52	1.93	3.42	1.41	1.83	2.51	1.28
L3SU (2)	1.86	0.70	2.74	1.49	2.04	1.64	2.09	1.06
L3UR (4)	1.39	2.01	2.15	2.79	1.57	2.48	2.06	1.96
L3RU (7)	0.85	1.23	1.33	2.91	0.78	2.12	0.76	1.45

* Speciation network sites are grouped as follows: L1 includes sites with latitudes below 39.77; L2 includes sites with latitudes between 39.77 and 42.95 and L3 includes sites with latitudes greater than 42.95. RU stands for rural sites, SU stands for suburban sites, UR stands for urban sites, defined according to the location setting field within the AQS database.

Table 3-1. Estimated primary vs. secondary organic carbon (microgram/m³) at speciation and IMPROVE sites using the OC/EC method (continued).

	Spring (March - May)		Summer (June - August)		Fall (September - November)		Winter (December - February)	
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary
IMPROVE								
ACAD1	0.35	0.35	0.60	0.79	0.16	0.64	0.48	0.32
AREN1	0.86	0.75	0.98	1.09	0.86	0.92	0.95	0.75
BOND1	0.90	0.53	0.88	0.78	0.81	0.79	0.74	0.40
BOWA1	0.39	0.50	0.79	0.72	0.46	0.51	0.43	0.24
CADI1	1.11	0.73	1.39	0.90	1.22	0.97	0.77	0.56
DOSO1	0.75	0.71	0.65	0.83	0.85	0.85	0.88	0.69
HEGL1	1.11	0.95	1.21	0.81	1.02	0.70	1.03	0.45
ISLE1	0.40	0.31	0.66	0.93	0.38	0.44	0.18	0.32
LIVO1	0.94	0.59	1.14	0.77	0.82	0.70	0.83	0.46
MACA1	1.05	0.87	1.36	1.17	0.97	1.16	1.04	0.58
MING1	1.00	0.66	1.31	0.89	1.23	1.36	1.01	0.89
MKGO1	1.00	0.58	1.27	1.17	0.99	0.76	0.99	0.58
QUCI1	0.90	0.55	0.99	1.11	0.85	0.68	0.93	0.44
SENE1	0.49	0.37	0.81	0.69	0.44	0.47	0.31	0.34
SHEN1	0.52	0.77	0.72	1.02	0.61	0.85	0.44	0.52
VOYA2	0.37	0.51	0.84	0.98	0.44	0.52	0.42	0.25

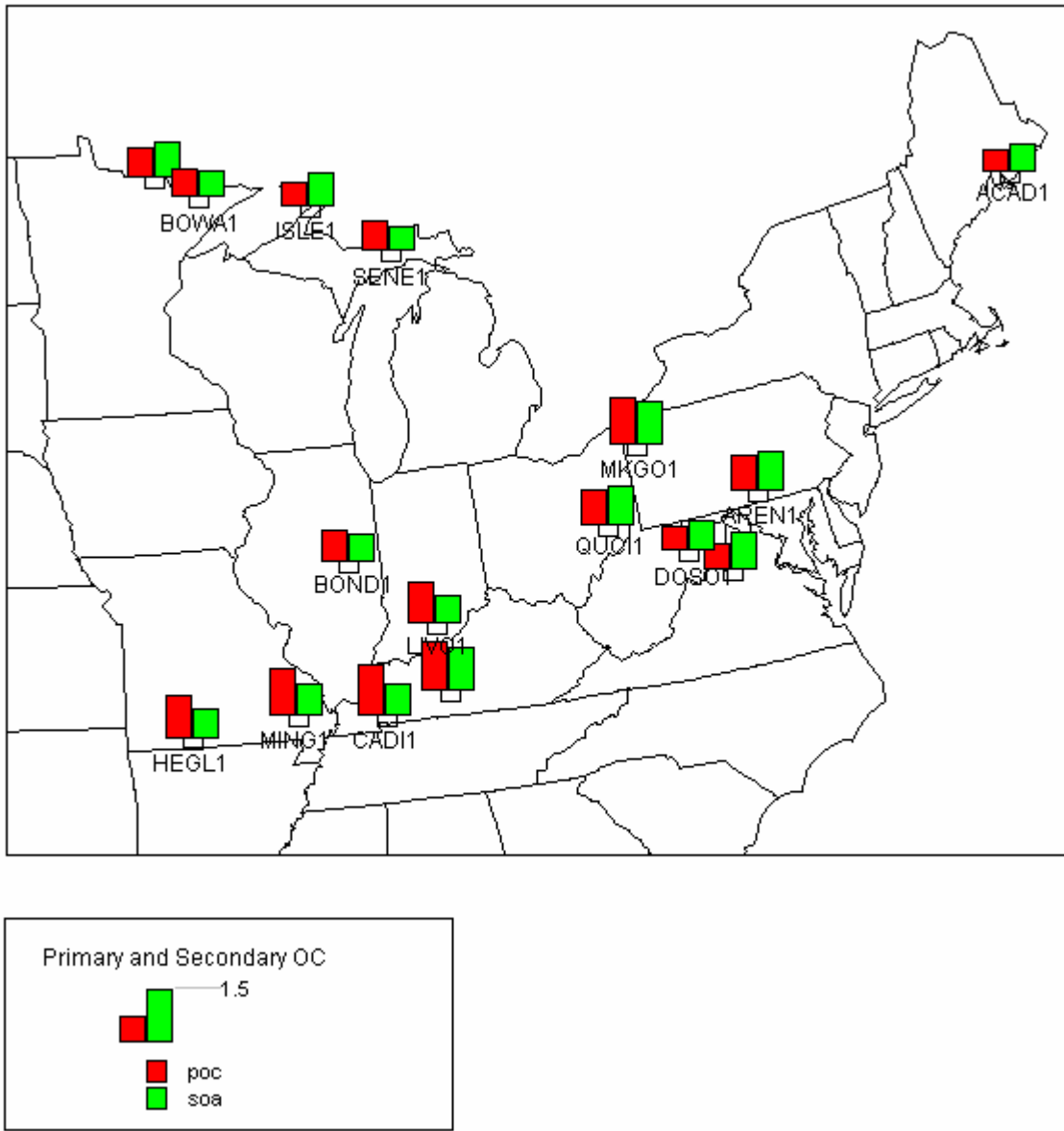


Figure 3-5. Summer primary and secondary OC (microgram/m³) at IMPROVE sites.

Because of the differences in analysis, speciation sites give higher estimates of OC and thus higher estimates of primary and secondary OC. Measurements at speciation sites also give lower concentrations of EC; therefore, estimates for the speciation sites are also expected to be sensitive to measurement errors of EC. The overall trend is for secondary OC to be higher than primary OC at speciation sites. The concentrations of secondary OC range from 1.5 to 3.9 $\mu\text{g}/\text{m}^3$ during summer, 1.6 to 3.5 $\mu\text{g}/\text{m}^3$ during fall, 1.1 to 3.4 $\mu\text{g}/\text{m}^3$ during winter, and 0.7 to 2.9 $\mu\text{g}/\text{m}^3$ during spring. The maximum concentration corresponds to 5.5 $\mu\text{g}/\text{m}^3$ organic material if a factor of 1.4 is used to account for the oxygen, hydrogen, and nitrogen in the organic material. Seven out of nine areas show a summer maximum of SOA, while the remaining two record higher fall concentrations. Also of interest is the seasonal cycle of primary OC. For 5 groups out of 9, primary OC is highest in the summer. Primary OC is highest in winter for the remaining groups, including urban, suburban, and rural sites with different latitudes. In any case, primary OC seems to be higher in the summer and winter seasons than during spring and fall, with only a few exceptions.

OC concentrations at IMPROVE sites are systematically lower than at speciation sites, including rural speciation sites. The overall trend at IMPROVE sites is different from speciation in that primary OC tend to be more important than secondary OC. At 11 out of 16 selected IMPROVE sites, secondary OC is highest in summer. The estimated secondary OC ranges from 0.7 to 1.2 $\mu\text{g}/\text{m}^3$ during summer. A few sites show maximum secondary OC concentrations in fall, when SOA seems to be more spatially variable, between 0.4 and 1.4 $\mu\text{g}/\text{m}^3$. More interesting is the seasonal distribution of primary OC. Virtually all IMPROVE sites investigated here record summer peaks in primary OC, although a fraction of secondary OC may be classified as primary if secondary OC is present on days with even the lowest OC/EC ratios, which is likely in a remote area. Further investigation will probably be needed to understand if the spatial variability in primary OC emissions, and if the relative magnitude of primary OC in winter vs. summer is related to the respective locations of the speciation and IMPROVE sites.

At this point, uncertainties in the sampling of semivolatile OC and the distinction between OC and EC leads to tremendous uncertainties in any analysis aimed to tease out the contributions of primary vs. secondary OC. The OC/EC method is based on the assumption that

primary carbonaceous aerosols are associated with a fixed OC/EC ratio. This assumption is acceptable for anthropogenic emissions, although it may limit the application of the method to specific seasons when the source mixture is not expected to change significantly. When biogenic emissions are important, the assumption may be inaccurate, since primary biogenic emissions may not be associated with EC at all. The OC/EC ratio method may also result in a fraction of secondary organic compounds being classified as primary, if a “base load of SOA” is always present at the location during a certain period, e.g., summer. With those caveats, several conclusions can still be drawn. Both primary and secondary aerosols are important in the Midwest RPO and surrounding states, although the relative concentrations are a function of site location or perhaps network sampling protocol, which should be investigated. Secondary OC tends to be high in summer, which is expected. Primary OC shows peak concentrations during summer at IMPROVE sites and has a secondary winter peak at speciation sites. Therefore, there may be some geographic variability in primary OC, especially during winter.

4. INORGANIC AEROSOLS

4.1 What are the relationships between the inorganic components, sulfate, nitrate, and ammonium?

Of the inorganic aerosol components, sulfate, nitrate, and ammonium constitute a significant fraction of $PM_{2.5}$ at many sites in the Midwest RPO area and surrounding states. Figure 2-1 shows that sulfate and nitrate are associated with different seasonal profiles. The equilibrium of particulate matter sulfate with gaseous sulfuric acid favors the particulate phase because of the low vapor pressure of sulfuric acid. Within the particulate phase, sulfate can exist as sulfuric acid, bisulfate, and sulfate, depending on the degree of neutralization. Cations are associated with bisulfate and sulfate. Typically, ammonium is the dominant cation in many parts of the North American continent. However, other cations, such as sodium, calcium, potassium, and magnesium may also serve to neutralize particulate sulfate. Compared to sulfuric acid, nitric acid is a weaker acid and is more volatile. The partitioning of nitric acid into the particulate phase as particulate nitrate is very sensitive to the availability of ammonium. Therefore, the formation of nitrate is inevitably related to the amount of sulfate due to the association of both anions to ammonium, and the amount of ammonium available for nitrate formation depends on the availability of other cations that may be associated with sulfate, such as sodium, calcium, potassium, and magnesium. The relationships of sulfate, nitrate, ammonium, and other cations are explored in this section.

Figure 4-1 shows the average anion and cation charges by month for sites in the speciation network. The total anion charge is calculated as $\text{sulfate} \times 2 + \text{nitrate} + \text{chloride}$. The total cation charge is calculated as $\text{ammonium} + \text{sodium} + \text{potassium} + 2 \times \text{magnesium} + 2 \times \text{calcium}$. These are the species known to participate in inorganic gas-aqueous-solid thermodynamic equilibria. Sulfate, nitrate and ammonium are also shown. While individual sites differ slightly in the exact shape of the seasonal profile, Figure 4-1 is a representative illustration of the profiles. Several observations can be made regarding the balance of charges. First, ammonium represents a large fraction of the cation charges in the particulate phase. The other cations, including sodium, calcium, potassium and magnesium, combine to account for only 6 to 16% of the positive

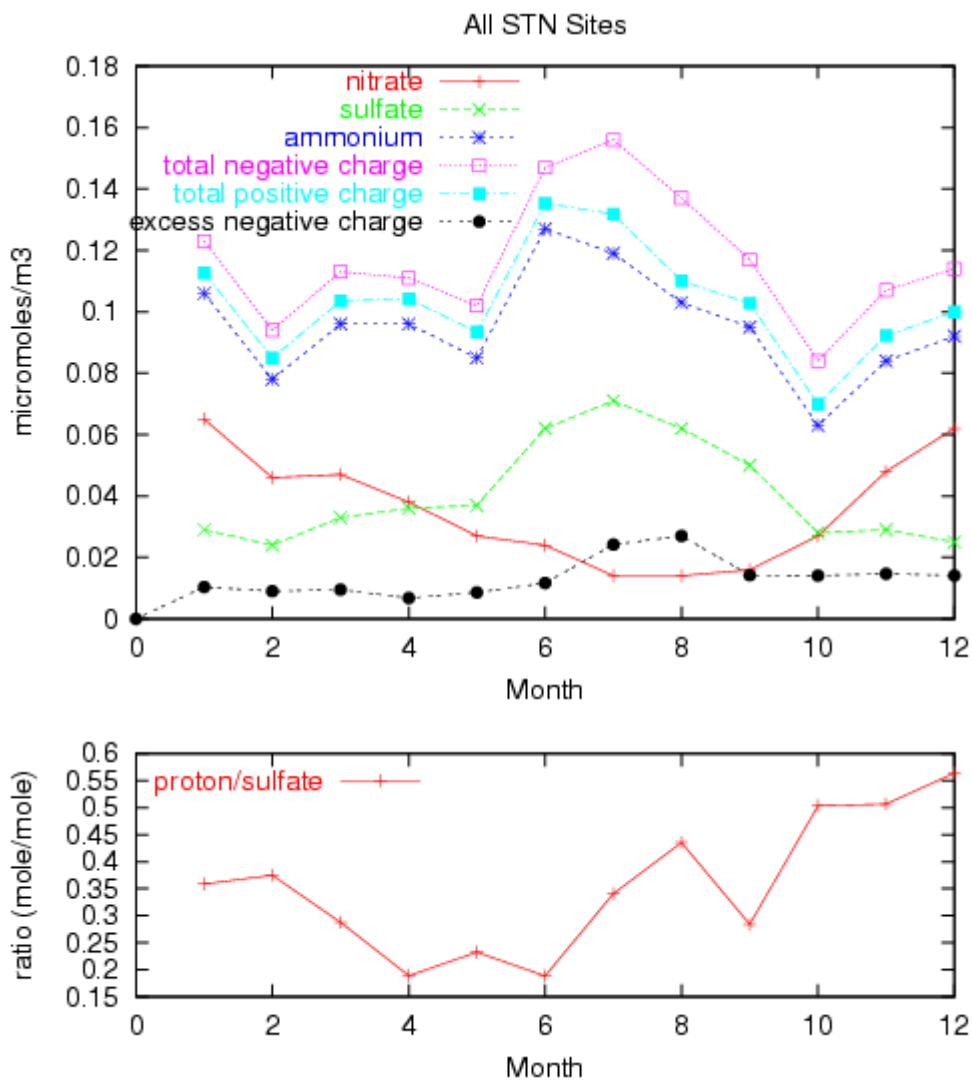


Figure 4-1. (Top) Monthly average concentrations of nitrate, sulfate, ammonium, total negative charge, total positive charge and excess negative charge at speciation sites within the Midwest RPO and in surrounding states. Total negative charge is calculated as the sum of chloride, nitrate and sulfate x 2. Total positive charge is calculated as the sum of ammonium, sodium, potassium, calcium x 2 and magnesium x 2. Excess negative charge is assumed to represent the concentration of protons. (Bottom) Molar ratios of negative charge to sulfate by month.

charges. Neglecting these species in the analysis of the formation of nitrate and sulfate will result in a small but non-negligible error. Second, the calculated positive charges (cations) are always less than the calculated negative charges (anions). The balancing charge is provided by protons, which means that either a fraction of sulfate exists as hydrogen sulfate (or sulfuric acid) or a fraction of nitrate exists as nitric acid in the particles. In any case, particulate nitrate can co-exist with partially neutralized sulfate in the speciation sites within the Midwest RPO and in surrounding states. The IMPROVE assumption of complete neutralization of sulfate and nitrate, which is used to reconstruct fine mass, does not always apply to sites in the Upper Midwest.

HNO_3 and HCl are quite volatile and their partition favors the gas phase, especially when temperature is high and relative humidity is low to moderate. Therefore, in the summer, particulate nitrate and chloride are likely to be associated with a cation other than proton. In this case, the protons (unbalanced charges in Figure 4-1) are associated with bisulfate and/or sulfuric acid. Despite the relatively high amount of excess negative charge attributed to protons, the degree of sulfate neutralization tends to be quite high during spring and early summer (low ratio of proton to sulfate; see bottom panel of Figure 4-1), mostly due to an abundance of sulfate relative to the unbalanced charges. The presence of a small amount of nitrate may be an indication that there is sufficient nitric acid and ammonia in the gas phase to drive the equilibrium formation of ammonium nitrate, despite the incomplete neutralization of sulfate.

In late fall and early winter, the ratio of proton to sulfate is quite high, consistent with significant concentrations of hydrogen sulfate relative to sulfate. Relaxing the assumption about the association of nitrate with proton due to lower temperatures, the winter situation may also be consistent with the possible presence of nitric acid in the particles, which is not neutralized by a cation. Without information on the concentration of the gaseous precursors, e.g., ammonia and nitric acid, it is difficult to evaluate if particulate nitric acid is formed, or if ammonium nitrate is formed in the presence of acidic sulfate. If ammonium nitrate is formed, the winter formation occurs at somewhat higher acidic sulfate concentrations than in the summer.

Blanchard and Tanenbaum (2004) found that particulate nitrate formation is not limited by the availability of ammonia for most samples at times when temperature and humidity favor the condensed phase in the Midwest RPO region.

Another intriguing possibility relates to the measurement errors of ammonium. Collett et al. (2004) studied the loss of ammonium on nylon filters at 4 IMPROVE locations during high nitrate seasons. They found significant losses of ammonium (10-34%, one-month average at these sites) especially in cases with warmer temperatures or significant diurnal fluctuations of temperature and relative humidity. Similar collection procedures of ammonium on nylon filters (slightly basic) at urban and rural speciation sites may be subject to volatilization (P. Solomon, 2004, personal communication). The apparent increase during summer of the excess negative charges, which are attributed to balancing charges of protons, can also be consistent with an increased volatilization of ammonium from PM samples collected on filters. Such a possibility needs to be evaluated in relation to the degree of neutralization of sulfate when ammonium nitrate can be formed.

Routine measurements of ammonium, sulfate, and nitrate are based on laboratory analyses of 24-hour average ambient samples collected on filter media. The deployment of a continuous ion chromatograph at Bondville provides an opportunity to further probe some of the hypotheses put forth. A preliminary data set May 2003 to January 2004 was obtained from LADCO (Kenski, 2004 personal communication) that contains hourly data of nitrate, nitric acid, sulfate, sulfur dioxide, ammonium, and ammonia (other species were measured, but data capture is poor for chlorine/chloride, nitrogen dioxide/nitrous acid (HONO)/nitrite). Monthly average concentrations of sulfate, nitrate, and ammonium are presented in Figure 4-2. These raw data were aggregated by month, considering only data points with simultaneous measurements of sulfate, nitrate, and ammonium. Data from Bondville indicate that ammonium exceeds the total negative charges associated with sulfate and nitrate, in contrast with Figure 4-1. Since the presence of another cation (e.g., chloride) is unlikely at this site, the excess positive charge (ammonium) cannot be easily explained. Further quality assurance may be needed for the continuous data set. The scatter plot of hourly data in Figure 4-3 shows a potential use of the

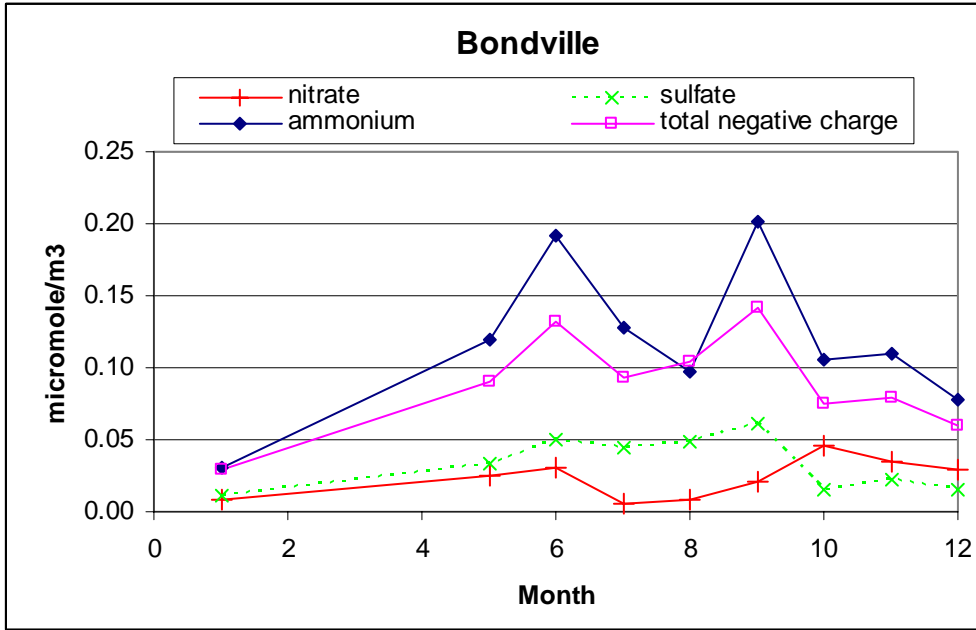


Figure 4-2. Monthly average concentrations of nitrate, sulfate, ammonium, and total negative charge at Bondville. Total negative charge is calculated as the sum of nitrate and sulfate x 2.

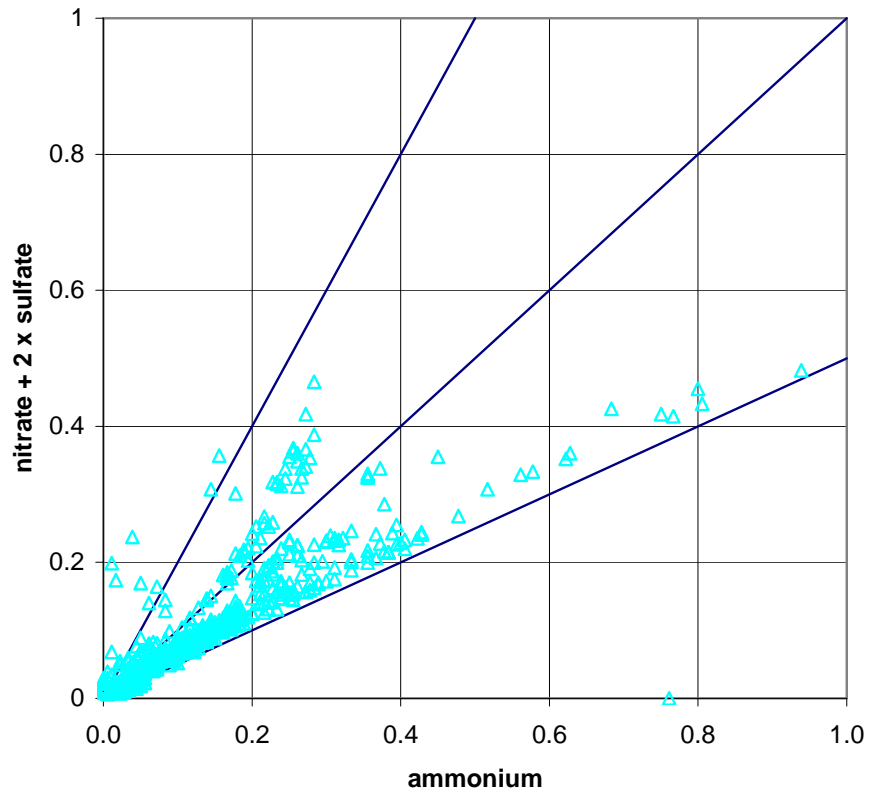


Figure 4-3. Scatter plot of hourly negative charges vs. ammonium (micromole/m³) at Bondville during summer 2003.

continuous data, i.e., to evaluate the variability of the ammonium-sulfate-nitrate equilibrium. It is interesting to note two distinct relationships between ammonium and sulfate and nitrate in this summer data set. Such relationships should be explored in greater detail with a final, quality assured dataset.

4.2 What are the possible responses of inorganic PM to the availability of sulfate, total (gas + particulate) ammonium, and total nitrate?

Although the participation of other anions and cations may affect the equilibrium of the ammonium-nitrate-sulfate system, the perturbations are expected to be small due to the relatively small contribution of these other ions to the overall ion balance of the particulate matter. Hence, it is informative to investigate the sensitivity of the ammonium-nitrate-sulfate system to the availability of individual components.

Simultaneous measurements of gaseous and particulate phase components are needed to establish the gas/particle equilibrium. The on-going project at LADCO to measure ammonia using ion chromatography and other methods will eventually provide additional data for the analysis. At this time, the most complete data set of ammonia, ammonium, nitric acid, nitrate, and sulfate (the vapor pressure of sulfuric acid is so low that its gas-phase concentration can be neglected compared to the particle-phase concentration) is obtained from the MARCH-Midwest field study (A. Hansen/I. Tombach, 2004, personal communication). Data are available for several Midwestern cities, including Athens (summer and winter), Charlotte (summer), Chicago (summer and winter), Cincinnati (summer and winter), Detroit (summer), and St. Louis (summer). The ammonium-nitrate-sulfate equilibrium is characterized by a gas ratio (GR), which is the ratio of the concentration of free ammonia (NH_3F) to total nitrate (HNO_3T). The equilibrium is also a function of temperature and RH, and is, therefore, distinctive for each location and season. Free ammonia is defined as the total concentration of gas and particulate ammonium minus the ammonium needed to completely neutralize the available sulfate (2 moles of ammonium are needed to neutralize one mole of sulfate).

Median HNO₃T varied spatially from 0.7 to 2.3 ppb during the summer and GR varied between 0.2 and 3.2. Athens showed the lowest median nitrate concentration but also the lowest GR. The highest median summer GR was recorded in Chicago, and the highest HNO₃T concentration was recorded in Cincinnati. Winter median HNO₃T ranged from 1.3 to 1.9 ppb, and GR from 0.3 to 1.3. In Athens, both winter and summer GR are low. In Chicago and Cincinnati, winter GR was lower than the corresponding summer value.

Ansari and Pandis (1998) investigated the response of PM to precursors as a function of GR and either HNO₃T or NH₃F. To investigate the response of PM on days with high PM concentrations, the values of HNO₃T, NH₃F, and GR are listed in Table 4-1 for each site and each season on the day with the maximum total PM_{2.5} concentration. In a few cases, the combination HNO₃T, NH₃F, and GR associated with the highest PM concentration is not representative of other high PM conditions at that location. A second entry is provided in Table 4-1 in those cases to illustrate the representative condition or the alternative condition from another high PM day (within the top 5 category). As shown below, these different conditions mostly do not result in different responses of PM in the summer, but do so in the wintertime for Chicago and Cincinnati.

Based on the HNO₃T, NH₃F, and GR values of high PM days, the responses of PM_{2.5} to sulfate according to Ansari and Pandis (1998) are summarized in Table 4-2. When relative humidity is low and temperature is high, ammonium nitrate is not formed very readily. Therefore, when the relative humidity is low during summer, reductions in sulfate yield the expected response at all locations. The expected response corresponds to the loss of sulfate and the associated ammonium (up to two moles of ammonium per mole of sulfate) as sulfate is decreased, without significant change in nitrate. In other words, ammonium nitrate formation is decoupled from sulfate formation in these summer cases.

When the relative humidity is higher, the ammonium nitrate equilibrium shifts towards the particulate phase and ammonium nitrate can form even when temperatures are high. In these cases, reductions in sulfate yield a non-linear response in Chicago, Cincinnati, Detroit, and St. Louis where the decrease in total PM is less than the decrease in ammonium sulfate. Some

Table 4-1. Total nitrate (HNO₃T), free ammonia (NH₃F) and gas ratio (GR) representative of days with high PM concentrations from the MARCH-Midwest database.

Location	Season (average temperature ⁽¹⁾)	Total nitrate (ppb)	Free Ammonia (ppb)	Gas ratio (ppb/ppb)
Athens, OH	Summer (67F)	2.0	< 0	< 0
Athens, OH	Winter (27F)	2.8	0.9	0.3
Charleston, WV	Summer (69F)	2.2	18	8.3
Chicago, IL	Summer (68F)	5.1	4.8	0.9
Chicago, IL	Winter (25F)	4.2	0.5 ⁽²⁾	0.1 ⁽²⁾
		3.7	5.2	1.4
Cincinnati, OH	Summer (67F)	3.5	2.1	0.6
Cincinnati, OH	Winter (27F)	5.5	3.0	0.5
		3.0	3.0 ⁽³⁾	1.0 ⁽³⁾
Detroit, MI	Summer (68F)	2.8	5.6	2.0
		3.5 ⁽³⁾	2.4 ⁽⁴⁾	0.7 ⁽⁴⁾
St. Louis, MO	Summer (74F)	5.0	0.1	0.01
		3.8	3.1 ⁽³⁾	0.8 ⁽³⁾

(1) Seasonal average temperatures are used to convert particulate concentrations to ppb (Source: NCDC)

(2) The winter day with maximum PM in Chicago is not representative because free ammonium is lower and GR is higher than other high PM days

(3) The top 5 highest PM concentrations are associated with two distinct types of free ammonium/GR conditions

(4) The summer day with maximum PM in Detroit is not representative because the gas ratio is higher than other high PM days

Table 4-2. Common responses of total PM to changes in sulfate at low (L), high (H) or all relative humidity conditions for several locations and seasons.

Location	Season	Expected ⁽¹⁾ (Removal of sulfate leads to removal of ammonium sulfate)	Non-linear ⁽²⁾ (Removal of sulfate leads to some formation of ammonium nitrate but overall decrease in PM)	Negative ⁽³⁾ (Removal of sulfate leads to formation of ammonium nitrate and overall increase in PM)
Athens, OH	Summer	All		
Athens, OH	Winter			All
Charleston, WV	Summer	All		
Chicago, IL	Summer	L	H	
Chicago, IL	Winter	All (high GR cases)		All (low GR cases)
Cincinnati, OH	Summer	L	H	
Cincinnati, OH	Winter		All (high GR cases)	All (low GR cases)
Detroit, MI	Summer	L	H	
St. Louis, MO	Summer	L	H	

(1) Expected response: $d \text{ PM} / d \text{ sulfate} = 1 - 1.34$

(2) Non-linear response: $d \text{ PM} / d \text{ sulfate} = 0 - 1$

(3) Negative response: $d \text{ PM} / d \text{ sulfate} = -0.28 - 0$.

ammonium nitrate is formed due to the availability of ammonia that was originally associated with sulfate.

During winter, when lower temperature favors the formation of particulate nitrate, the nonlinear response is more common than the expected response. In fact, a negative response is estimated to be prominent in Chicago, Cincinnati, and Athens. If most of the ammonium is tied up in particulate phase and gaseous nitric acid is available, a maximum of 2 moles of nitrate (MW = 62) will be formed per mole of sulfate removed (MW = 96). Thus, removing sulfate results in a net gain in PM mass. Conversely, the addition of sulfate may result in a decrease in total PM_{2.5}. To varying degrees, the non-linear and negative responses are indicative of ammonium sensitivity in the formation of nitrate in winter.

In Athens during the summer, there is little free ammonia and total nitrate to form ammonium nitrate, and the lack of sensitivity of PM to either ammonia or nitrate indicates that ammonium nitrate is unlikely to be formed in significant quantities when either component increases (Tables 4-3 and 4-4). This behavior is also common at other urban areas when the temperature is high and the relative humidity is low because little ammonium nitrate can be formed. When relative humidity is high, some ammonium nitrate is formed in most of the Midwestern cities in the March Midwest study. At four out of the five urban areas other than Athens, the formation seems to be sensitive to both total nitrate and free ammonia at high RH (Tables 4-3 and 4-4). Non-linear response to both HNO₃T and NH₃F indicates that both may become the limiting reagent in this regime. In Charleston, nitrate formation is more sensitive to HNO₃T than NH₃F, which is consistent with the abundance of free ammonia measured during conditions with high PM_{2.5} formation.

Table 4-3. Responses of total PM to changes in free ammonia (gas + particulate ammonia – 2 x sulfate) at low (L), high (H) or all relative humidity conditions for several locations and seasons.

Location	Season	No response⁽¹⁾ (Removal of ammonia does not affect PM. Either no ammonium nitrate is formed or system is very nitric acid sensitive)	Non-linear⁽²⁾ (Removal of ammonia removes some ammonium nitrate based on equilibrium)	Very sensitive⁽³⁾ (Removal of ammonia removes ammonium nitrate; system is sensitive to ammonia)
Athens, OH	Summer	All		
Athens, OH	Winter			All
Charleston, WV	Summer	All ⁽⁴⁾		
Chicago, IL	Summer	L	H	
Chicago, IL	Winter	L,H (high GR cases)	H (high GR cases)	All (low GR cases)
Cincinnati, OH	Summer	L	H	
Cincinnati, OH	Winter		All (high GR cases)	All (low GR cases)
Detroit, MI	Summer	L	H	
St. Louis, MO	Summer	L	H	

(1) No response: $d \text{ PM} / d \text{ ammonium} = 0 - 0.2$

(2) Non-linear response: $d \text{ PM} / d \text{ ammonium} = 0.2 - 3.5$

(3) Very sensitive response: $d \text{ PM} / d \text{ ammonium} = 3.5 - 4.7$

(4) High PM conditions near non-linear response zone.

Table 4-4. Responses of total PM to changes in total nitrate at low (L), high (H) or all relative humidity conditions for several locations and seasons.

Location	Season	No response⁽¹⁾ (Removal of nitric acid does not affect PM. Either no ammonium nitrate is formed or system is very ammonia sensitive)	Non-linear⁽²⁾ (Removal of nitric acid removes some ammonium nitrate based on equilibrium)	Very sensitive⁽³⁾ (Removal of nitric acid removes ammonium nitrate; system is sensitive to nitric acid)
Athens, OH	Summer	All		
Athens, OH	Winter	H	L	
Charleston, WV	Summer	L		H
Chicago, IL	Summer	L	H	
Chicago, IL	Winter		All (low GR cases)	All (high GR cases)
Cincinnati, OH	Summer	L	H	
Cincinnati, OH	Winter	All (low GR cases)	All (high GR cases)	
Detroit, MI	Summer	L	H	
St. Louis, MO	Summer	L	H	

(1) No response: $d \text{ PM} / d \text{ nitrate} = 0 - 0.1$;

(2) Non-linear response: $d \text{ PM} / d \text{ nitrate} = 0.1 - 0.9$

(3) Very sensitive response: $d \text{ PM} / d \text{ nitrate} = 0.9 - 1.27$.

In winter, ammonium nitrate formation seems to be quite sensitive to NH₃F under at least some conditions conducive to the formation of PM at all three locations with measurements. However, a non-linear response to NH₃F is predicted under some conditions in Cincinnati. Some conditions in Chicago prove unresponsive to changes in NH₃F, but respond to changes in total nitrate (non-linear to very sensitive response). High PM conditions in Athens and Cincinnati tend to be less responsive to HNO₃T.

Blanchard and Tanenbaum (2004) found that particulate nitrate formation is not limited by the availability of ammonia for most samples at times when temperature and humidity favor the condensed phase in the Midwest RPO region, even though they noted that individual samples were ammonia-limited. By the definition of Blanchard and Tanenbaum (2004), particulate nitrate formation is not limited by the availability of ammonium for samples having excess ammonium ($\text{gas} + \text{particulate ammonium} - 2 \times \text{sulfate} > \text{gas} + \text{particulate nitrate}$) or having $\text{GR} > 1$. In Table 4-1, we note that many of the highest PM_{2.5} cases studied correspond to ammonium sensitivity by the definition of Blanchard and Tanenbaum (2004). In addition, nitrate may increase under median conditions with sulfate decrease at a few locations, indicating some interactions via ammonium if not sensitivity. The sensitivity to ammonia under conditions corresponding to high concentrations, especially winter, is not unexpected based on the finding that wintertime aerosols may be more acidic than summertime. Additional sampling of these species, especially at rural areas, would help clarify the seasonality of the ammonia limitation issue.

4.3 Can current information provide insights into the formation processes of sulfate and nitric acid?

Sulfate. Atmospheric oxidation of sulfur dioxide to sulfate takes place in the gas phase via the reaction of SO₂ with OH and in cloud droplets when SO₂ is oxidized by O₃, H₂O₂ or O₂ (catalyzed by trace metal ions). When sulfate is formed in the gas phase and condense onto particles; sulfate predominantly resides in particles with diameters less than 0.5 microns. Cloud processing of sulfate typically leads to sulfate concentrations in slightly larger particles with

diameters between 0.5 and 1 microns (Hering and Friedlander, 1982; McDade et al., 2000). Data from Detroit, MI (Cahill et al., 2002) provide some basis for assessing the source of sulfate.

Size resolved PM samples were collected in three-hour time periods between February 28 and April 10, 2002, and analyzed for 28 elements. Figures 4-6 of Cahill et al. show the time series of sulfate in three size bins (1.15 to 2.5 microns, 0.34 to 1.15 microns, and 0.1 to 0.34 microns). During this period, sulfate concentrations in particles between 1.15 and 2.5 microns were small ($< 0.1 \mu\text{g}/\text{m}^3$) except for a few concentration spikes of up to $0.45 \mu\text{g}/\text{m}^3$. Sulfate concentrations in particles between 0.34 and 1.15 microns typically ranged from <0.1 to $0.5 \mu\text{g}/\text{m}^3$, except for several concentration spikes of 1.5 to $3 \mu\text{g}/\text{m}^3$. Sulfate concentrations associated with the smallest particles ranged from <0.1 to $0.5 \mu\text{g}/\text{m}^3$, and no spike of high concentrations was observed in this size range.

Sulfate found in the smallest size bin corresponds fairly well to gas-phase oxidation of sulfur dioxide and subsequent condensation of the low vapor-pressure sulfuric acid. During the sampling period, gas-phase formation seems to be a fairly consistent source of sulfate. The 0.34 to 1.15 size bin corresponds to sulfate that has experienced cloud processing. Note that in addition to oxidation reactions in the aqueous phase to produce new sulfate, cloud processing also changes the size distribution of existing sulfate. Therefore, sulfate residing in a larger size fraction is not in itself conclusive evidence that the sulfate has been produced in aqueous-phase reactions in clouds. Nonetheless, the sulfate time series for the 0.34 to 1.15 micron size section contains spikes that are many times the background concentrations in this section and much larger than corresponding concentrations in smaller size sections. These spikes are consistent with aqueous production of sulfate particles.

Data from Pittsburgh are consistent with both gas-phase and intermittent aqueous-phase production of sulfate. It may be useful to collect further size-segregated data for this type of analysis, especially for the summer season when sulfate is high and for areas that may be more subject to transport. In a focused study, back trajectories and meteorology along the back trajectory can also be analyzed to provide supplemental information regarding the production pathways.

Nitrate. The formation of particulate nitrate requires the availability of nitric acid and some cation (e.g., ammonium). Nitric acid is formed in the oxidation of nitrogen dioxide (NO_2) via a number of chemical reactions. In the gas phase, NO_2 is oxidized by OH to form nitric acid. Alternatively, O_3 can convert NO_2 to NO_3 . NO_3 can react with NO_2 to form N_2O_5 , which reacts with water to form nitric acid. There are also heterogeneous reactions that convert NO_2 , NO_3 , and N_2O_5 to HNO_3 . Since NO_3 radicals photolyze, the NO_3 pathways tend to be viable at night. The OH reaction tends to occur during the day, as OH is removed at night and cannot typically be replenished without sunlight. Therefore, diurnal variations of nitrate concentrations may indicate the dominant process for nitrate production. Recent analyses of wintertime nitrate formation in the California Central Valley indicate daytime nitrate formation as an afternoon nitrate peak. This observation is consistent with the OH + NO_2 reaction. However, above the surface layer, there is also evidence of evening nitrate formation via the O_3 reactions. As the mixing layer collapses in the evening, surface level O_3 is quickly titrated away by surface NO_x emissions, especially near urban areas and mobile sources. Elevated O_3 concentrations can be retained throughout the evening to act as an oxidant for the production of nitric acid. Such a possibility of aloft nitrate production needs to be investigated for the Upper Midwest.

5. WHAT CAN BE INFERRED FROM ALOFT DATA ABOUT THE TRANSPORT AND/OR FORMATION OF PM?

An aloft measurement database is compiled based on measurement flights in 2001, 2002, and 2003. According to Schauer (2002), the 2001 Wisconsin DNR aircraft data suffered from flow rate problems, which resulted in inconsistent PM cut points and increased detection limits for carbon measurements. Even without sampling mishaps, the analysis of aircraft data is subject to a number of caveats. First, the 2001 PM samples from the Purdue aircraft were collected with a cut point between 7 and 9 microns; the cut point of the 2002 and 2003 data is not available in the data base, but should be closer to 2.5 microns due to the installation of new equipment (M. Allen, Wisconsin DNR, personal communication, 2004). Second, flights typically took place during the day, and aloft data are unavailable at night. Third, aircraft data are either instantaneous (specific location and very short averaging time on the order of seconds) or integrated (averaged over the duration of flight (typically several hours) and locations covered by the flight path); in comparison with surface data, which are point measurements of intermediate (1 hour) to longer (24-hour) averaging time.

5.1 Upper Midwest flights (Regional flight route for the WI aircraft)

For this analysis, we obtained PM composition data for flights conducted during 2001 and 2002. PM composition is collected as integrated samples, and represents a spatially averaged composition along the flight path. Of interest to the Upper Midwest Class I areas is a series of Wisconsin DNR flights that passed through Wisconsin and over several of the Great Lakes (Figure 5-1). In Figure 5-2, the concentrations of several PM components are displayed for the aircraft measurements and for several of the surrounding rural sites. Consider the period of fall and winter 2002, aloft sulfate and ammonium concentrations were quite low and not very variable. On the other hand, the major components of PM during this period, nitrate and OC, were quite variable.

During this fall and early winter period in the Upper Midwest, aloft sulfate concentrations were generally higher than surface level concentrations. One exception was on 11/4/2002 when

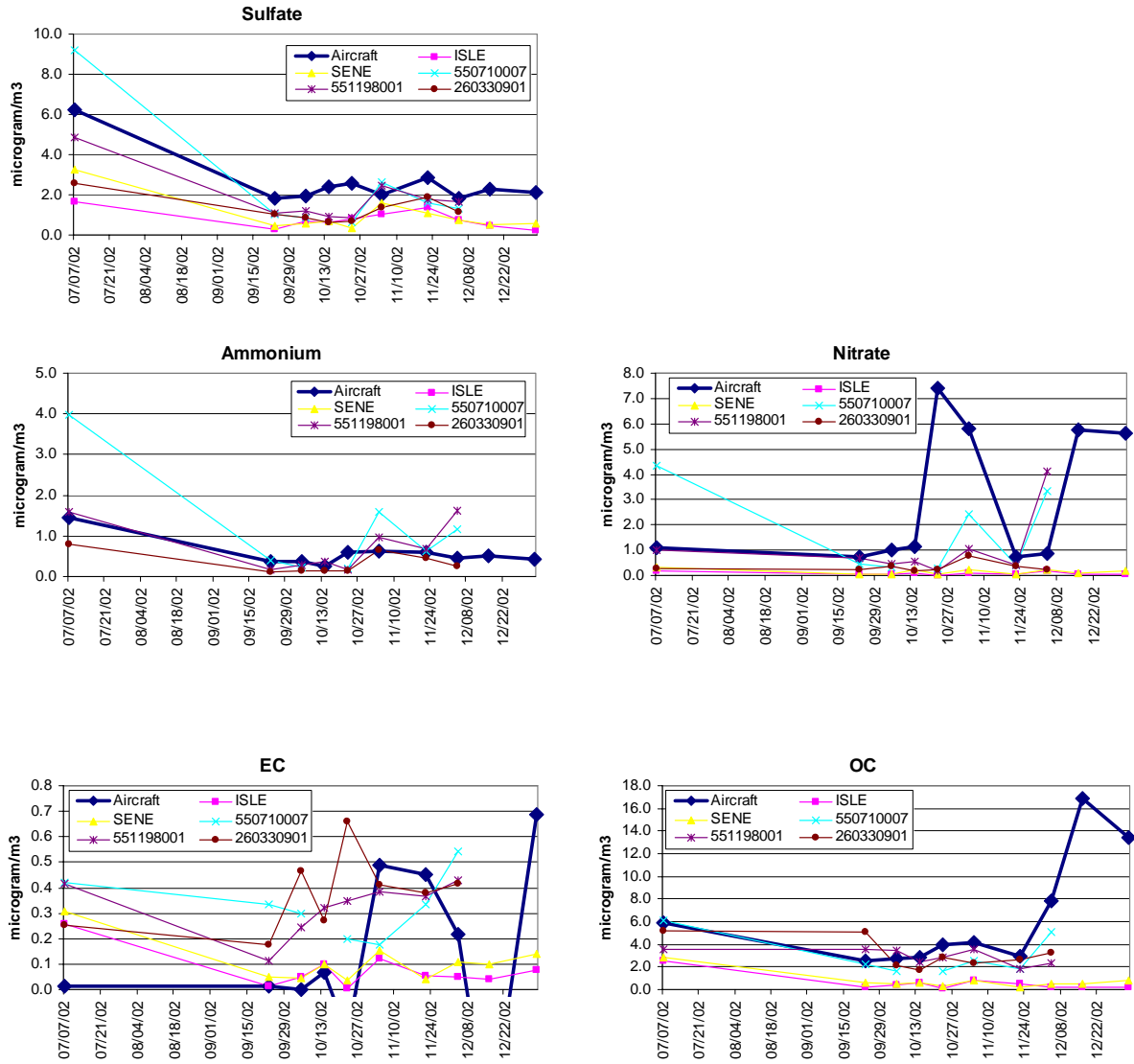


Figure 5-2. Concentrations of PM components aloft and at ground level at several nearby monitoring sites for the Wisconsin regional flights. SENE and ISLE are IMPROVE sites at Seney National Wilderness and Isle Royale National Park. 550710007 is a speciation monitor in Manitowoc, WI. 551198001 is a speciation monitor at Perkinstown, WI. 260330901 is a speciation monitor in Saute Ste. Marie, MI.

the surface concentrations at two rural Wisconsin sites were similar to the aloft concentration. The other exception was on 7/7/2002 when the concentration at the lakeshore site at Manitowoc, WI (550711007) exceeded that measured aloft. That aloft concentrations are higher than surface concentrations implies that conditions conducive to the downward movement of air increase the surface concentrations of sulfate at the Upper Midwest sites. Elevated concentrations aloft are also consistent with long-range transport of sulfate and/or SO₂ that is converted to sulfate as it is transported.

Ammonium concentrations aloft were similar to surface concentrations. On the days and for the sites where aloft sulfate was less than surface sulfate, the ammonium concentrations showed the same relative concentrations. The surface concentrations at the two Wisconsin sites on 12/4/2002 were higher than the aloft concentrations. The ammonium is associated with nitrate, which showed elevated concentrations. While nitrate formation at the surface sites on 12/4/2002 was probably in the form of ammonium nitrate, the elevated nitrate concentration aloft observed on 10/23/2002 was not associated with significant ammonium concentrations. The different forms of nitrate deserve further investigation, including the possibility of an aloft formation process that may not require the presence of ammonium.

Elemental carbon is a primary species that is emitted predominantly at the surface. Therefore, aircraft measured concentrations were typically lower than surface concentrations. Organic carbon concentrations aloft were similar to those at the speciation sites, and higher than those at the IMPROVE sites due to the differences in measurement procedures.

In the comparison of aircraft and surface data, we made the following assumptions: (1) All sulfate, nitrate, ammonium, OC, and EC reside in PM_{2.5}; (2) aloft concentrations change slowly with time, such that the flight duration can be considered representative of the daily average. Contingent upon those assumptions, we note that sulfate, nitrate, ammonium, OC, and EC measured aloft can differ significantly from surface concentrations measured at rural sites. Aloft concentrations are not always representative of the regional concentrations at the surface, despite lower variability aloft due to the lack of influence of emissions (except stack emissions).

Instead, consistent vertical gradients of several components may be indicative of the role played by vertical mixing in governing pollutant concentrations at the surface.

5.2 Other flights

The concentrations of several PM components measured aloft during different flights are presented in Figure 5-3 by flight route. Along several of the southern routes of the Purdue aircraft, fairly extreme concentrations of sulfate and OC were sometimes observed. The highest concentrations of sulfate and OC (and EC, not shown) were observed on 6/22/2002 during two flight segments (9:30-10:30; 12:00-16:00) of the Purdue airplane. On the same day, the Wisconsin aircraft was also in the air during daylight hours and collected data along a different flight route along the shore of Lake Michigan. These two flight routes are shown in Figure 5-4. The concentrations recorded by the Wisconsin aircraft were somewhat representative of the 24-hour average concentrations recorded at surrounding surface sites, especially sulfate concentrations. Nitrate concentrations were higher aloft than at the surface, but ammonium concentrations were lower. OM concentrations were higher aloft, although EC concentrations were higher at ground level. The Purdue aircraft recorded extremely high concentrations for sulfate, OM, and EC at 66, 175, and 6 $\mu\text{g}/\text{m}^3$, respectively. The maximum 24-hour concentrations at any surface sites in the Midwest were 21, 11 and 1.6 $\mu\text{g}/\text{m}^3$ for these species. If the surface concentrations reflect the rough magnitude of the daily average values aloft, those extreme readings indicate the significant temporal variability that may also exist aloft or measurement problems (PM collected on June 23 and June 25 along the same routes (LMI) show a marked decrease in sulfate and OC concentrations in Figure 5-3).

The differences in the aloft concentrations between these two flights are mirrored by a South-to-North gradient at the surface for sulfate and organic matter, as shown in Figure 5-5. Both surface and upper air transport were important mechanisms for distributing fine particulate sulfate and OC from South to North on that day.

While the gradient of pollutant concentrations from South to North on June 22 was extreme, it is by no means unique. Regional flight patterns were designed to investigate Class I

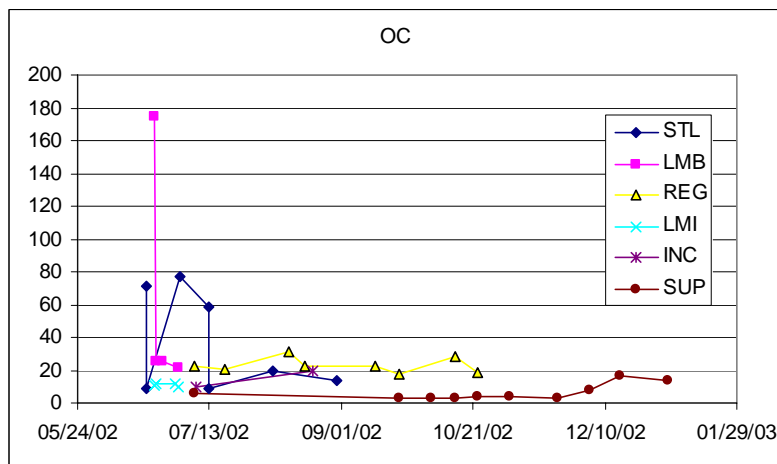
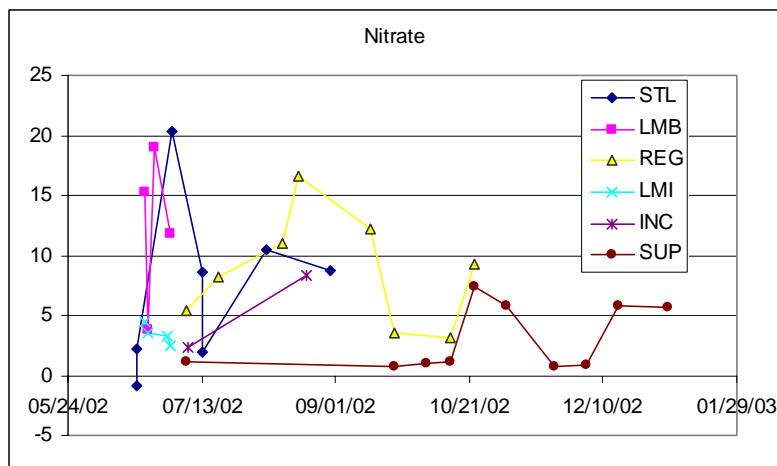
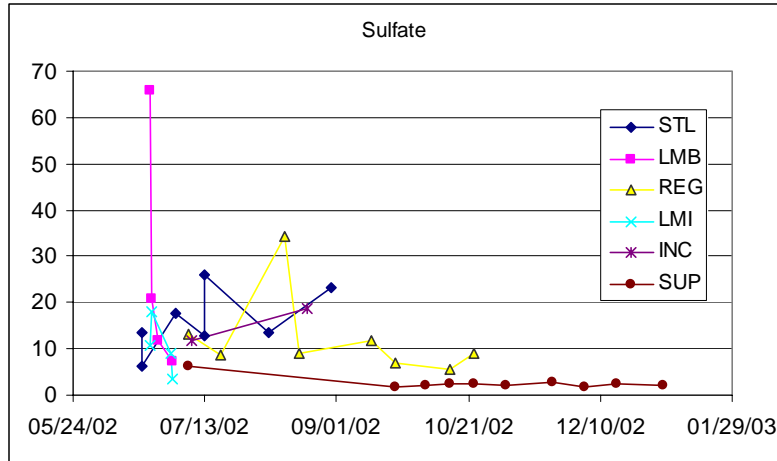


Figure 5-3. Sulfate, nitrate and OC concentrations recorded on Wisconsin and Purdue aircraft during 2002 grouped by routes. SUP and LMI are the regional and Lake Michigan routes for the WI aircraft; REG and LMB are the regional and Lake Michigan routes for the Purdue aircraft; STL are flight routes to St. Louis, and INC represent intercomparison flights.

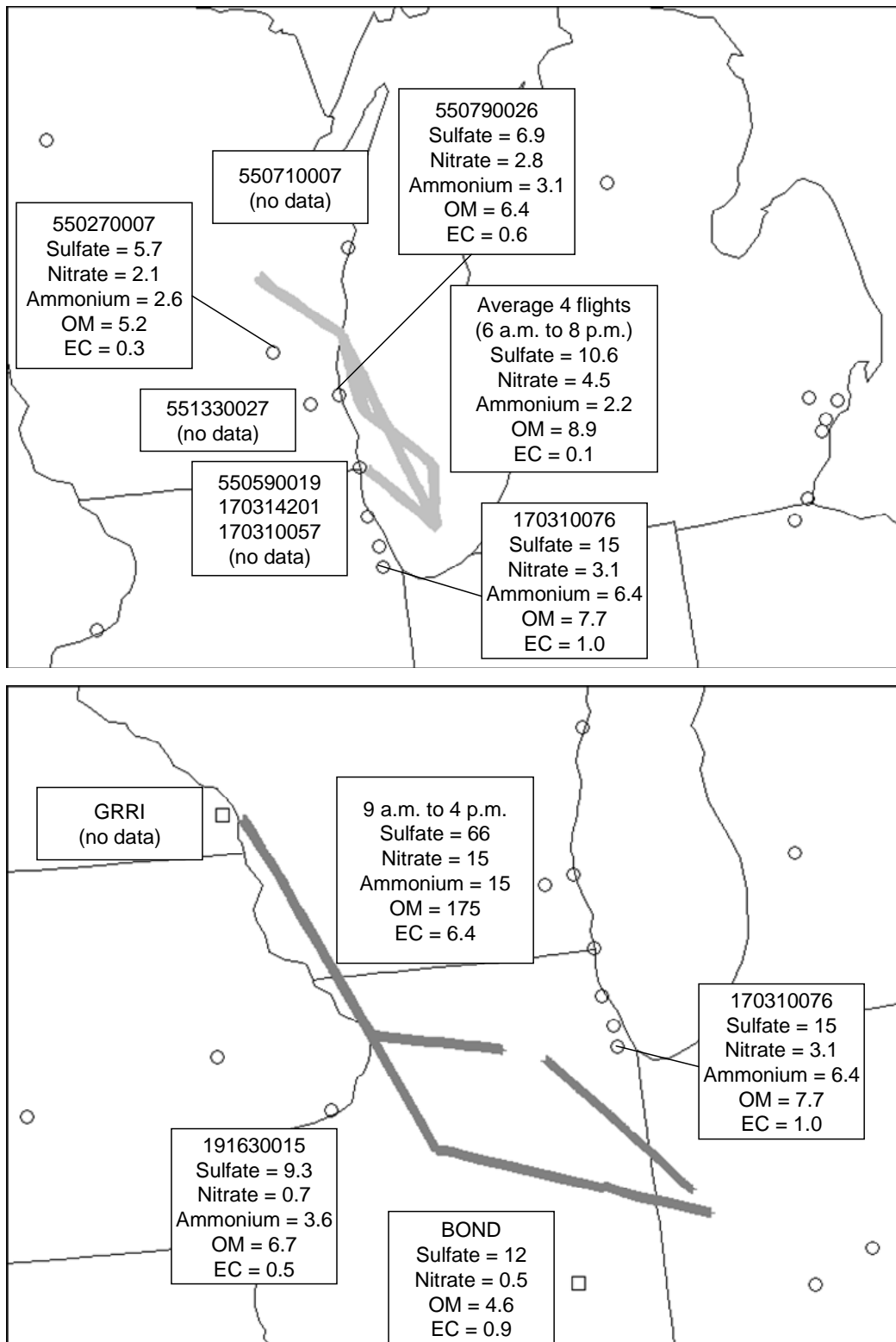


Figure 5-4. Flight paths of the Wisconsin aircraft (top) and the Purdue aircraft (bottom) and concentrations at surrounding surface sites.

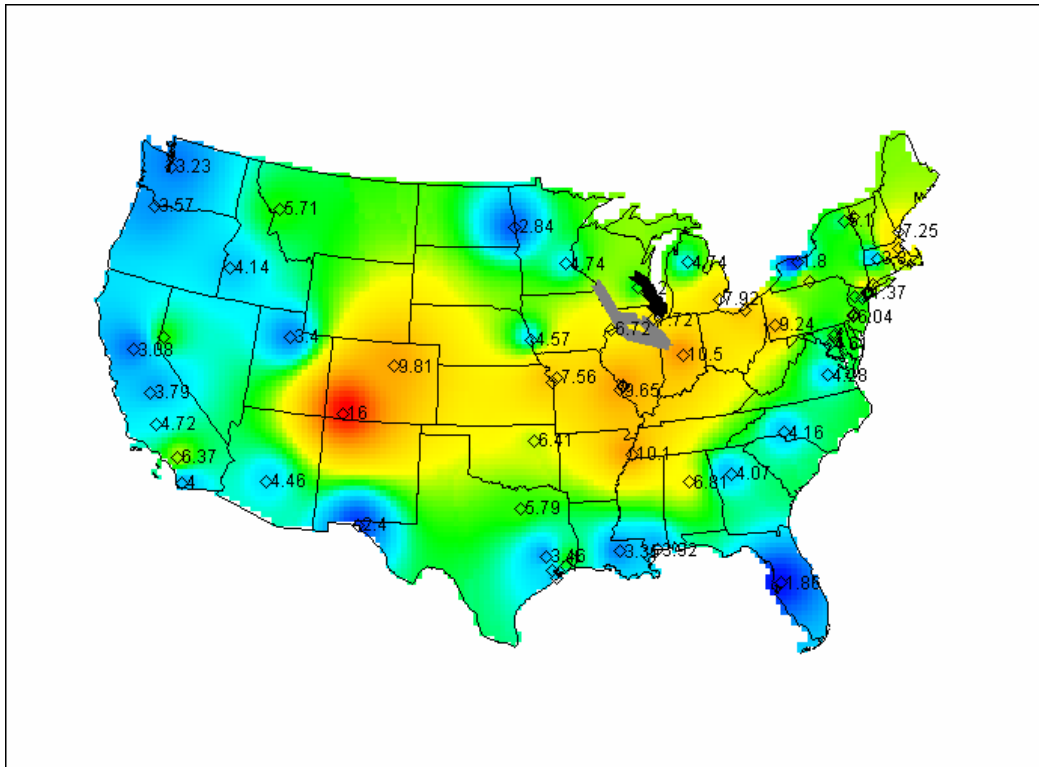
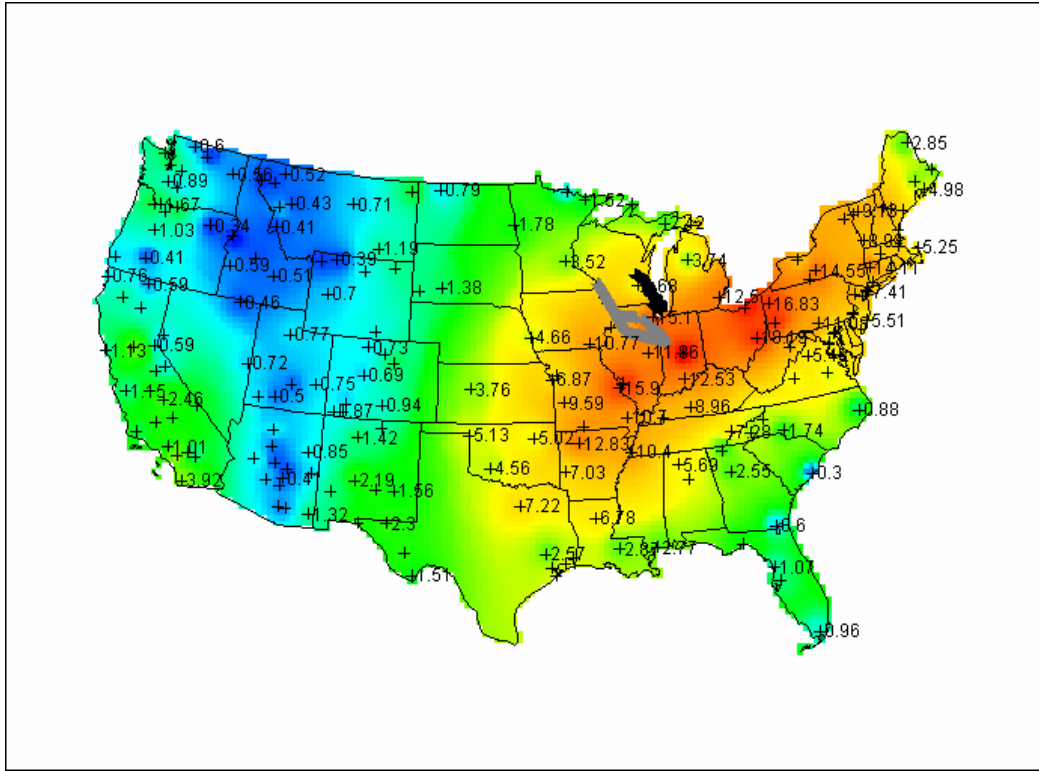


Figure 5-5. Spatial distributions of sulfate (IMPROVE and speciation) and OC (speciation sites only) on June 22.

areas in the upper Midwest (Wisconsin flight route to Isle Royale National Park and Seney National Wilderness) and nearby Class I areas (Purdue flight route to Mammoth Cave National Park and Dolly Sods Wilderness). Unfortunately, due to missing data from one or the other plane or change of flight routes, data are available for comparison for only one (July 7) of the 12 summer days scheduled for regional flights in 2002. On that day, the planes were in the air during different time of the day, and sampling time overlapped only one hour in the morning. Two days in the fall were selected instead as a case study. The concentrations of elemental carbon, nitrate, organic carbon, and nitrate measured on these regional flights are plotted in Figure 5-6. Surface concentrations at the Class I areas are also shown. On both days, aloft concentrations measured along the Purdue aircraft's southern regional route were higher than those measured along the Wisconsin regional route for organic carbon, sulfate, and nitrate. Concentrations of elemental carbon were small aloft. The South-to-North gradient is also observed in the surface measurements.

Aloft concentrations tend to be higher than concentrations at the surface for sulfate, nitrate, and organic carbon, over both regional flight routes. The aloft-surface difference is more significant for nitrate and organic carbon than for sulfate. Sulfate production in clouds may be a partial explanation for the higher concentrations of sulfate aloft. While there is typically not enough ammonium present in aloft particles to neutralize both sulfate and nitrate aloft, nitrate is formed. Nitric acid is measured in the WI aircraft. From the 2003 summer data, nitric acid concentrations were frequently elevated, indicating that availability of ammonia may be limiting the formation of ammonium nitrate aloft. Winter data are more limited, but HNO_3 concentrations aloft may be lower during winter than summer. This data can be analyzed in greater detail for individual flights to gain further insights. The source of aloft organic carbon, either primary or secondary, is currently unknown.

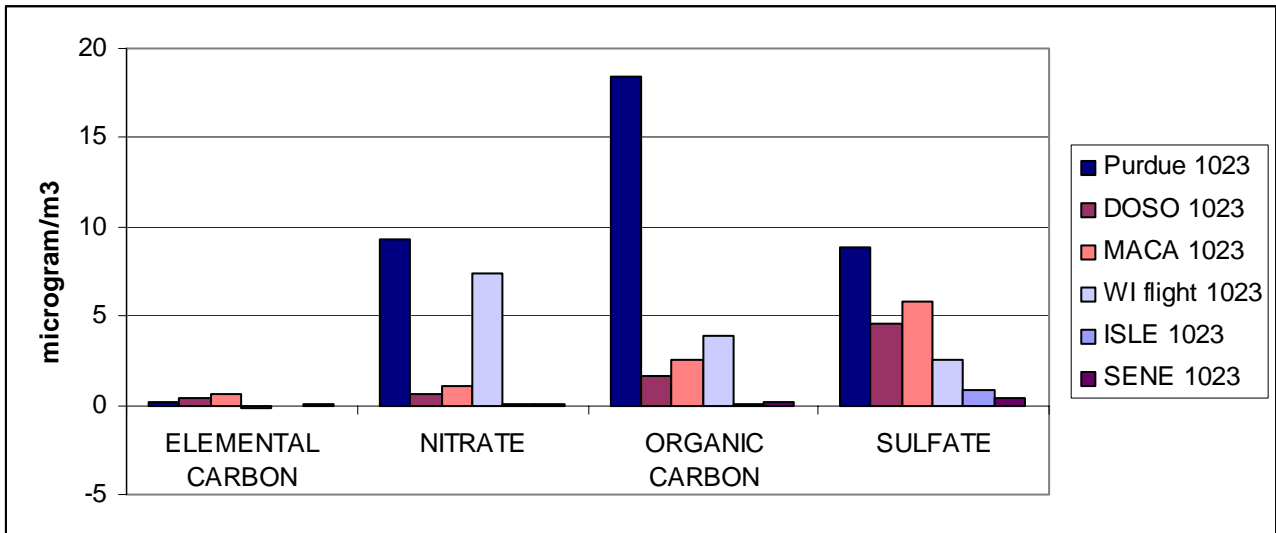
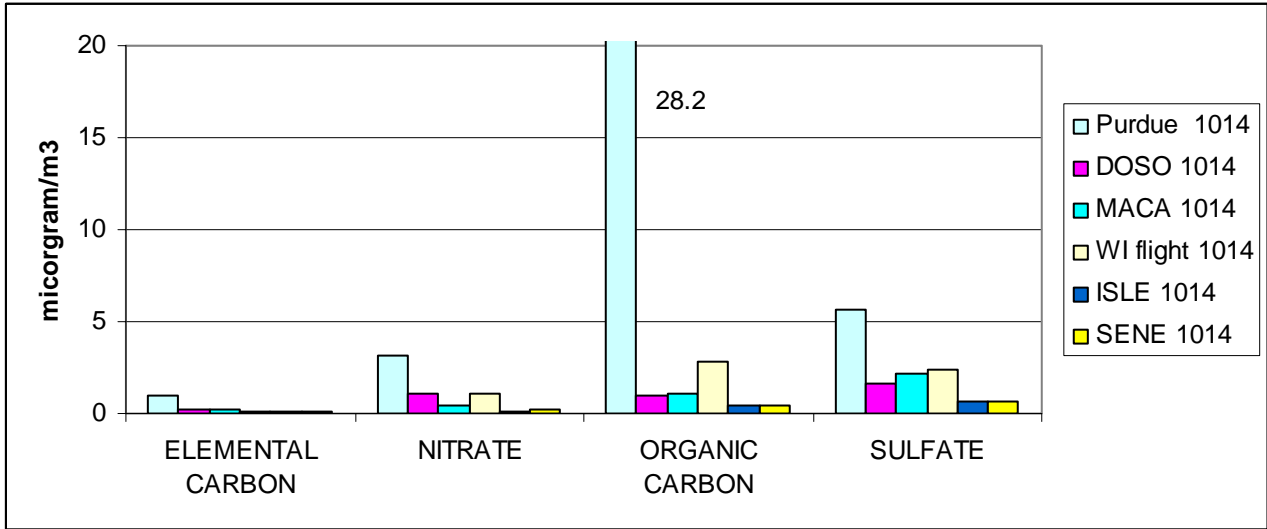


Figure 5-6. Measured concentrations of elemental carbon, nitrate, organic carbon, and sulfate for the Purdue and Wisconsin flights flying regional patterns and related surface concentrations at 4 Class I areas on October 14 and 23, 2003.

6 ANALYSIS OF TRANSPORT PATHWAYS

6.1 Meteorological analyses by STI

During 2003, staff at Sonoma Technology, Inc. (STI) in Petaluma, CA prepared six reports for the EPA that document high PM_{2.5} episodes in 2003. These reports focus on episodes in the Midwest and Great Lakes regions. While they do not address haze and reduced visibility directly, the meteorological conditions that contribute to high PM_{2.5} and ozone episodes are strongly correlated with poor visibility and overall air quality. Therefore, a summary of STI's findings is given below to shed more light on (1) the source regions that contribute to overall poor air quality in the Great Lakes region (and reduced visibility, by association) and (2) the regional meteorological conditions that contribute to episodes of poor air quality.

Each of STI's six reports summarizes one multi-day episode of poor air quality in the Midwest and Great Lakes regions. Each episode is 3-7 days in length, and the episodes occur during February-August 2003. In the reports, air quality is determined from observed PM_{2.5} concentrations and the daily 24-hr PM_{2.5} Air Quality Index (AQI) at about 50 stations throughout the Midwest and Great Lakes regions. The AQI is a categorization of 24-hr PM_{2.5} concentration ($\mu\text{g m}^{-3}$) into five levels: good, moderate, unsafe for sensitive groups (USG), unhealthy and very unhealthy. Each episode usually begins with good air quality throughout the Midwest followed by one or more days of degrading air quality. Air quality levels at their worst in each episode are typically moderate to USG for most cities, with a few cities showing unhealthy levels. The episodes end with one day of good air quality, usually after a significant change in the meteorology that clears the region of polluted air. The reports use a variety of meteorological data to describe the evolution of each episode, one day at a time.

Although the PM_{2.5} observations are concentrated around densely populated areas, the time and spatial scales of air transport in the Midwest and Great Lakes regions imply that even Class I wilderness areas would experience episodes of air pollution on many of the same days. The effect on Class I area air quality should be moderated however. Urban areas have additional sources of PM_{2.5} (e.g., cars, industry), so the build up of pollutants during a several day period

can be more severe than in remote Class I areas. However, stagnated atmospheric flow will generally increase particulate matter and reduce visibility and air quality, whether in urban or Class I areas. In cases where the transport of pollutants is significant (discussed below), the air quality in Class I areas will also bear the effects of the non-local pollutants.

The STI reports, taken together, bring out some themes and trends that are applicable to visibility concerns in the Great Lakes region.

- Stable atmospheric conditions (i.e., surface high pressure) stagnate the flow and trap pollutants and their transport within the boundary layer.
- Surface temperature inversions inhibit vertical mixing and concentrate pollutants within the boundary layer.
- Winds, even light winds, from a predominately southerly direction generally transport warmer, more polluted air into the region. Transport of polluted air can occur by winds within the surface layer. Polluted air may also be carried aloft over longer distances and gradually brought down to the surface layer (over a period of days) by generally sinking conditions in the atmosphere.
- Stationary fronts are particularly effective at concentrating pollutants on the warm (usually south) side of the front.
- Any process which increases vertical mixing, whether local convection (small-scale) or large-scale upward motion from an approaching synoptic weather system will ventilate the boundary layer and reduce pollutant concentrations.
- Clearing a region of pollutants is generally a complete process where a wholesale change of air masses occurs in a matter of hours, whereas pollutant buildup and degrading air quality often occurs gradually over the course of several days.

In our previous analysis, we suggested that transport from as far away as Colorado could contribute to poor air quality in the upper Midwest. The STI reports do not refute this finding, but do not directly support it either. The day-by-day narrative format of their reports does not allow direct evaluation of the effects of multi-day transport. But given the slow evolution of weather systems that accompany episodes of poor air quality and the repeated patterns of daily transport present in their reports, long-range transport seems very plausible. Further, their reports show that in addition to transport from the southwest (e.g., Colorado and Iowa) suggested in our previous analysis, transport from the south and southeast are also likely to carry more polluted air.

6.2 Additional analyses

Using visibility observations at three sites in the Great Lakes region (Boundary Waters-BOWA, Seney-SENE and Isle Royale-ISLE), clear and hazy cases have been identified during the period Dec 1999-Apr 2003. Two of the hazy cases from the most recent 1.5 years of the record of visibility observations are presented below. On 25 June 2002, PM concentrations at SENE, ISLE, and BOWA were 24.0, 9.9, and 10.1 $\mu\text{g}/\text{m}^3$, respectively. On 1 March 2003, PM concentrations at SENE, ISLE, and BOWA were 22.2, 15.2, and 7.2 $\mu\text{g}/\text{m}^3$, respectively.

- **Case of June 25, 2002**

Figure 6-1 shows two surface analyses, including fronts and precipitation, for the evening before June 25th (upper panel) and the morning of June 25th (lower panel). These times were chosen to show the meteorological conditions in the 12 hours preceding the day with poor visibility.

Notice that a stationary front (wavy front with alternating blue & red line segments) is draped across the Great Lakes region and continues into the mid-Atlantic states. The front originates at a weak center of low pressure over Minnesota's Canadian border. This stationary front moves little over the Great Lakes in the 12 hours preceding Jun 25th, only sliding to the north a few tens of miles. The associated low pressure system is weak and moving slowly, and

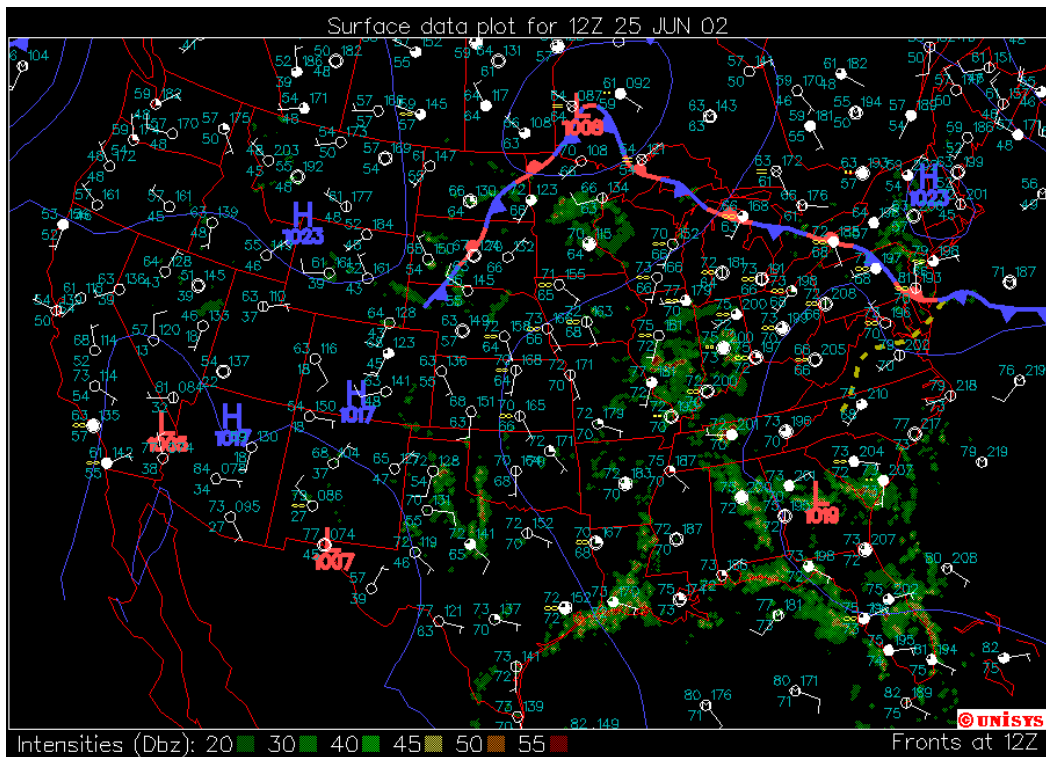
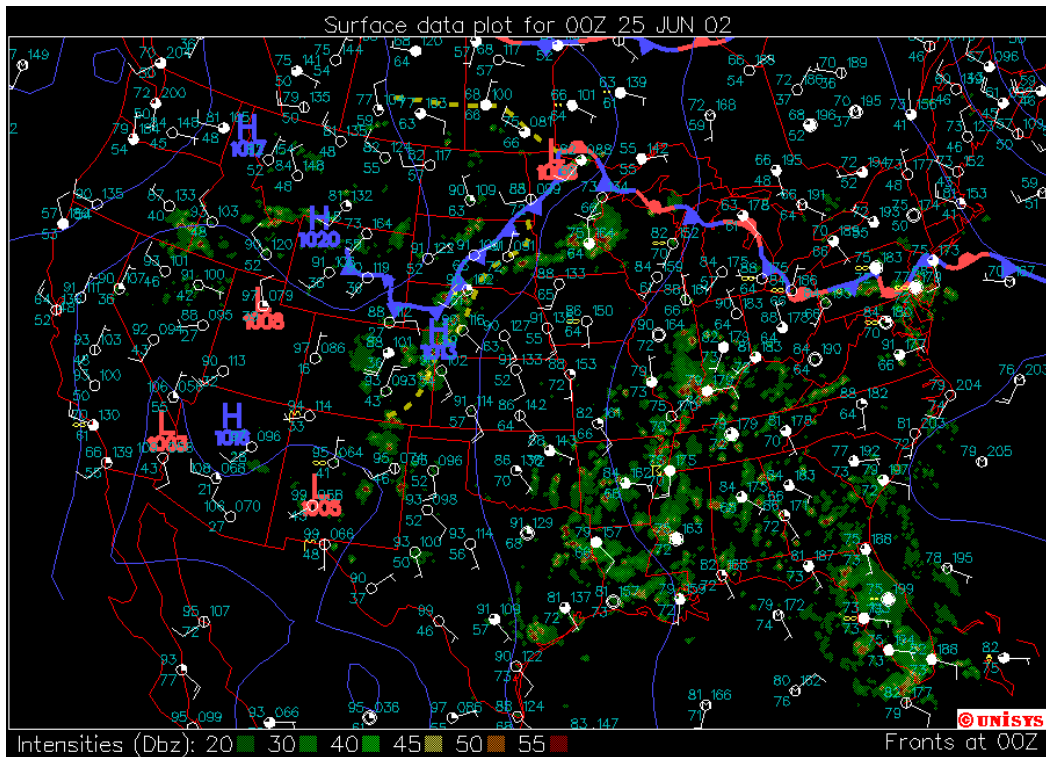


Figure 6-1. Surface analyses for 0000 UTC June 25, 2003 (7:00 p.m. CDT June 24) (top) and 1200 UTC June 25, 2003 (7:00 a.m. June 25, 2003) (bottom) (source:<http://weather.unisys.com>).

the weak cyclonic circulation gradually but steadily transports polluted air from the states south of the Great Lakes to the north. Converging winds on either side of the stationary front make the front a locus along which polluted air can be concentrated.

Figure 6-2 shows the corresponding upper air meteorological analysis for the dates in Figure 6-1. The upper air charts show typical summertime conditions: weak gradients and slow moving features. The flow at 850 hPa (about 1.5 km AGL) over the Midwest region is controlled by a high pressure system over the East coast. Transport during the 12 hours preceding the 25th and during the 25th (not shown) is mostly from the south and southwest, and is generally sinking gradually (influence of high pressure). All of these elements conspire to concentrate pollutants around the stationary front for an extended period (i.e., more than 24 hours).

- **Case of March 1, 2003**

Figure 6-3 shows two surface analyses, including fronts and precipitation, for the evening of February 27th (upper panel) and the morning of February 28th (lower panel). The depicted conditions are representative of the meteorological conditions for the 3-day period between February 27 and March 1. The slow moving patterns contribute to a significant build up of pollutants seen on March 1.

As in the previous case, a stationary front is present over the Great Lakes region. The front rests in a weak and extended trough of surface low pressure oriented roughly southwest to northeast. This weak trough is embedded in a larger high pressure system whose center is just north of the Canadian boarder and which is advancing slowly to the south. The combination of a weak trough of low pressure (read “converging winds”) embedded in a larger environment of high pressure (read “sinking air” and “capped boundary layer”) provides an excellent environment in which to concentrate pollutants in the trough. In the two days preceding March 1st (not shown), surface winds from the south and southeast transported pollutants into the upper Midwest. The subsequent formation of a stationary front embedded within a high pressure system provided the means to concentrate these plus other local pollutants. The upper air charts

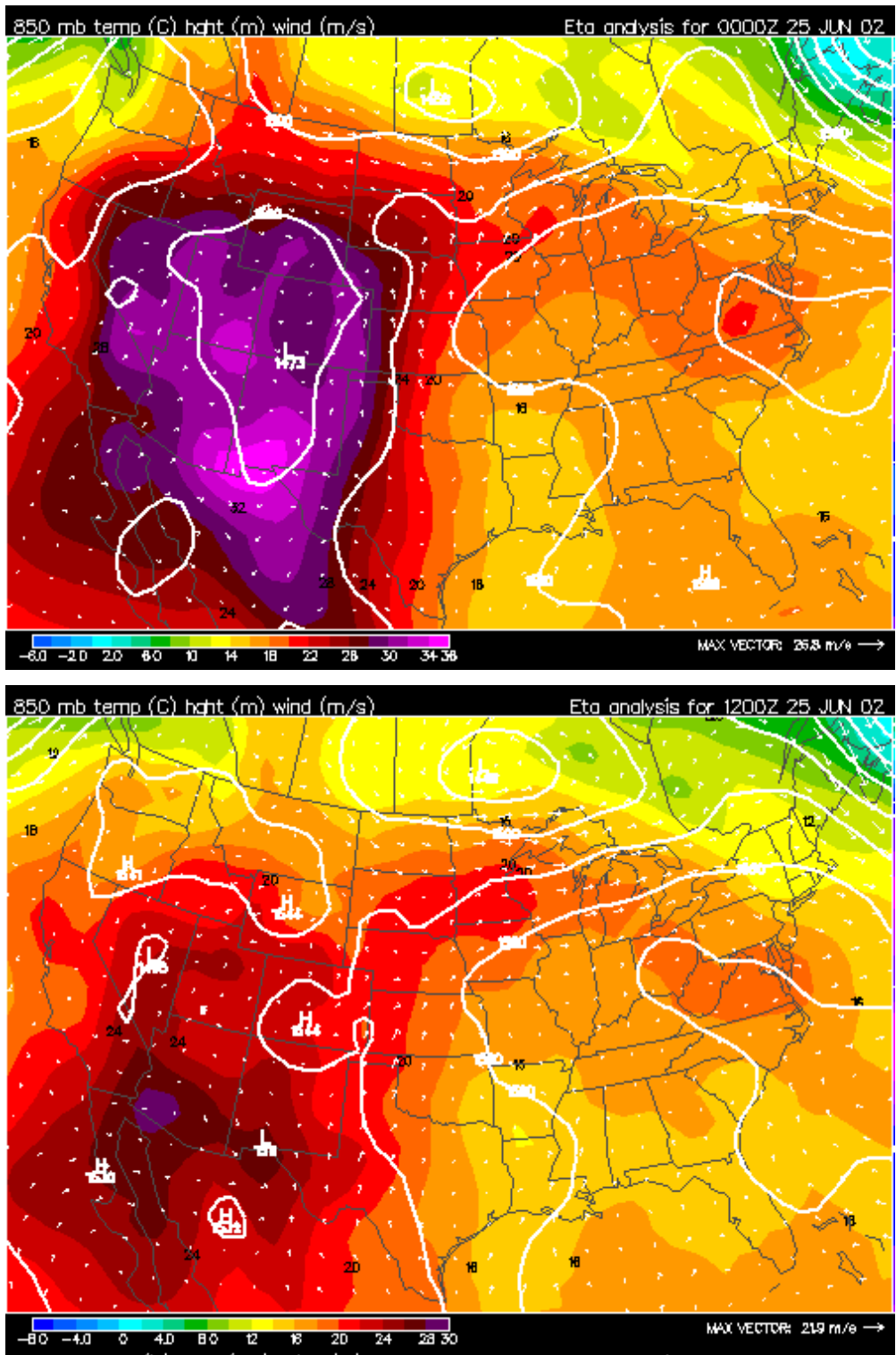


Figure 6-2. Upper air charts (850 hPa) for 0000 UTC June 25, 2003 (7:00 p.m. CDT June 24) (top) and 1200 UTC June 25, 2003 (7:00 a.m. June 25, 2003) (bottom) (source:<http://weather.unisys.com>).

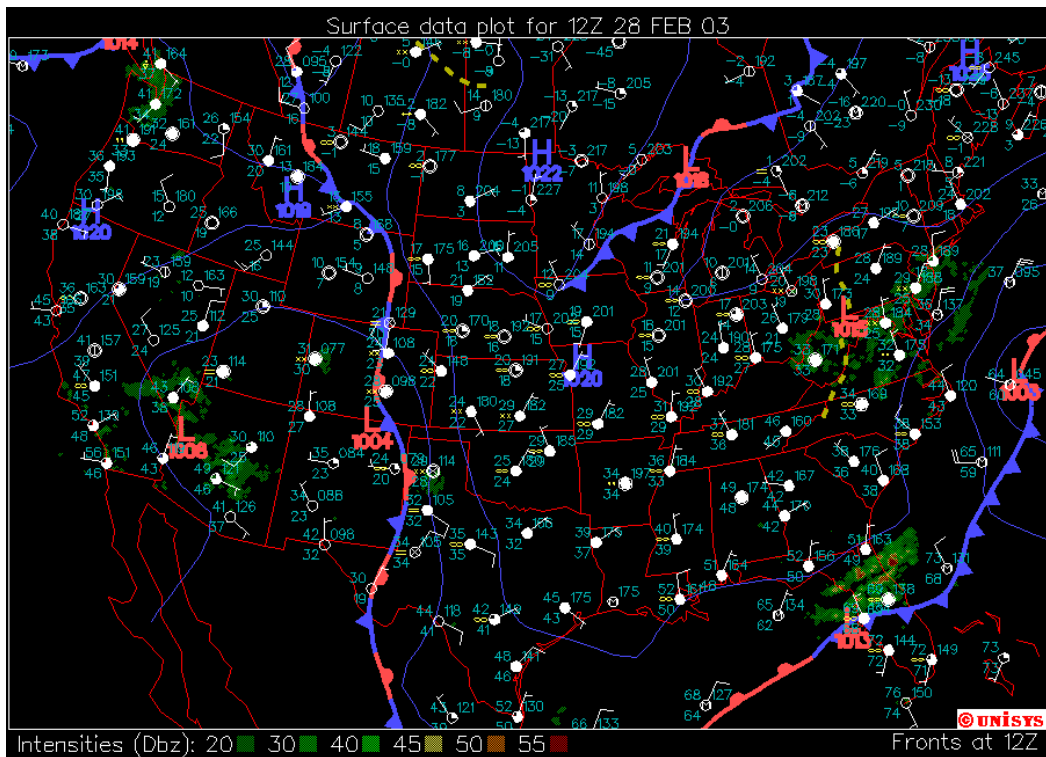
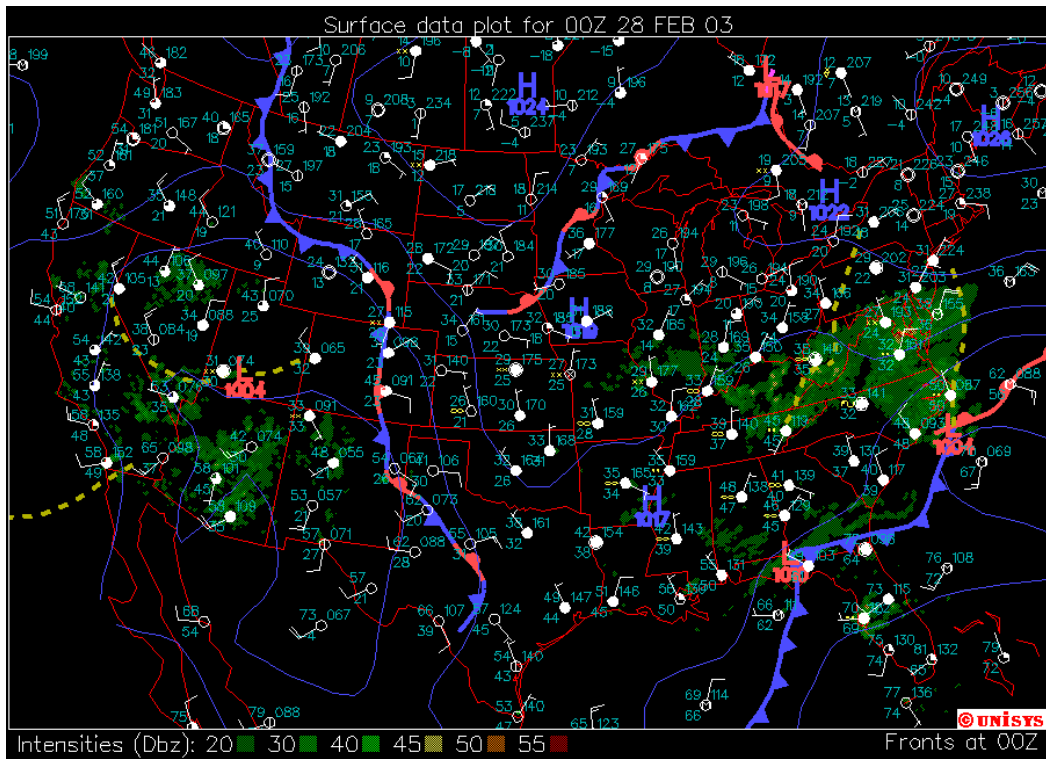


Figure 6-3. Surface analyses for 0000 UTC February 28, 2003 (6:00 p.m. CST February 27) (top) and 1200 UTC February 28, 2003 (6:00 a.m. February 28, 2003) (bottom) (source:<http://weather.unisys.com>).

(Figure 6-4) do not show any meaningful transport at upper levels. As in the first case, the fields are generally flat over the upper Midwest and features are moving slowly.

While the June 25th case shows transport of pollutants more clearly than the March 1st case, both cases provide evidence that long-range pollutant transport contributes to hazy conditions in the Great Lakes region. These cases confirm that the findings of the STI reports are generally applicable to the Great Lakes region Class I. The magnitude of pollutant levels in the Great Lakes Class I areas are likely to be lower than those reported for the urban areas in the STI reports. Nonetheless, the meteorological mechanisms and time scales shown in the STI reports are very well reflected in hazy episodes observed in Class I areas of the Great Lakes.

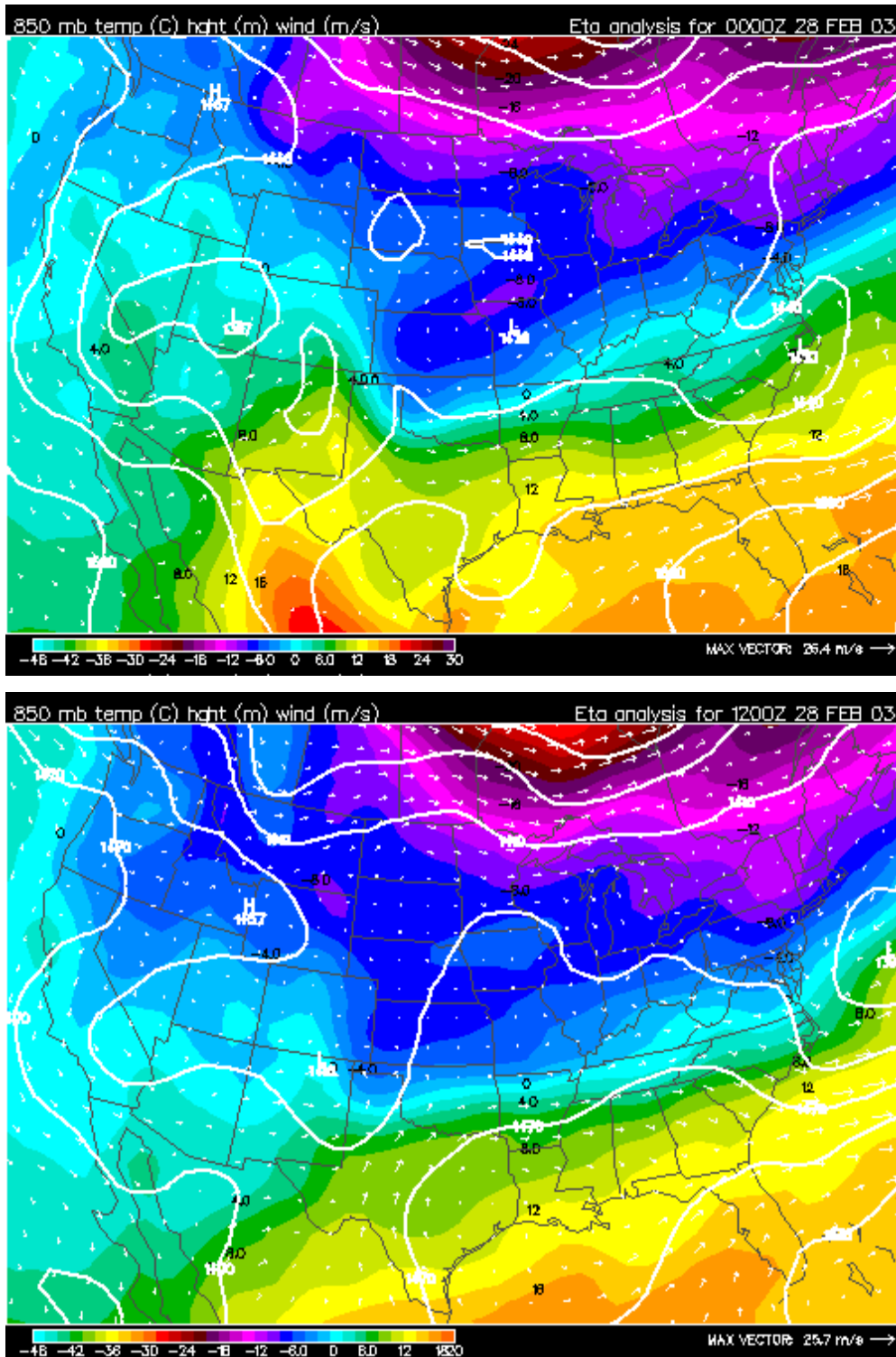


Figure 6-4. Upper air charts (850 hPa) for 0000 UTC February 28, 2003 (6:00 p.m. CST February 27) (top) and 1200 UTC February 28, 2003 (6:00 a.m. February 28, 2003) (bottom) (source:<http://weather.unisys.com>).

7. URBAN EXCESS

The February 2004 report by LADCO concluded that sulfate tends to be regionally distributed whereas nitrate (especially winter) and organic compounds (winter and summer) tend to be more prevalent at urban sites in Chicago, Cincinnati, Cleveland, Detroit, Gary, Indiana, Milwaukee, and St. Louis than at surrounding rural sites. A case study was performed for Indianapolis, IN. The speciation site 180970078 at Washington Park was used to determine the representative urban concentrations. Another speciation site in Henry County, 180650003, with rural designation, is located 30 miles East-North-East of Indianapolis. Two IMPROVE sites, Bondville (BOND) and Livonia (LIVO) are located 120 miles West and 90 miles South of Indianapolis, respectively. Concentrations at Washington Park were compared with those at rural sites on days with valid data at the sites considered.

The rural site at Henry County came on line early 2002. Considering the two speciation sites using data from 2002 and 2003, the mean difference of sulfate, nitrate, ammonium, OC, and EC are 0.12, -0.02, 0.05, 1.12, and 0.25 $\mu\text{g}/\text{m}^3$, respectively (Table 7-1). Therefore, organic carbon shows the most significant excess at the urban site, followed by elemental (black) carbon, while the inorganic components do not show a significant urban excess on average.

The average difference between the urban and rural sites for summer and winter are contrasted in Table 7-1. For sulfate, the difference between urban and rural sites is higher in the winter, with a difference of 0.3 $\mu\text{g}/\text{m}^3$ relative to an urban concentration of 3.8 $\mu\text{g}/\text{m}^3$ on average, than in summer. Otherwise, the urban excess is not significant for this component. Nitrate shows an interesting trend. During summer, the urban area records less nitrate (1.8 $\mu\text{g}/\text{m}^3$) than the rural area (2.6 $\mu\text{g}/\text{m}^3$). This may be due to the rural site's location, which may be downwind of the urban area. The higher summer concentration at the rural site is the result of photochemistry of urban emissions. In this case, the locally produced nitrate enters the particulate phase when it reacts with ammonia, which seems to be available during summer near Indianapolis. Accordingly, ammonium is also higher at the rural site. Organic and black carbon both show higher urban excess in summer than in winter at this site; a similar observation was made for organic carbon in the LADCO report.

Table 7-1. Average differences ($\mu\text{g}/\text{m}^3$) between urban Indianapolis and nearby rural speciation site for summer, winter, and all seasons for several PM components.

Species	Summer (% of urban concentrations)	Winter (% of urban concentrations)	All seasons (% of urban concentrations)
Sulfate	-0.17 (-4%)	0.30 (8%)	0.12 (0.3%)
Nitrate	-0.64 (-41%)	0.45 (10%)	-0.02 (-0.9%)
Ammonium	-0.28 (-11%)	0.22 (11%)	0.05 (2%)
Organic carbon	1.37 (25%)	1.06 (27%)	1.12 (26%)
Black carbon	0.32 (47%)	0.22 (36%)	0.25 (41%)

Carbon measurement procedures at speciation monitors and IMPROVE monitors differ in their distinction between elemental (black) and organic carbon. Therefore, a direct comparison between the speciation site in Indianapolis and the surrounding IMPROVE sites cannot be made for organic and black carbon. Total carbon is more comparable between the two networks, despite unresolved differences in their blank correction procedures. Ammonium measurements are not taken at IMPROVE sites. A comparison of sulfate, nitrate and total carbon is presented in Table 7-2.

The urban excess of sulfate in this analysis may be confounded by the overall gradients of sulfate, which are fairly significant S-N direction in the summer near Indianapolis and in the E-W direction for the annual data and the summer data (see Figure 7-1).

The maximum nitrate difference is observed in winter at both IMPROVE sites. During winter, urban areas seem to record higher nitrate than the surrounding rural areas (see Figure 7-2). Of the three rural sites considered here, Livonia is located to the South of Indianapolis and the urban-rural difference may be confounded by a regional gradient in the same direction. Therefore, the best estimate of the urban excess for winter nitrate is 0.5 (Henry County) to 0.75 (Bondville) $\mu\text{g}/\text{m}^3$. Unlike the speciation site at Cook County, the IMPROVE sites are far enough removed from Indianapolis to be less impacted by the photochemistry of urban emissions in summer. Using nitrate concentration data at Bondville and Livonia, summer urban excess at Indianapolis is approximately 0.51 to 0.62 $\mu\text{g}/\text{m}^3$.

The urban excess of total carbon is 3.1 to 3.2 $\mu\text{g}/\text{m}^3$, using IMPROVE sites to estimate rural concentrations. Excess concentrations are observed throughout the year. Speciation data from Washington Park and Cook county (Table 7-1) gives an excess of 1.4 $\mu\text{g}/\text{m}^3$ for total carbon, which is less than half of the estimate obtained using the IMPROVE data. Some difference between these estimates may be due to the lack of blank correction for the speciation monitors and the blank corrected IMPROVE data. This range of values, 1.4 to 3.2 $\mu\text{g}/\text{m}^3$, appears to be a reasonable estimate of the urban excess of total carbon.

Table 7-2. Average differences ($\mu\text{g}/\text{m}^3$) between urban Indianapolis and nearby IMPROVE sites for summer, winter, and all seasons for sulfate, nitrate, and total carbon.

Species	Summer (% of urban concentrations)	Winter (% of urban concentrations)	All seasons (% of urban concentrations)
Sulfate @ BOND (W)	2.00 (26%)	0.59 (20%)	1.21 (25%)
Nitrate @ BOND (W)	0.51 (37%)	0.75 (17%)	0.44 (17%)
Total carbon @ Bond (W)	3.9 (65%)	3.4 (68%)	3.2 (63%)
Sulfate @ LIVO (S)	-0.80 (-10%)	0.30 (11%)	-0.05 (-1%)
Nitrate @ LIVO (S)	0.62 (46%)	1.77 (39%)	1.07 (40%)
Total carbon @ LIVO (S)	3.6 (60%)	3.1 (63%)	3.1 (60%)

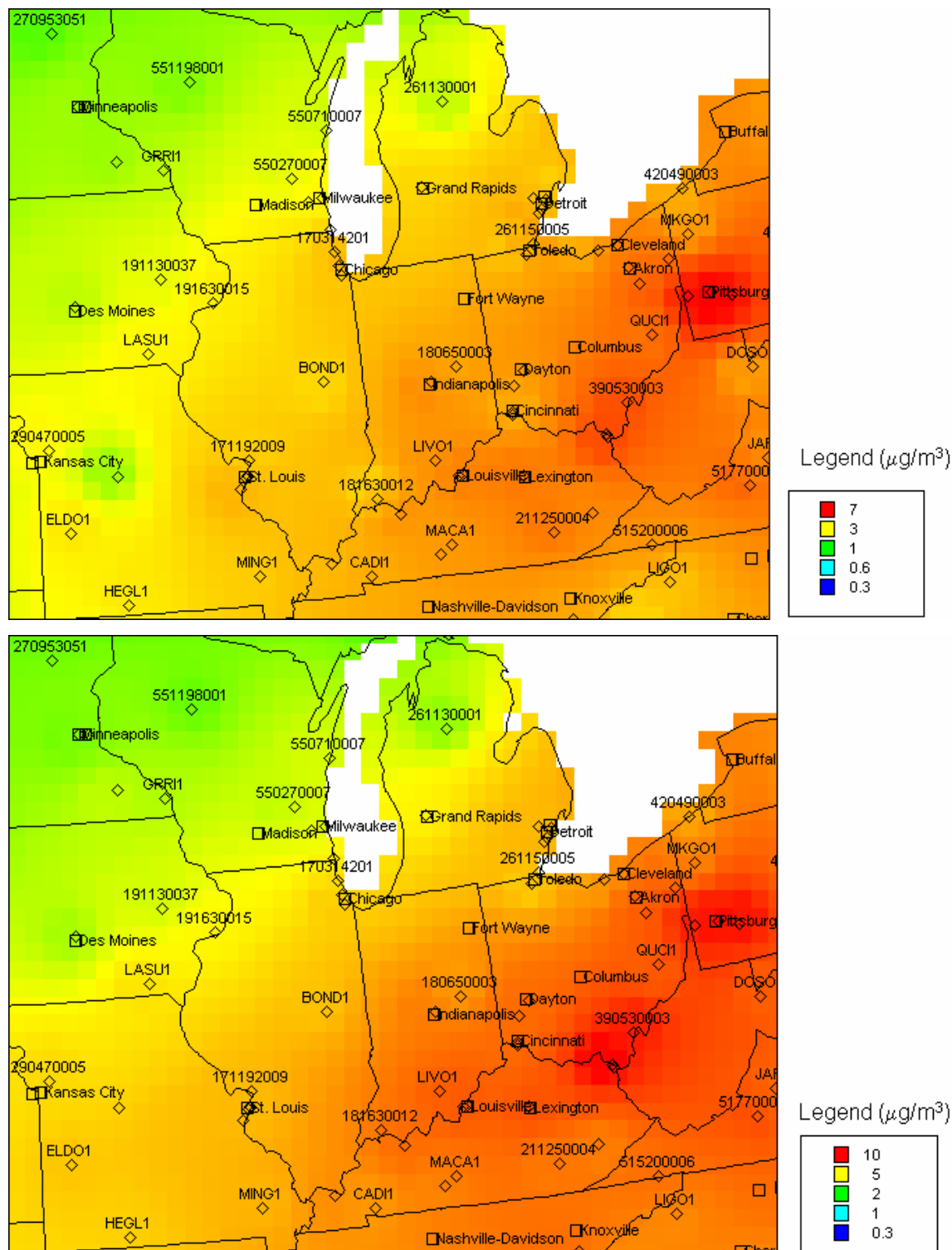


Figure 7-1. Sulfate gradients around Indianapolis: all data (top), summer data (bottom).

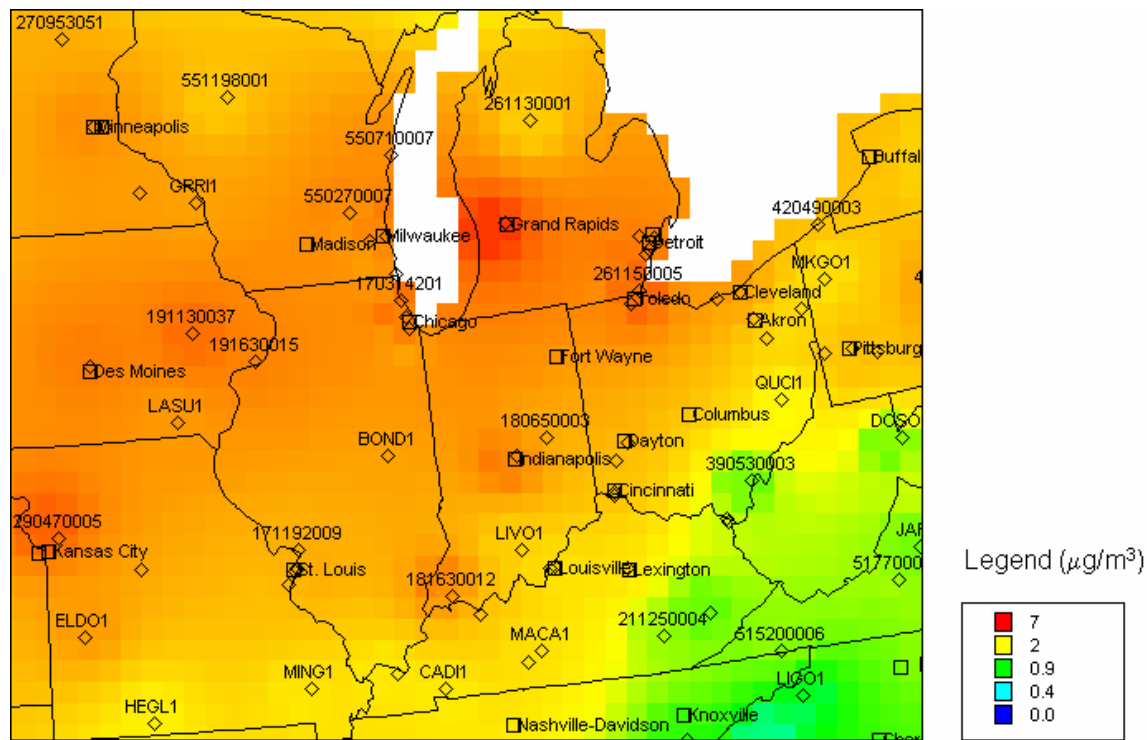


Figure 7-2. Nitrate gradients around Indianapolis during winter.

8. UPDATES TO CONCEPTUAL MODEL

8.1 PM composition

A clear understanding of the PM composition as a function of season is emerging from the recent IMPROVE data collected at the Upper Midwest Class I areas. Seney Wilderness Area and Isle Royale National Park share some PM characteristics with Boundary Waters Canoe Area. The contributions of sulfate and organic matter are significant throughout the year, especially in the summer. Nitrate represents a solid contributor, especially in winter. The annual concentrations of sulfate and nitrate at the Class I areas in Michigan are higher than those at the Minnesota site. The Michigan Class I areas also show a stronger PM seasonal cycle than the Minnesota site, resulting from a stronger sulfate cycle that peaks in the summer.

8.2 Transport

As a group, the Upper Midwest Class I areas are fairly isolated from other IMPROVE sites South of the Great Lakes in terms of daily concentrations. VOYA, BOWA, ISLE, and SENE all correlate with their neighbors on a daily basis with respect to sulfate and OC. The strongest OC correlation is observed in the between, BOWA and VOYA, and VOYA and ISLE also share a moderate correlation for OC. Sulfate correlations, on the other hand, are stronger among the sites south of the Great Lakes. Monthly correlations indicate that the Upper Midwest Class I areas correlate with a few sites to the South, suggesting long-range transport of sulfate and organic compounds to these sites.

Transport from the South as a source of polluted air is supported by meteorological analyses. While we do not discount longer range transport from as far as CO due to the lifetimes of time particles, areas South of the Great Lakes affect the Upper Midwest Class I areas via both surface and upper air transport. Upper air transport can be a source of inorganic and organic PM at the Upper Midwest Class I areas, judging from aircraft measurements of high concentrations of sulfate, nitrate, and OC aloft.

8.3 Formation of ammonium nitrate

Blanchard and Tanenbaum (2004) found that ammonium nitrate formation is not limited by the availability of ammonia for most samples at times when temperature and humidity favor the condensed phase. Our case studies taken from highest PM samples from several urban areas indicate that ammonium sensitivity is quite prevalent under those conditions. The chemical regime and response of ammonium nitrate to precursors have significant spatial and seasonal variability within the Upper Midwest.

At present, there is no information available to support an analysis regarding the formation pathways of nitric acid.

8.4 Formation of sulfate

Limited speciated PM composition data from Pittsburgh indicate that sulfate is formed from the gas-phase reaction ($\text{SO}_2 + \text{OH}$) and intermittently from aqueous-phase reactions. Decreasing sulfate trends in the past have been correlated with reductions of SO_2 emissions. Non-linearities due to oxidant limitation become less important as SO_2 concentrations decrease because the system tends towards being SO_2 limited. Therefore, future reductions in SO_2 should continue to lead to sulfate reductions.

8.5 Organic compounds

The organic mixture at Seney Wilderness is characterized by a preponderance of biogenic organic compounds during the late spring to early fall months. Anthropogenic sources are more dominant during the colder months based on the alkane Carbon Preference Index calculated from the data of Sheesley and Schauer (2004).

Current estimates of the secondary portion of organic carbon range from 35% to 80%. This estimate is subject to measurement errors in OC, including inconsistent procedures between

networks and measurement artifacts (volatilization as well as adsorption). In many cases, the data do not show an expected seasonal cycle.

Uncertainties regarding OC emissions and SOA formation prevent at this moment the investigation of the chemical regimes associated with the production of secondary OC.

9. RECOMMENDATIONS FOR FUTURE WORK

A clearer conceptual model is emerging based on the analyses of newly acquired air quality data. Nonetheless, a number of knowledge gaps have also evolved during the course of this study. We highlight here some of the recommended measurement and analyses activities that will help address critical questions. LADCO is already pursuing many of these data gathering activities, which should provide good insights when the data set is quality assured and analyzed.

9.1 Top priorities

The lack of closure in the mass balance of PM_{2.5} composition raises significant doubts in the analyses that are conducted using the data in question. Two major issues need to be resolved as soon as possible.

Ammonium-sulfate-nitrate closure. In the analysis of inorganic aerosol components, we encountered a mystery of ion balance. In short, the absence of sufficient cations to balance the measured sulfate and nitrate is a question that needs to be addressed. Before delving into the implications, one possibility that should be carefully investigated is a sampling artifact for ammonium (volatilization of ammonium from alkaline nylon filters that retain nitrate and sulfate better than ammonium). Once we can be assured of the quality of the ammonium data, we should explore the closure of the ion balance. Possibilities include (1) the presence of other cations (besides known soil components, ammonium, and proton), (2) the formation of ammonium nitrate in an environment that contains acidic sulfate (sulfuric acid or ammonium bisulfate), (3) the formation of nitric acid particles, possibly in a high RH environment, including aloft.

A preliminary data set from the LADCO-sponsored continuous ammonium-nitrate sulfate measurements at Bondville suggests that ammonium may be present in concentrations exceeding the concentration of negative charges provided by nitrate and sulfate. At present, there is no obvious explanation for the excess cations, and additional quality assurance may be needed to

confirm the observation. This data set can potentially be used to analyze short time-scale fluctuations of the ionic balance.

Organic mass. Some studies have recommended using multiplier values as high as 2.6 to convert from OC to OM. The conversion factor of 1.4 that is generally used to estimate OM from IMPROVE measurements is almost certainly inappropriate. As a result, the role of OM will increase in importance in the Upper Midwest. Therefore, we recommend measurements of OM composition to determine the most appropriate conversion factor for the Upper Midwest Class I areas.

Differences in the OC/EC methodology of two different networks (speciation vs. IMPROVE) prevent the full exploitation of the data in our analyses. Key questions that need to be addressed include (1) the possibility of sampling evaporative losses of OC, especially for the summer, (2) the possibility of adsorption of organic gases on filters (and the subtraction of back filter measurements for IMPROVE but not for EPA's speciation network), (3) which measurement may be closer to the ambient OC concentrations, and (4) possible ways to correct one or both sets of measurements so that they provide comparable quantities, (5) other methodologies, including continuous measurements.

9.2 Moderate priorities

Soil. Soil is a minor component of PM in the Upper Midwest Class I area; therefore, it is not considered among the most pressing priorities. However, the composition of soil should be explored to help reduce the uncertainties in the composition of PM. Soil also provides a source of cations that interact with anions formed in the atmosphere (see discussion above on inorganic ion closure).

The following measurements and analyses are recommended to study the sources and response of PM components, and should be supported by an accurate characterization of the relative importance of the PM composition.

Sulfate. Measurements of sulfate associated with different particle sizes provide some insights into the origin of sulfate particles. The present analysis is based on one site in Pittsburgh during a limited duration of time. It may be of interest to study the particle size distribution of key aerosol components during different seasons, e.g., sulfate during summer, and at both urban and rural locations within the Midwest RPO. The intermittent formation of sulfate by aqueous-phase chemistry is a hypothesis that can be confirmed using case studies combined with back trajectories and meteorological analyses.

Nitrate. Diurnal variability of total nitrate (gas + particle) should be assessed to determine the chemical pathways for the local formation, if any, of nitrate. The pathway information is important for determining the sensitivity of nitrate to the control of oxidants, if oxidants are the limiting reagent, which is likely for wintertime scenarios. Based on the finding in California where aloft nitrate formation can also take place, information of the diurnal concentrations aloft should also be collected, if feasible. Aloft measurements are available for both nitrate and HNO_3 over Upper Midwest from the Wisconsin aircraft. These measurements represent spatial averages over the duration of one or more flight segments. Additional temporal resolution, including nighttime samples, may be useful for the evaluation of nitrate formation pathways.

Ammonium/Nitrate/Sulfate Interactions (a.k.a Sensitivities). Considering only the ammonium-nitrate-sulfate equilibrium, more co-located measurements are needed for sulfate, nitrate, ammonium, ammonia, and nitric acid to analyze the sensitivities of the thermodynamic equilibrium. Representative rural areas should be a focus of future analyses. The ion chromatography data collected at Bondville and to be collected at Northbrook will provide an excellent opportunity for the sensitivity analyses after the uncertainties of the measurements are better characterized. PM data needed for this analysis should be available from the top priority measurements recommended above to establish mass balance.

Organic Compounds. Current knowledge is incomplete regarding the sources of OC in rural areas. Spatial differences of the annual cycle of OC vs. EC seen in the OC/EC analysis could be explored using ambient measurements at different locations. The source apportionment

analysis performed using the Seney speciated OC data provides some information of the overall trends of sources but does not provide good enough signal-to-noise ratio to draw quantitative conclusions. It is possible that the state-of-the-science organic measurements are insufficient to meet the data needs for a source apportionment based on OC markers. An alternative method based on Principal Component Analysis has been used to decipher the sources of OC based on different groups of OC and EC that evolved at different temperatures (e.g., Kim and Hopke, 2004). Such a method involves the reanalysis of existing data, and should be pursued to corroborate the source apportionment results based on speciated OC data.

More fundamental research may be needed in terms of the differences in biogenic emissions (e.g., terpene composition) and the SOA formation potential of different kinds of forests (e.g., boreal vs. temperate). In addition, information regarding primary biogenic emissions is needed to address the question of primary vs. secondary organic aerosols.

Transport/source areas. The current analysis indicates that areas to the south and southwest of the Great Lakes act as source areas for polluted air mass, especially for sulfate, which is more regionally distributed than PM and OC. Sulfate is most likely formed on a regional scale closer to its source area and transported both at the surface and aloft. This conceptual model can be verified using 3-D modeling studies as well as forward and back trajectory studies on test cases selected for regional modeling.

9.3 Low Priorities

Aircraft data. Aircraft data have a potential to provide significant insights; and analyses of existing data can improve the conceptual model in terms of transport and potential source area. However, we recommend additional aircraft data collection as a low priority until reliable measurements can be made aloft. We were unable to explore the use of aircraft data in detail due to a number of measurement caveats that may be difficult to eliminate at this time. Areas of improvement include particle size cutoff in the aircraft data, coordination of temporal extent measurement (possibly with the use of shorter time-scale monitors at key surface locations). Correcting the data may be possible but will involve additional uncertainties due to assumptions

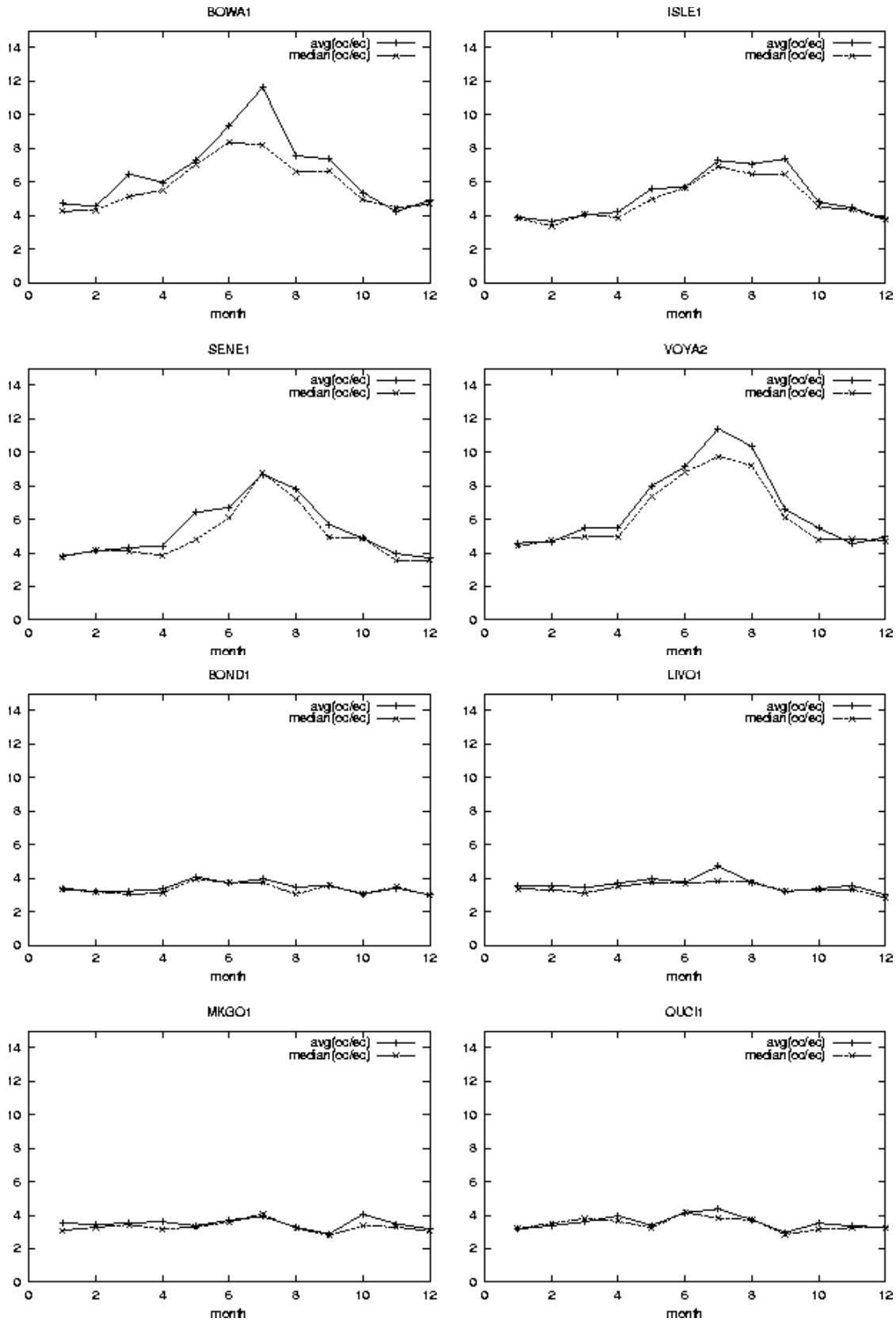
in the distribution of particles. We have not attempted any use of the continuous nephelometer data as surrogate to compare against surface PM data. Some re-thinking of the coordinated collection of aircraft and surface data may be useful in generating a dataset that is more comparable and more meaningful to analyze. There are indications that aloft concentrations may be higher than regional surface concentrations of sulfate, nitrate, and OC. However, such a suspicion cannot be confirmed without data covering the same period of time. Only then can inference be made about the importance of aloft transport on surface concentrations. Once the importance of aloft transport is verified, measurements can be designed to investigate formation processes aloft, including nitrate formation (HNO_3 measurements are already taken on board the Wisconsin aircraft; additional measurements, such as NH_3 , may be applicable).

H_2O_2 . H_2O_2 , together with HNO_3 , serve as indicators for photochemical regimes for oxidants. Measurements of H_2O_2 should be arranged in the case where the formation of sulfate, nitrate, or secondary organic compounds is shown to be sensitive to oxidants.

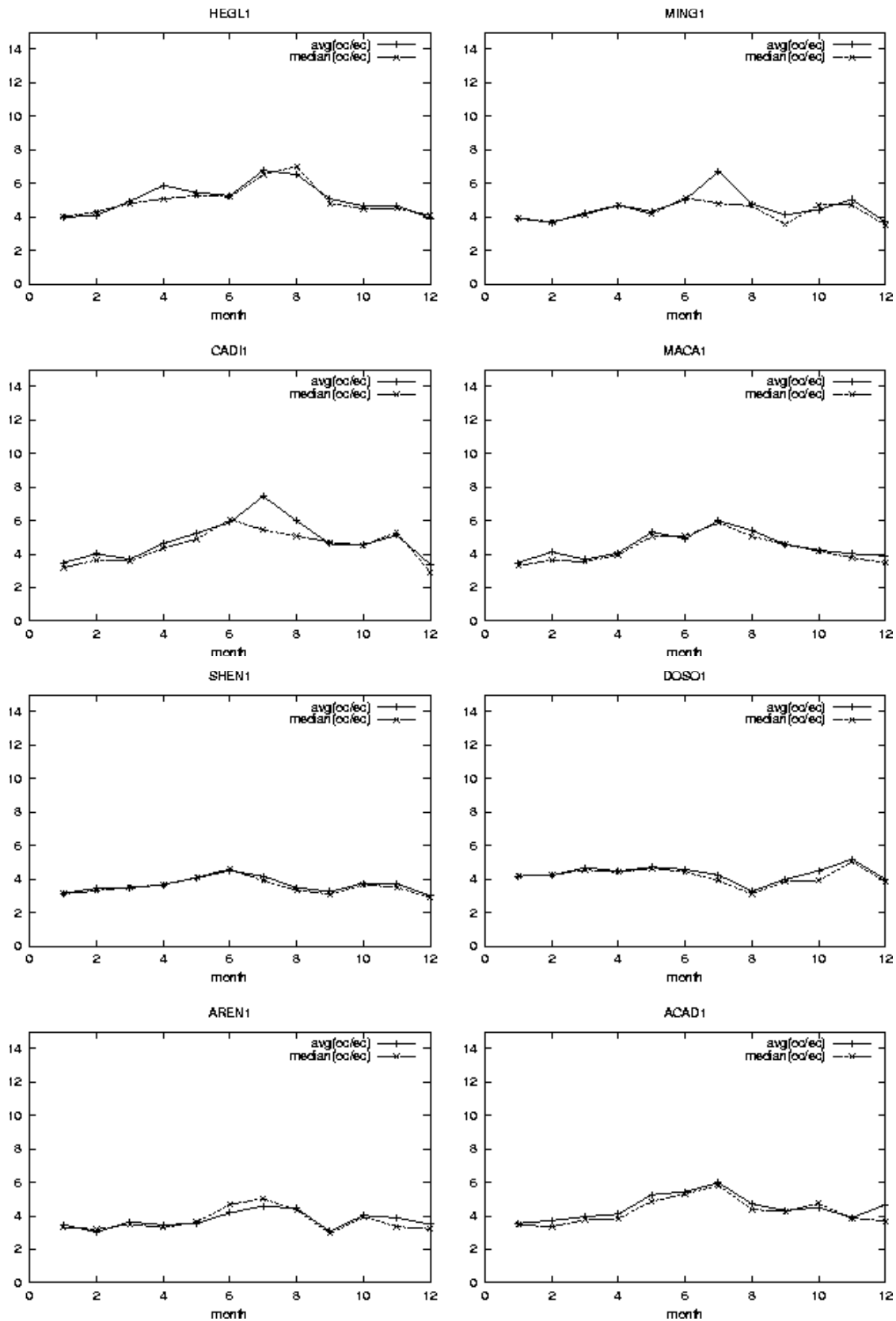
10. REFERENCES

- Ansari, A.S., and S.N. Pandis, 1998. Response of inorganic PM to precursor concentrations, *Environ. Sci. Technol.*, **32**, 2706-2714.
- ARA, 2004. "Analysis of Particulate and Visibility Related Data within the LADCO Region", Report to LADCO.
- Blanchard, C.L S.J. Tanenbaum, 2004. The effects of changes in sulfate, ammonia, and nitric acid on fine PM composition at monitoring sites in Illinois, Indiana, Michigan, Missouri, Ohio, and Wisconsin, 2000-2002, final report to LADCO.
- Brown, S.G., P. Herckes, L. Ashbaugh, M.P. Hannigan, S.M. Kreidenweis and J.L. Collett, 2003. Characterization of organic aerosol present in Big Bend National Park, Texas, *Atmos. Environ.*, **36**, 5807-5818.
- Cahill, T.A., et al., 2002 Analysis of size, time, and compositionally resolved aerosols in Detroit, Michigan, Feb.25 – April 10, 2002
- Chow, J. et al., 2001. Comparison of IMPROVE and NIOSH carbon measurements, *Aerosol Sci. Technol.* 34, 23
- Collett, J.L., T. Lee, X. Yu, B. Ayres, S. Kreidenwies, 2004. Characterizing biases in Speciation Network measurements of fine particle ions concentrations. 97th Annual AWMA Conference and Exhibition, June, 2004, Indianapolis, IN.
- Didyk, B. M., Simoneit, B. R. T., Pezoa, L. A., Riveros, M. L., Flores, A. A., 2000. Urban aerosol particles of Santiago, Chile: organic content and molecular characterization. *Atmos. Environ.*, **34**, 1167-1179.
- Hering, S.V. and S.K. Friedlander, 1982. Origins of sulfur size distributions in the Los Angeles Basin, *Atmos. Environ.*, **16**, 2647-656.
- Kim, E. and P.K. Hopke, 2004. Improving source identification of fine particles in a rural northeastern U.S. area utilizing temperature-resolved carbon fractions, *J. Geophys. Res.*, **109**, doi: 10.1029/2003JD004199.
- LADCO, 2003. "PM_{2.5} in the Upper Midwest", June 2, 2003.
- LADCO, 2004. "PM_{2.5} in Urban Areas in the Upper Midwest", February 12, 2004.

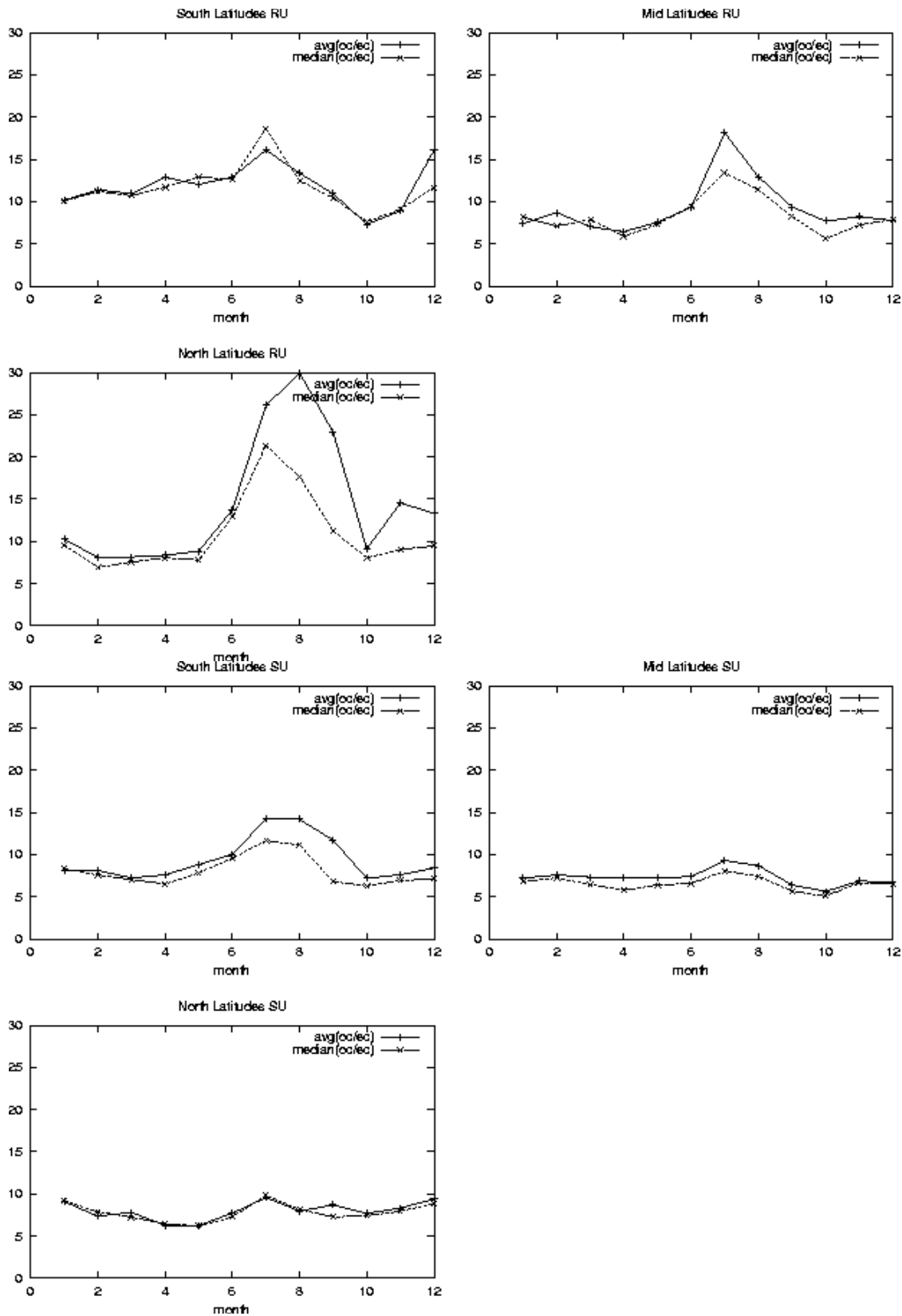
- MACTEC, 2004. "Analysis of Air Quality Data Collected near Tribal Lands in Minnesota, Wisconsin, and Michigan" with addendum "Analysis of Particulate and Visibility-Related Data within the LADCO region", report to LADCO.
- McDade, C., I. Tombach, S. Hering, N. Kriebel, 2000. Analysis and simulation of wintertime light scattering by urban aerosol in Dallas-Fort Worth, *J. Air Waste Manage. Asso.*, **50**, 849-857.
- Pang, Y., N.L. Eatough, J. Wilson, D.E. Eatough, 2002. Effect of semivolatile material on PM_{2.5} measurement by the PM_{2.5} federal reference method sampler at Bakersfield, CA, *Aerosol Sci. Technol.*, **36**, 289-299.
- Park, R.J., D.J. Jacob, M. Chin and R.V. Martin, 2003. Sources of carbonaceous aerosols over the United States and implications for natural visibility, *J. Geophys. Res.*, **108**, 4355, doi:10.1029/2002JD003190.
- Pun, B., C. Seigneur, M. Leidner, P. Karamchandani, S. Roe, R. Strait, K. Thesing, J. Wilson and M. Mullen, 2001. Scoping Study for Regional Haze in the Upper Midwest. Midwest Regional Planning Organization, Des Plaines, IL.
- Rice, J. et al. (2004) STN/IMPROVE Comparison Study, EPA Model Performance Evaluation Workshop, March 2004
- Seigneur, C., B. Pun, K. Lohman and S.-Y. Wu, 2003. Regional modeling of the atmospheric fate and transport of benzene and diesel particles, *Environ. Sci. Technol.*, **37**, 5236-5246.
- Sheesley, R.J. and J.J. Schauer, 2004. Source Apportionment of Atmospheric Fine Particulate Matter Collected at the Seney National Wildlife Refuge, Final Report, LADCO.
- Simoneit, B. R. T., 1978. The organic chemistry of marine sediments. *Chemical Oceanography*, J.P. Riley and R. Chester, eds. New York, Academic Press, **7**, 233-311.
- Simoneit, B. R. T., 1989. Organic matter of the troposphere- V. Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chem.*, **8**, 251-275.
- Turpin, B. and H. Lim, 2001. Species contributions to PM_{2.5} mass concentrations; revisiting common assumptions for estimating organic mass, *Aerosol Sci. Technol.*, **35**, 602-610.



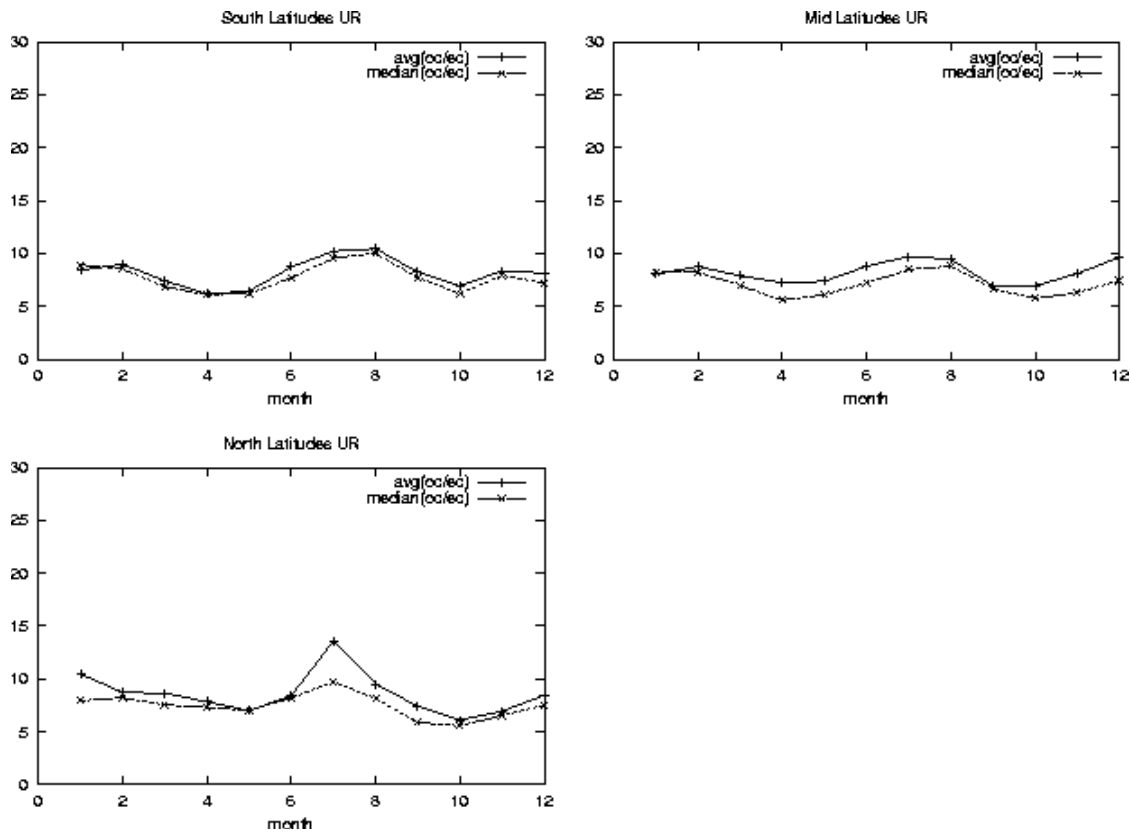
Appendix A. Monthly OC/EC ratios at selected IMPROVE sites.



Appendix A. Monthly OC/EC ratios at selected IMPROVE sites (continued).



Appendix B. Monthly OC/EC ratios at groups of speciation sites (North: latitude ≥ 42.95 ; Mid: $39.77 \leq$ latitude < 42.95 ; South: latitude < 39.77).



Appendix B. Monthly OC/EC ratios at groups of speciation sites (North: latitude ≥ 42.95 ; Mid: $39.77 \leq \text{latitude} < 42.95$; South: latitude < 39.77) (continued).