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MIDWEST URBAN ORGANICS STUDY: LESSONS LEARNED

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Over 60 counties in the Upper Midwest were deemed nonattainment (as of December 17, 2004) for the particulate matter less than 2.5 microns ($PM_{2.5}$) National Ambient Air Quality Standards (NAAQS). The primary goal of the Midwest Urban Organics Study is to understand the sources of organic carbon mass (OM)[1] concentrations in the Upper Midwest based on special measurements (during calendar year 2004) and subsequent data analyses, including source apportionment. Because OM accounts for 25% to 36% of the total $PM_{2.5}$ mass (**Figure 1** shows data, on average, for 2004) in the urban areas studied (i.e., Northbrook, Cincinnati, Indianapolis, Detroit, Cleveland, and St. Louis), identifying the sources of OM is necessary to develop effective $PM_{2.5}$ control strategies.

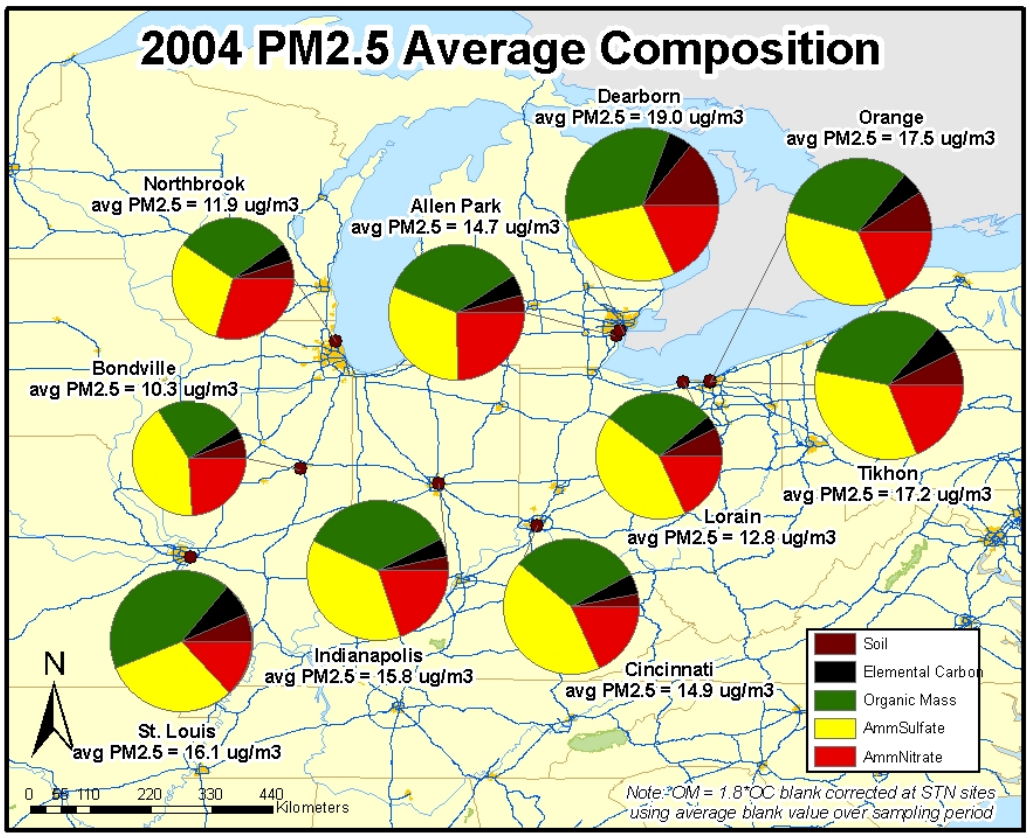


Figure 1. Map of monitoring sites and $PM_{2.5}$ average composition during 2004. OM is calculated as 1.8*OC and is blank-corrected at STN sites using the average blank value over the sampling period. No OM or elemental carbon (EC) was measured at Granite City. Ammonium sulfate, ammonium nitrate, and soil were calculated using standard Interagency Monitoring of Protected Visual Environments (IMPROVE) equations.[2]

[1] OM is defined as 1.8 times the measured organic carbon (OC).
[2] IMPROVE (2004) Overview of IMPROVE and visibility. Available on the Internet at <http://vista.cira.colostate.edu/improve/Overview/Overview.htm> last accessed June 15, 2005.

OM comes from local and regional sources, including gasoline vehicles, diesel vehicles, industrial point sources, wood burning, and biogenic emissions, and consists of a complex mixture of hundreds of compounds. OM is both primary (directly emitted from emissions sources) and secondary (formed in ambient air from emissions of gaseous and semi-volatile precursors) and is, therefore, difficult to predict from emission inventories alone and to apportion among sources. Thus, control strategies are needed for primary OM emissions and for the precursor emissions to secondary OM. The following discussion summarizes the key findings from this study.

1. How do OM concentrations vary spatially?

Urban $PM_{2.5}$ mass and OM concentrations varied among the cities, but the relative composition of $PM_{2.5}$ was very similar from city to city (see Figure 1). The $PM_{2.5}$ mass and OM concentrations at the rural Bondville site were significantly lower than at the urban core sites, indicating that localized influences were important at the urban monitors. The OM concentrations at Bondville were typically 40-60% of the urban concentrations, indicating that local sources of OM are important in urban areas.

- Average $PM_{2.5}$ concentrations varied by up to 60% among the urban sites in 2004 (**Figure 2**). This observed spatial pattern in $PM_{2.5}$ concentrations is consistent with the proximity of the monitors to sources and trends in previous years. Among the sites included in this study, the $PM_{2.5}$ concentrations during 2004 were, on average, 0-4 $\mu g/m^3$ above the NAAQS. The highest annual average $PM_{2.5}$ concentrations in this study were measured at the Dearborn site, which is located in the heart of the Detroit industrial area. The lowest concentrations in 2004 were observed at Northbrook and Lorain (Cleveland).
- At the rural Bondville site, ammonium sulfate and soil concentrations were similar to those observed at urban sites, but OM and ammonium nitrate concentrations were lower. This difference shows the regional nature of ammonium sulfate and soil and the importance of local sources on OM and ammonium nitrate.
- In 2004, OM accounted for 3-7 $\mu g/m^3$ at the cities included in this study (**Figure 3**). OM concentrations were highest (on average, above 5 $\mu g/m^3$) at Dearborn, Allen Park, Indianapolis, St. Louis, and Cleveland (Orange and Tikhon), while OM concentrations at Cincinnati, Northbrook, and Lorain were lower (3-4 $\mu g/m^3$). The highest OM concentrations were observed at the Dearborn site, and the lowest concentrations were observed at the Bondville site. The spatial variability in OM also indicated that local emissions are important. Because OM is a large portion of the $PM_{2.5}$ mass at all the sites, a significant reduction in OM could aid the region in reaching attainment for $PM_{2.5}$.
- Large intra-city variation was also observed in Detroit and Cleveland, where data from multiple monitors were analyzed. Thus, while urban excess is observed when compared to the rural site, local excess driven by local sources is also evident. These inter- and intra-city variations have important implications for control strategy design.

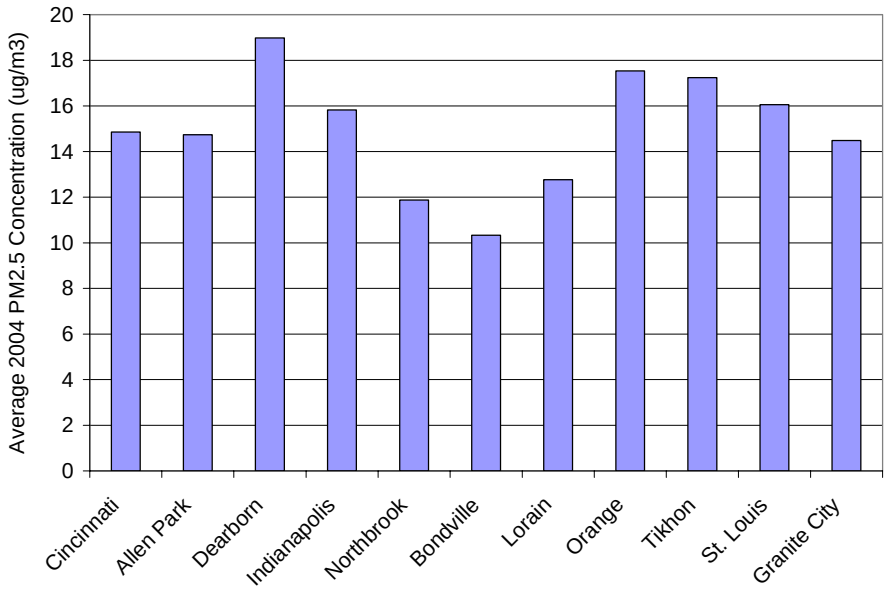


Figure 2. Annual average $PM_{2.5}$ mass concentrations during 2004 at the sites investigated in this study.

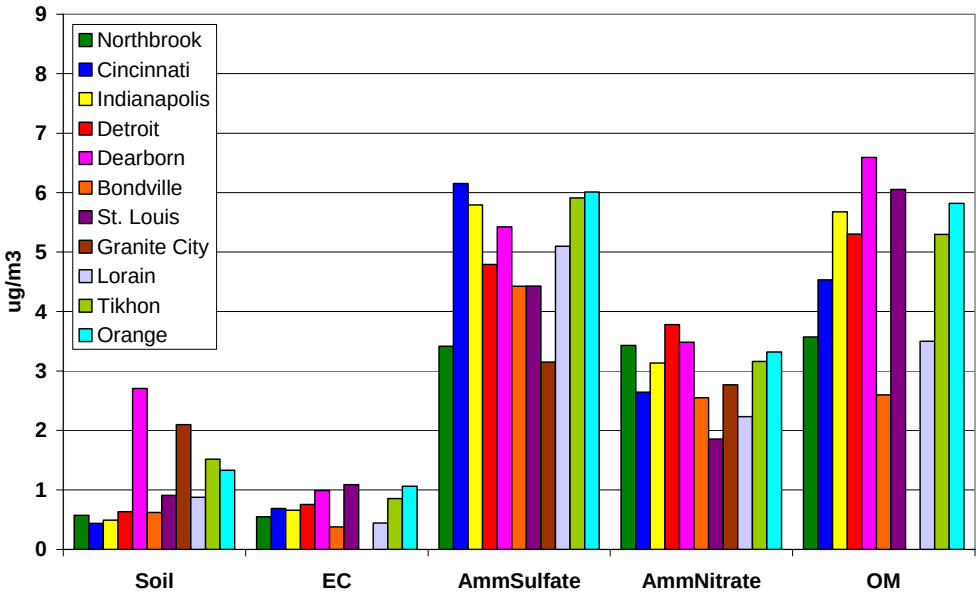


Figure 3. $PM_{2.5}$ composition during 2004 at the sites in this study. OM is blank-corrected at STN sites using the average blank concentration and is calculated as 1.8*OC. No OM or EC was measured at Granite City. Ammonium sulfate, ammonium nitrate, and soil were calculated using standard IMPROVE equations.[3]

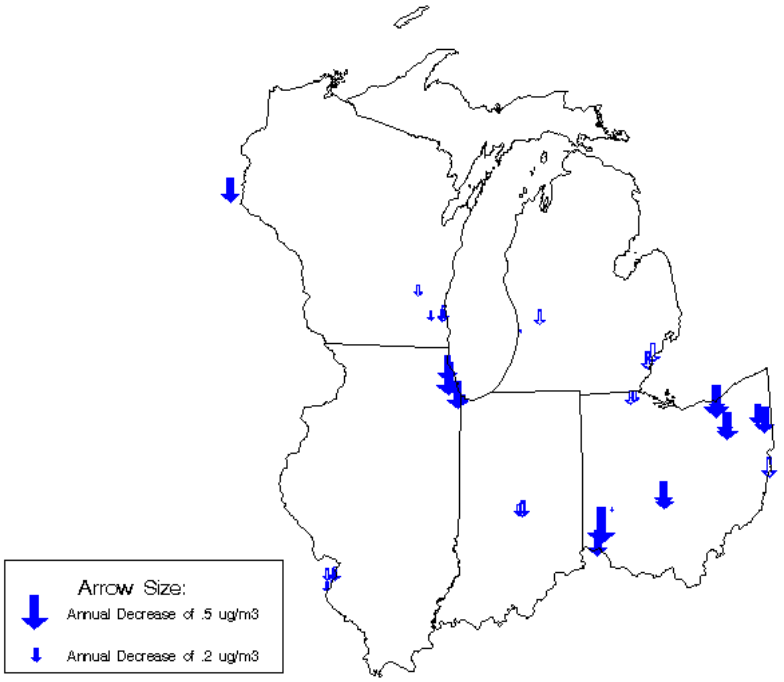
[3] IMPROVE (2004) Overview of IMPROVE and visibility. Available on the Internet at <http://vista.cira.colostate.edu/improve/Overview/Overview.htm> last accessed June 15, 2005.

2. How do OM concentrations vary temporally?

Temporal variations in OM concentrations aid in understanding the sources contributing to OM; this understanding can then be used to select control strategies.

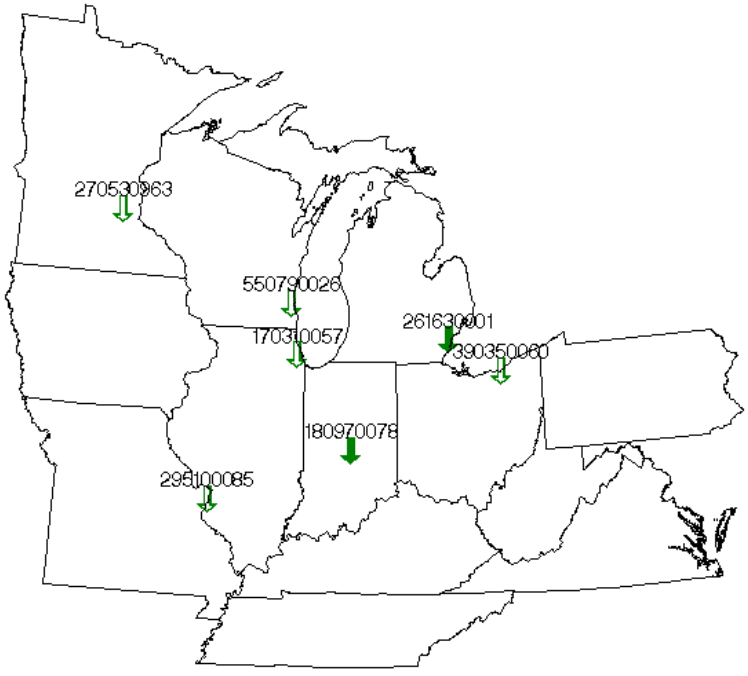
- $PM_{2.5}$ and OM concentrations decreased over the last few years. Trends in Federal Reference Method (FRM) $PM_{2.5}$ and STN OC are shown in **Figure 4**. An example illustrating annual average composition for Indianapolis is shown in **Figure 5**. While concentrations in 2004 were lower, it is likely representative of recent and current conditions, so data from multiple years can be combined, comparisons among sites can be performed, and controls suggested in this study are pertinent to other years.
- OM typically exhibited higher mass during summer (**Figure 6**), indicating that secondary organic aerosol (SOA) is a likely influence of OM. As expected, sulfate concentrations were higher during summer, while nitrate concentrations were higher during winter, which is consistent with formation processes (i.e., sulfur dioxide [SO_2] oxidation to sulfate is enhanced by the hydroxyl radical; nitric acid conversion to particle nitrate is favored in cool conditions). Burning concentrations were generally higher during summer, but not significantly higher. Soil concentrations were also higher during spring and summer and lowest during winter, as expected.
- OM concentrations did not show a significant day-of-week pattern. This is consistent with the importance of gasoline vehicle emissions of OM. Day-specific emission inventories show that on a 24-hr average basis, gasoline-fueled motor vehicles do not typically exhibit strong day-of-week biases. In contrast, EC concentrations typically are significantly lower on weekends than weekdays because diesel-fueled vehicle activity, an important contributor to EC, is significantly reduced on weekends. No day-of-week trends are expected for most large industrial sources, windblown soil, and SOA. Some burning sources, such as agricultural burning and wildfires, are not expected to show day-of-week trends, but residential wood burning may exhibit a day-of-week trend. At Bondville, no day-of-week pattern was observed in any $PM_{2.5}$ component, which is expected for a site mostly impacted by transported material.

(a)



Solid arrows show statistically significant trends, empty arrows show trends that are not statistically significant.
Size of arrow is proportional to magnitude of trend

(b)



Solid arrows show statistically significant trends, empty arrows show trends that are not statistically significant.

Figure 4. Annual trends in (a) FRM $PM_{2.5}$ based on daily (every third day) sampling in 1999-2005 and (b) OC at STN sites.

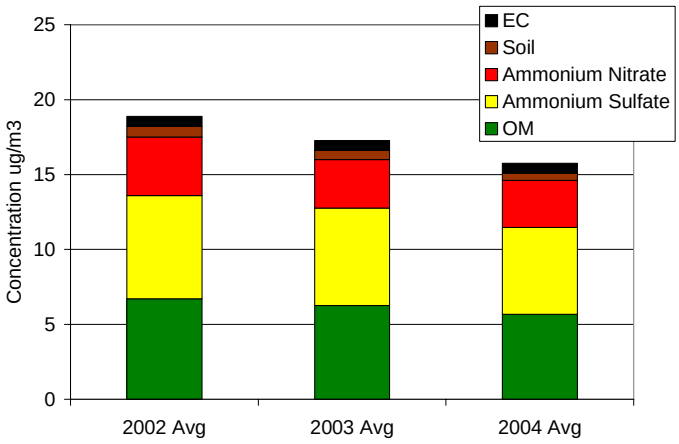
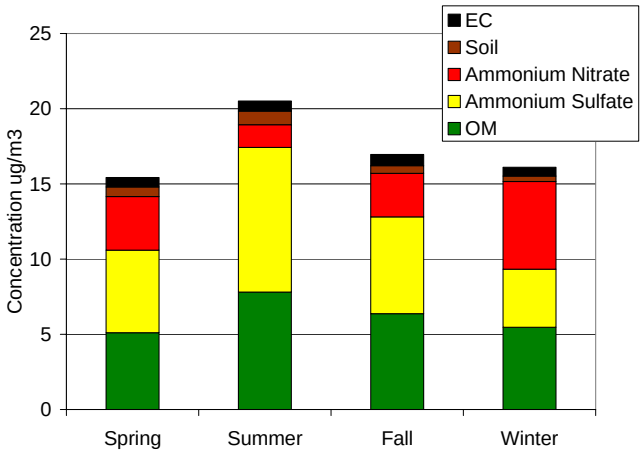


Figure 5. Average composition by year at Indianapolis. Other sites showed a similar trend.

(a)



(b)

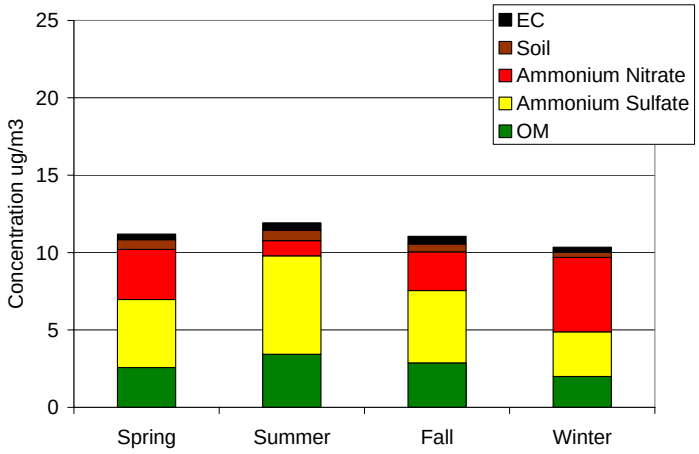


Figure 6. Average seasonal variation in OM and other $PM_{2.5}$ mass components at (a) Indianapolis (2002-2004) and (b) Bondville (2002-2004).

3. What are the major anthropogenic sources of OM? How confident are we in the source attribution?

Several approaches were taken to assess the sources of OM using receptor models. Positive matrix factorization (PMF) was applied to Speciation Trends Network (STN) and IMPROVE data to identify and quantify major and minor sources of $PM_{2.5}$ mass and OM. Chemical mass balance (CMB) was applied to monthly composite samples of speciated organics to better understand mobile source and burning contributions. The largest anthropogenic source of OM was mobile sources. Results are summarized in **Table 1** and **Figure 7**, along with an estimate of confidence in the results.

- Based on the source apportionment approaches considered in this study, the major sources of OM are (1) mobile sources, including on-road and non-road, gasoline and diesel, and smoking (high-emitting) and non-smoking vehicles; (2) burning (both residential wood combustion and wildfires); (3) industrial sources; and (4) SOA. Other sources include soil, vegetative detritus, and construction (Cincinnati only). Contributions from mobile and industrial sources are greater at urban sites than at rural sites. Burning is more important at the rural site than at the urban sites, while secondary OM can constitute up to 30% of the OM at all sites.
- Analysis of the data from sites in Cleveland (Orange, Tikhon, Lorain) and Detroit (Allen Park, Dearborn) showed significant intra-city variation, illustrating the important influence of emissions from local sources on $PM_{2.5}$ and OM.
- Primary local and secondary sources are important to $PM_{2.5}$, although primary local sources, including mobile and industrial sources, are generally more important to OM than transport or secondary sources in the urban areas.

Table 1. Summary of 2004 contributions (percent) to OM by CMB and PMF analyses, average OM (µg/m^3) used in PMF and CMB analyses from STN/IMPROVE and UW, and average OM blank values ± standard deviation for STN and UW OM data. Boldface type and green cells indicate apportionments with the highest confidence, italic type and red cells indicate apportionments with the lowest confidence, and apportionments with regular type and yellow cells designate medium confidence. Ranges represent error estimates based on OM conversion of CMB results and bootstrapping of PMF results.

Source	Analysis	Allen Park	Indianapolis	Cincinnati	Northbrook	St. Louis	Bondville
Mobile	CMB, PMF	**35%-57%**	**33%-64%**	**13%-33%**	**25%-33%**	**48%-68%**	8%-15%
Burning	CMB, PMF	2%-**25%**	2%-**27%**	**12%-17%**[a]	**14%-21%**	**17%-19%**[a]	**10%-44%**
Industrial[b]	PMF	5%-12%	9%-19%	13%-20%	9%-13%	*8%-18%*	*14%-23%*
Secondary	Inferred from CMB, PMF	25%-29%	16%-26%	33%-40%	35%-38%	*10%-18%*	*37%-46%*
Other (soil, detritus, construction, etc.)	CMB, PMF	**2%-5%**	**2%-6%**	**4%-12%**	**1%-7%**	**2%-5%**	2%-22%
OM average (µg/m^3)	STN/IMPROVE for PMF	**5.30**	**5.68**	**4.53**	**3.57**	**6.06**	**2.60**
OM average (µg/m^3)	UW TOT[c] analysis for CMB	**5.35**	**5.25**	**4.85**	**4.43**	**6.65**	**2.81**
OM blank values ± standard deviation (µg/m^3)	STN	**1.67 ± 0.74**	**1.69 ± 0.65**	**2.03 ± 0.36**	**1.85 ± 0.5**	**N/A**	**N/A**
OM blank values ± standard deviation (µg/m^3)	UW TOT analysis	**0.12 ± 0.04**	**0.18 ± 0.10**	**0.14 ± 0.12**	**0.14 ± 0.05**	**0.21 ± 0.13**	**0.12 ± 0.12**

[a] Not identified with PMF; only CMB results are shown.
[b] Industrial does not include OM associated with coal.
[c] TOT = Thermal Optical Transmittance

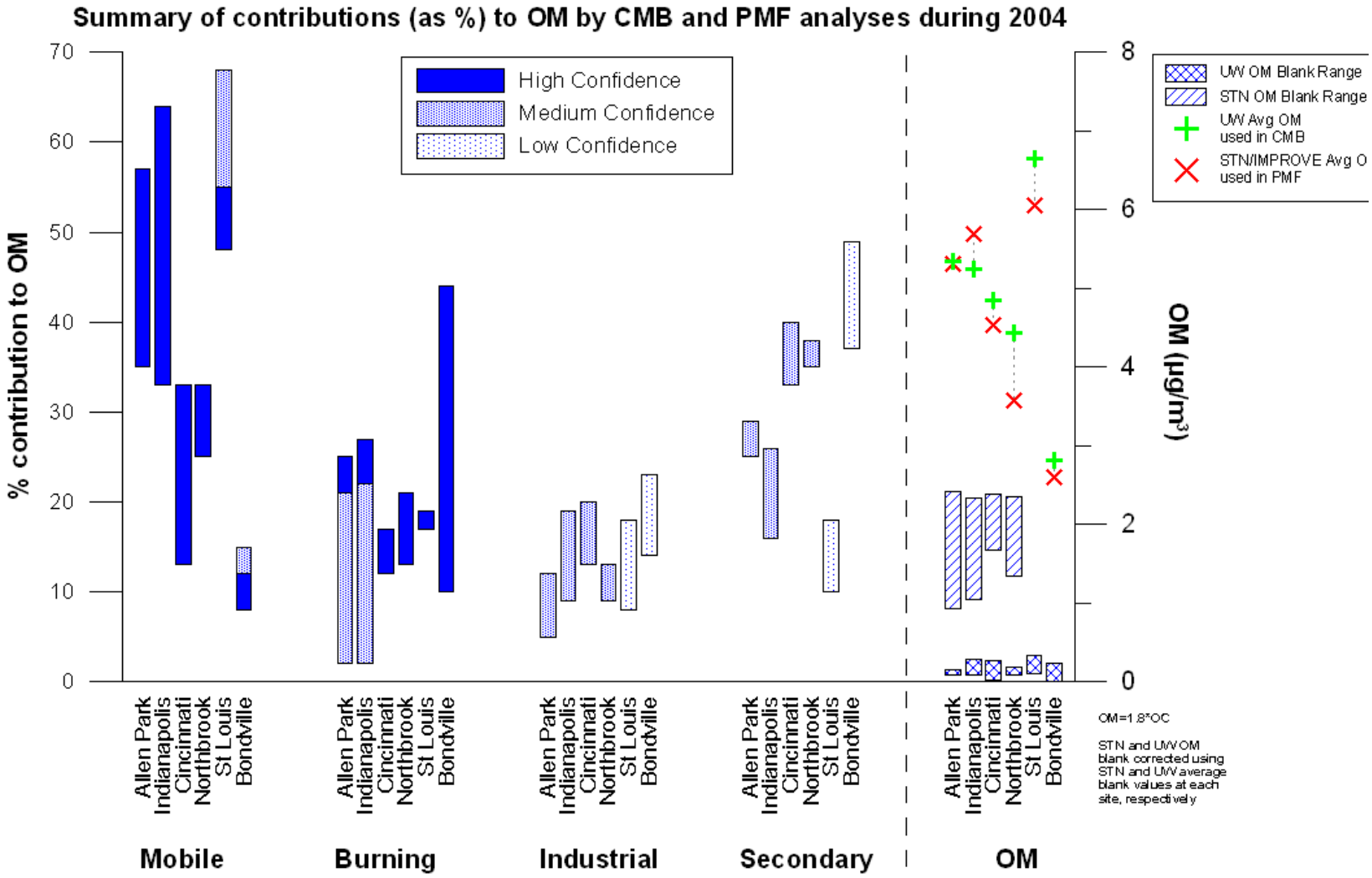


Figure 7. Summary of contributions (percent) to OM by CMB and PMF analyses, average OM (µg/m^3) concentrations from UW and STN data used in CMB and PMF analyses, respectively, and average OM blank values ± standard deviation during 2004. Ranges represent error estimates based on OM conversion of CMB results and bootstrapping of PMF results.

4. What are the regulatory implications of the source attribution findings?

Given the magnitude of OM concentrations (i.e., about 30% of the $PM_{2.5}$ mass on an annual average), state implementation plans (SIPs) for $PM_{2.5}$ should include control programs for OM. However, the lack of understanding of the sources of and control strategies for OM has been a problem. Source apportionment in this study identifies the important OM sources in the region. Although the states should consider possible control programs for these sources, further study and measurements to improve the source identifications and quantification, and to assess the effectiveness of any OM control program, are recommended.

5. What control programs will reduce OM concentrations?

Mobile sources are typically the largest contributors to OM, but are difficult to regulate because many of the regulations need to be applied on a national, rather than regional, scale. Burning is a major portion of the primary $PM_{2.5}$ emission inventory for the Midwest; but while important, burning is typically less than 25% of the OM, on average. Industrial sources, not commonly associated with OM in previous ambient data analyses, were also found to be important contributors to OM, consistent with the emission inventory. Selected control options are discussed by emission category.

Mobile sources

- *Changes in gasoline and/or diesel fuel composition.* This strategy would immediately affect all vehicles in the region that operate on such fuels. Separate analyses have shown that a decrease in OM was observed in Washington, D.C., coincident with implementation of reformulated gasoline (RFG), although a direct link between the fuel change and the ambient OM decline was not established.[4] Additional work on this subject could be conducted to better understand the impact of fuel composition changes in other locations.
- *Additional or modified inspection/maintenance (I/M) programs,* particularly targeting cars more than five years old, especially high-emitting vehicles. Similar to I/M programs that have been implemented in several areas, the objective would be to identify (and repair) vehicles that are likely to have the highest emissions.
- *Diesel retrofit programs,* which would impact both OM and EC as well as air toxics, such as polycyclic aromatic hydrocarbons (PAHs) and diesel particulate matter (DPM). Voluntary programs have been implemented in California and elsewhere and rely on economic incentives for participation. The U.S. Environmental Protection Agency (EPA) is planning controls on PM from diesel vehicles, which may affect OM and EC from diesel emissions.

[4] Brown S.G. and Hafner H.R. (2005) Preliminary study of the impact of past fuel changes on ambient organic carbon concentrations in $PM_{2.5}$. Prepared for the Lake Michigan Air Directors Consortium, Des Plains, IL, by Sonoma Technology, Inc., Petaluma, CA, STI-903520.03-2867, December.

Non-industrial sources

- *Retrofits on residential burning sources*, which would impact both OM and EC during winter (assuming the majority of burning in winter comes from local residential wood burning). However, this strategy would not likely affect burning OM in summer when residential wood burning is minimal.
- *A "no burn-day" program*, which could help reduce high $PM_{2.5}$ concentrations on fall and winter days when burning can account for over 1 $\mu g/m^3$ of the $PM_{2.5}$ mass.
- *Controls on construction equipment and dust*. At Cincinnati, emissions of OM, EC, and dust from large local construction projects accounted for 10% of the total mass and OM. These controls would likely be effective at the Taft St. site in Cincinnati specifically, but may not be as effective at other sites unless nearby construction activity is planned.

Industrial sources

- *Industrial emission controls for PM (and thus OM)*, targeting combustion sources at industrial facilities. OM associated with industrial metals is evident in the ambient data; when more is known about the source profiles, specific controls could be designed. Additionally, the emission inventory indicates that much of the PM in a local area likely originates from a small number of facilities; therefore, these facilities could potentially be the best candidates for additional measures.
- *Development of specific industrial source profiles*. These specific profiles would enable better quantification of specific source influences on OM and air toxics such as PAHs.

Co-benefits from other controls

- Future controls targeting air toxics and/or ozone precursors, such as diesel emission controls and changes in fuel regulations, may also provide a benefit in the reduction of ambient OM concentrations. Further examination of control programs in other areas, such as RFG, could be conducted to better understand if these programs would reduce OM.
- Nitrate is also 25% to 30% of the $PM_{2.5}$ mass and is controllable from NO_x and ammonia reductions. Issues include availability of ammonia and transport of ammonia for local formation versus transport of particulate nitrate, and the emission inventory can be used to better understand the mobile-versus-industrial split of NO_x.

6. How do high $PM_{2.5}$ concentration days compare to average conditions?

In addition to investigating the data on average, a few case studies of high $PM_{2.5}$ concentration days were conducted to investigate potential differences in composition on those days. Typically, the composition on the highest $PM_{2.5}$ concentration days had a higher contribution from ammonium sulfate and/or OM compared to average-condition days. High $PM_{2.5}$ concentrations also occurred during winter at Northbrook and were dominated by ammonium nitrate. Therefore, control measures targeting sulfate, OM, and ammonium nitrate will likely provide the most benefit to reduce high $PM_{2.5}$ concentrations.

7. What are the next steps?

Additional measurements and data analyses are needed to increase certainty in source apportionment analyses, better understand the spatial and temporal trends of sources, and assist policymakers in developing refined control measures. By pursuing additional measurements and analyses to develop a useable long-term data set, the impact of specific regulations can be quantified to ensure accountability. Selected "next steps" follow:

- *Improve temporal resolution of carbon data.* Diesel and burning are important contributors to both $PM_{2.5}$ and air toxics, and source apportionment efforts would be more certain with further understanding of the spatial and diurnal, day-of-week, and seasonal patterns. This understanding can be gained by expanding the use of continuous instruments, such as Aethalometers™, that provide real-time black carbon (BC) data and are being deployed in some urban areas, or other continuous OC and EC measurement alternatives.
- *Improve spatial resolution near key sources.* Local sources, including mobile and industrial sources, are important contributors to OM at sites with high $PM_{2.5}$ concentrations. Additional studies to assess the impact of local sources in high $PM_{2.5}$ concentration areas, including source apportionment updated with additional data, would better quantify individual source contributions to $PM_{2.5}$ in these high concentration areas.
- *Determine site-specific emission factors for burning and industrial sources.* Source attribution analyses depend on emission factors that are applicable to an area and season. Additional monitoring to develop source profiles would give better certainty in the quantification of these sources.
- *Concentrate efforts to fully understand the sources of $PM_{2.5}$ and their trends in future nonattainment areas.* Based on current regulations and ambient concentrations, a number of areas in the region will likely remain classified as nonattainment in 2010 and 2015. An examination of the relationships between historical $PM_{2.5}$ concentrations in the context of source apportionment results with historical emissions data may help in the development of improved control strategies.
- *Synthesize existing results.* In addition to the analyses in this study, a number of other researchers have investigated data at similar sites. These results should be synthesized and distilled to give policymakers a more complete picture of $PM_{2.5}$ and OM in the Upper Midwest. This synthesis of information would be especially useful in heavily studied urban areas such as Detroit and St. Louis.
- *Increase certainty in burning emissions, emissions activity, and burning's impact on $PM_{2.5}$.* Burning is important to OM, but the specific sources and their activity is not understood well. Both better wood burning activity data and analysis of continuous data would help in understanding the temporal and spatial trends of burning and, thus, the most effective control measures.
- *Evaluate inter- and intra-urban variability.* Variability was seen in $PM_{2.5}$ mass, OM, and source contributions among sites within an urban area as well as between urban areas. These differences are important to understand because local sources are likely key contributors to many of these differences. If only a small number of monitoring sites are

in exceedance, control measures could be adopted that address the specific sources affecting these sites.

- *Evaluate the emission inventory in the context of the source apportionment results.* The emission inventory for the areas in and around each city should be compared to the results from this study. The overall average examination of the emission inventory does not capture urban/rural differences that are important to consider when determining changes that may need to be implemented in the inventory.
- *Develop a monitoring strategy to assess the effectiveness of any new control measures.* To quantify the impact of control measures, a consistent data record before and after implementation of the control measure is needed. Thus, a measure of accountability can be quantified to ensure that control measures are effective.
- *Improve information about mobile sources.* Mobile sources are important at all urban sites, but additional data are needed to fully understand and quantify the mobile sources. This includes development of representative source profiles, especially for smoking vehicles, as well as collection of continuous data such as BC and/or PAH. Improved source profiles will help quantification with CMB. Collection of continuous data will help quantify diurnal patterns, the relationship of carbonaceous aerosol with meteorology, and the contribution of mobile sources to OM by PMF application.