2.0 CONCEPTUAL MODEL

EPA guidance for performing a $PM_{2.5}$ attainment demonstration recommends developing a Conceptual Model that contains a conceptual description of the potential processes, sources and other factors that contribute to exceedances of the $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) in the region (EPA, 2007a). Below we present a Conceptual Model for $PM_{2.5}$ exceedances in the St. Louis nonattainment area (NAA) in support of the 2012 St. Louis $PM_{2.5}$ State Implementation Plan (SIP). The focus of this Conceptual Model is on the annual $PM_{2.5}$ NAAQS that is the subject of this SIP, although there are also some analysis for 24-hour $PM_{2.5}$ presented as well. The Conceptual Model presented below is based primarily on work performed by Turner and co-workers (2007a,b,c,d).

2.1 INTRODUCTION

The St. Louis area currently violates the National Ambient Air Quality Standard (NAAQS) for the annual average concentration of ambient fine particulate matter ($PM_{2.5}$, particulate matter smaller than 2.5 μm aerodynamic diameter). The States of Missouri and Illinois have examined, adopted, or are in the process of adopting control strategies to bring the area into compliance with this air quality standard. As part of this effort, a detailed description has been developed of the emissions, meteorology and atmospheric processes that modulate $PM_{2.5}$ concentrations. This "conceptual model" for $PM_{2.5}$ over the St. Louis area helps to guide the development and application of chemical transport models (CTM) and receptor-based models that are discussed later in this document. These models are necessary for quantitatively understanding source-receptor relationships which is the foundation needed for evaluating control strategy scenarios (Vickery, 2004). The conceptual model is focused on the information needed to support the development and implementation of control strategies to meet the annual average $PM_{2.5}$ NAAQS. It intentionally excludes factors and processes that influence certain metrics of air quality but have marginal significance in the context of the mass concentration based annual-average standard (e.g., homogeneous nucleation leading to high ultrafine number concentrations). Figure 2-1 shows the elements that go into the development of a conceptual model which is necessarily dynamic and must be refined as new knowledge becomes available. Content and presentation of the conceptual model for $PM_{2.5}$ over St. Louis closely follows the framework used by Vickery (2004) for nine North American geographic regions. This framework includes descriptions of the following:

1. annual and seasonal levels of $PM_{2.5}$ in relation to the mass-based standards;
2. compositional analysis of $PM_{2.5}$;
3. meteorological influences;
4. atmospheric processes contributing to $PM_{2.5}$;
5. sources and source regions contributing to the principle chemicals of concern; and
6. implications to the St. Louis $PM_{2.5}$ SIP.

The domain of interest for this conceptual model is the $PM_{2.5}$ nonattainment area (Figure 2-2) that includes: Franklin, St. Charles, Jefferson, St. Louis and City of St. Louis counties in Missouri; Madison, St. Clair, and Monroe counties in Illinois; and the township of Baldwin, Illinois. Contributions from emissions within the nonattainment shall be considered "urban scale influences" and "local source influences" while contributions from emissions outside the

nonattainment area will be considered "regional source influences" The differential between "local" versus "urban" influences occurs in regards to whether specific sources near a monitor contribute the $PM_{2.5}$ at that monitor (e.g., an industrial source located adjacent to the monitor) versus more dispersed urban source contributions to $PM_{2.5}$ concentrations (e.g., motor vehicles).

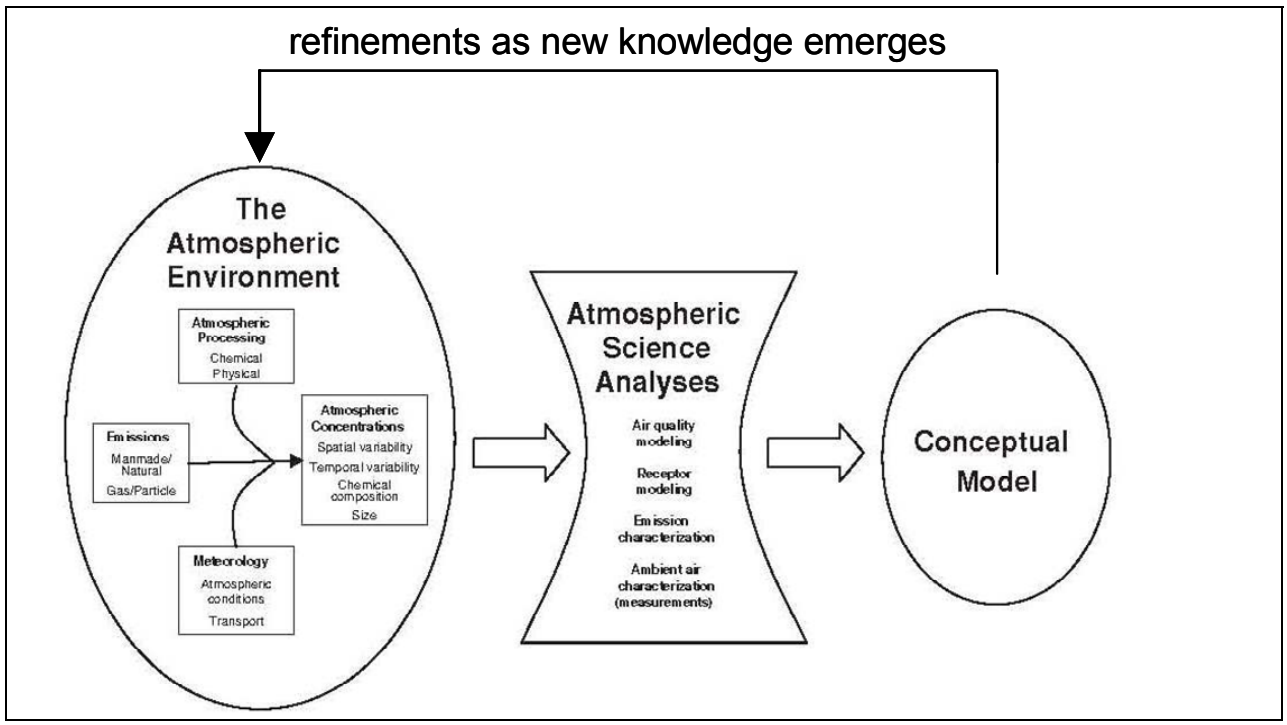

Figure 2-1. Development of a conceptual model (adapted from Vickery, 2004).

Figure 2-2. $PM_{2.5}$ nonattainment area for the St. Louis (MO-IL) region.

2.2 SUMMARY OF ANNUAL/SEASONAL $PM_{2.5}$ LEVELS IN THE ST. LOUIS NAA

The St. Louis nonattainment area (NAA) currently violates the annual average $PM_{2.5}$ NAAQS. In 2006, the United States Environmental Protections Agency (EPA) promulgated a revision to the 24-hour $PM_{2.5}$ NAAQS, reducing the threshold value from 65 to 35 μg/m^3. However, this $PM_{2.5}$ State Implementation Plan (SIP) is designed to address the 15 μg/m^3 annual and 65 μg/m^3 24-hour $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). Table 2-1 summarizes the annual metrics (98th percentile for the 24-hour standard, average of quarterly means for the annual standard) for all monitoring sites in the St. Louis area and also presents the monitor-specific 2002-2004 and 2003-2005 "design values" (three-year average of the annual metrics) for comparison to the NAAQS. Twelve of the fourteen compliance monitors that use the Federal Reference Method (FRM) for measuring $PM_{2.5}$ mass concentrations within the NAA are used for comparisons to the annual-average NAAQS. For the 2003-2005 period, two sites (Granite City and East St. Louis) exceeded the annual average $PM_{2.5}$ NAAQS of 15 μg/m^3 and five sites were in the range 14-15 μg/m^3, whereas no sites violated the 65 μg/m^3 24-hour $PM_{2.5}$ NAAQS. Nonattainment areas have not been designated for the new 35 μg/m^3 24-hour $PM_{2.5}$ standard but currently two sites, both in Granite City, exceed the 35 μg/m^3 standard and five sites are within 1 μg/m^3 of the standard.[1] Figure 2-3 shows the St. Louis area $PM_{2.5}$ compliance monitoring network 2003-2005 monitor-specific design values for those sites used for comparisons to the annual-average NAAQS.

Table 2-1. Annual concentration metrics and three-year average design values for $PM_{2.5}$ monitors in the St. Louis area (from Missouri DNR).

	24-hr Std = 35 μg/m^3 98th percentile				Design Values		Annual Mean Std = 15.0 μg/m^3				Design Values	
	98th percentile						Annual Mean					
St. Louis -MO	2002	2003	2004	2005	02 - 04	03 - 05	2002	2003	2004	2005	02 - 04	03 - 05
West Alton	35.0	35.5	30.2	38.5	33.6	34.7	14.0	14.0	11.9	15.2	13.3	13.7
Margaretta	35.5	31.5	26.5	40.0	31.2	32.7	14.3	13.5	12.1	15.3	13.3	13.6
Blair Street	36.5	32.0	27.9	40.3	32.1	33.4	15.4	14.1	13.2	16.1	14.2	14.5
South Broadway	36.5	33.2	28.5	38.6	32.7	33.4	15.3	14.4	13.1	15.9	14.3	14.5
Mound Street	35.9	33.2	30.3	40.8	33.1	34.8	15.6	14.7	13.6	15.9	*	*
Clayton	35.6	31.5	25.6	43.5	30.9	33.5	14.6	13.6	12.2	15.5	13.5	13.8
Sunset Hills	34.0	30.5	27.9	37.7	30.8	32.0	13.0	13.0	11.6	14.6	12.5	13.1
Arnold	39.8	34.2	27.0	39.9	33.7	33.7	15.0	14.0	12.6	15.4	13.9	14.0
St. Louis -IL												
VFW	44.6	38.0	35.3	41.2	39.3	38.2	19.6	18.1	16.2	18.9	*	*
Granite City	42.9	40.8	35.4	44.1	39.7	40.1	17.7	17.5	15.4	18.2	16.9	17.0
Alton	34.5	31.5	28.9	45.1	31.6	35.2	14.7	14.0	11.5	16.0	13.4	13.8
Wood River	33.9	31.6	30.0	41.2	31.8	34.3	15.1	14.0	13.2	16.0	14.1	14.4
E. St. Louis	40.9	32.6	30.2	39.6	34.6	34.1	16.6	14.8	14.7	17.1	15.4	15.5
Swansea	37.2	34.2	26.6	37.9	32.7	32.9	15.1	14.3	13.2	16.0	14.2	14.5

*middle-scale site… not for comparison to annual average NAAQS

[1] The 24-hour $PM_{2.5}$ NAAQS is 35 μg/m^3 with values 35.1–35.4 μg/m^3 rounding to 35 μg/m^3, which is not a violation of the standard.

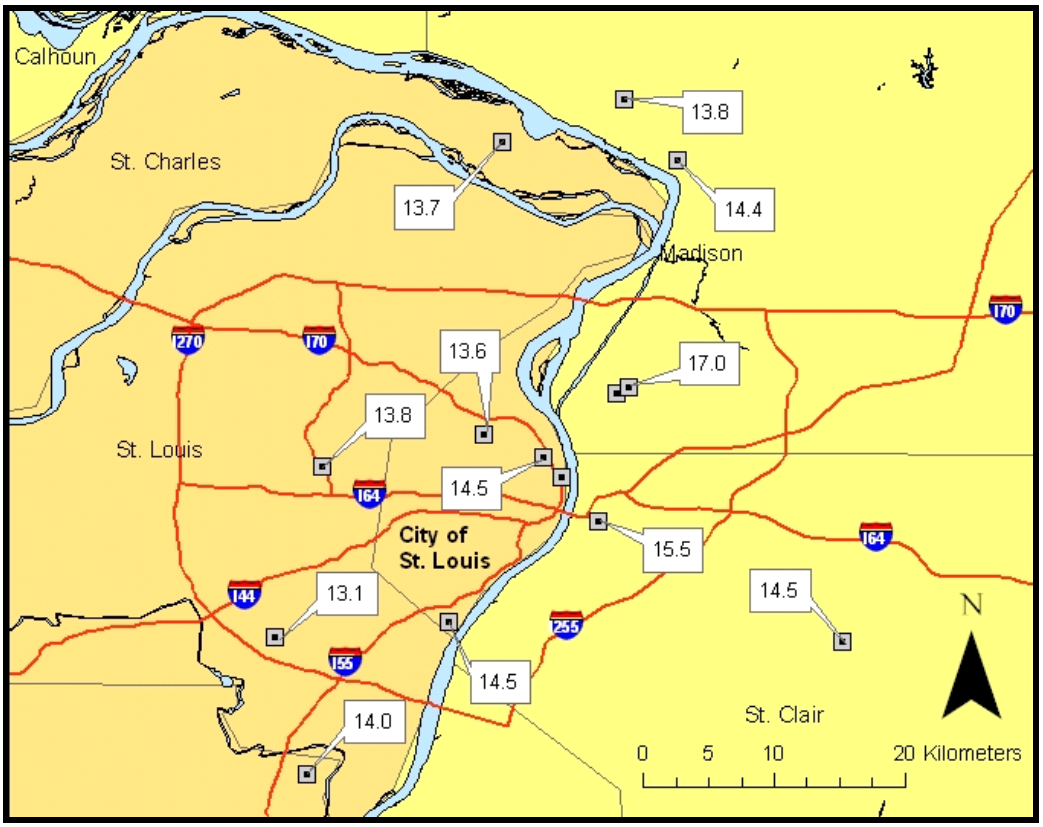

Figure 2-3. $PM_{2.5}$ mass concentrations at the FRM network sites in the St. Louis area, 2003-2005 design values.

Annual $PM_{2.5}$ concentrations are relatively high even at the rural sites that might represent regional contributions to the St. Louis urban $PM_{2.5}$ burden. Three-year average $PM_{2.5}$ concentrations within the nonattainment area for 2003-2005 ranged from 13.1 to 17.0 $\mu g/m^3$ while the average concentration at Bonne Terre (MO)[2], a rural site approximately 100 km south of the City of St. Louis urban core, was 11.3 $\mu g/m^3$.

Figure 2-4 displays the daily $PM_{2.5}$ FRM concentration data for the Margaretta Street station (City of St. Louis, MO with annual value of 13.6 $\mu g/m^3$ in figure 2-3) from 1999 to 2004. This site was chosen for demonstration because it is near the urban core yet has relatively few impacts from near-field "local" sources. The daily-average $PM_{2.5}$ NAAQS of 35 $\mu g/m^3$ was exceeded on 1.8% of the days. The two days exceeding 50 $\mu g/m^3$ were July 4-5, 2002, corresponding to fireworks events. About half of the remaining 21 days that exceeded 40 $\mu g/m^3$ occurred as clusters of two-to-three consecutive days rather than single days. This pattern is consistent with multiday, episodic behavior observed for $PM_{2.5}$ concentrations.

[2] Bonne Terre $PM_{2.5}$ gravimetric mass concentration are based on a Teflon filter of the speciation sampler deployed at Bonne Terre is not a Federal Reference Method sampler.

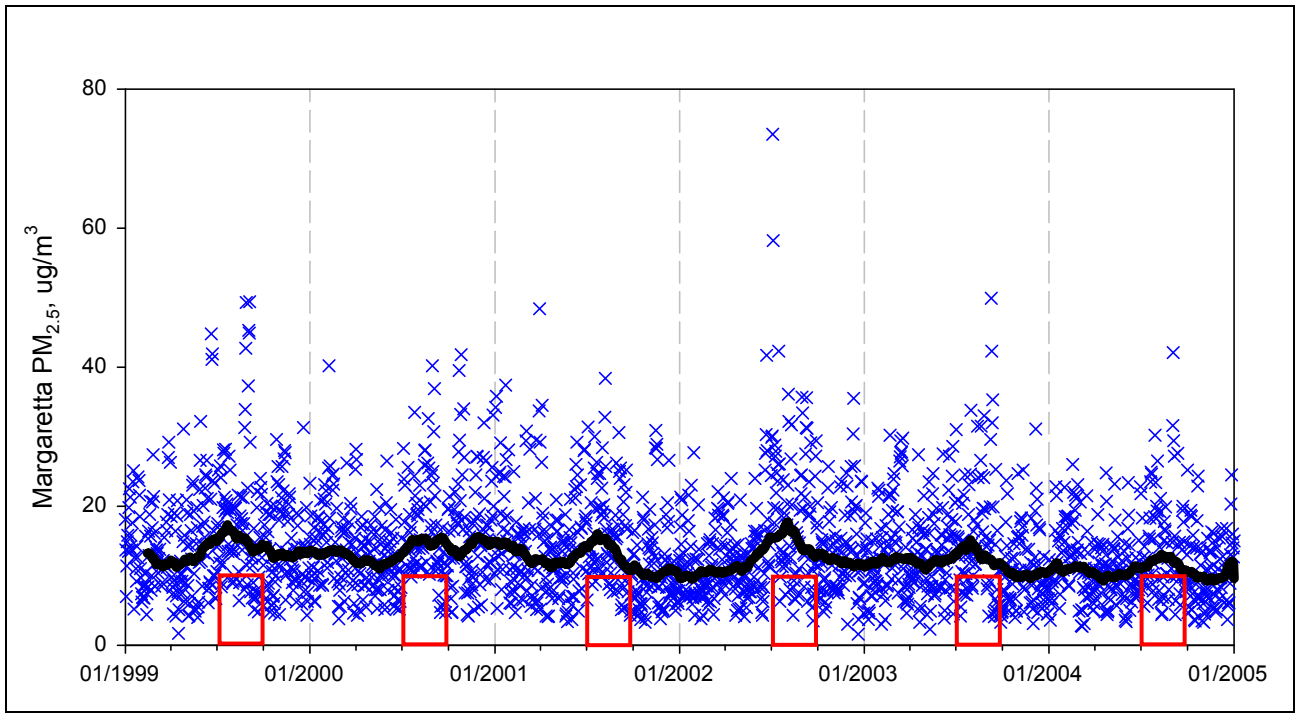

Figure 2-4. Daily $PM_{2.5}$ FRM mass concentration for the Margaretta Street (City of St. Louis, MO) monitoring station from 1999 to 2004. The black line is the centered 90-day geometric mean concentration and the red rectangles correspond to 3rd quarter and concentrations less than 10 µg/m^3

There is some seasonal variation in $PM_{2.5}$ with the summertime typically, but not always, exhibiting the highest average concentrations (Figure 2-5). Overall, the seasonal variation is modest. There are also year-to-year variations in $PM_{2.5}$. Figure 2-6 shows the cumulative distributions of daily $PM_{2.5}$ FRM concentration data for the Margaretta Street station for 1999 and 2004. These distributions are nearly linear in log-probability space, which suggests they are nearly lognormal over a large range of concentration. Both concentration distributions deviate from lognormal behavior at high concentrations. In 1999 the peak concentrations are higher than expected for lognormal behavior ("A" in Figure 2-6) while in 2004 the peak concentrations are lower than expected for lognormal behavior ("B" in Figure 2-6). Not only were peak concentrations lower in 2004 compared to 1999, but also the entire distribution was shifted to lower concentrations. Figure 2-5 (red rectangles) exhibits an elevated baseline for summertime $PM_{2.5}$ concentrations from 1999 to 2001 and to some extent through 2003. In 2004, however, there are several relatively low concentration days in the summer and the lower annual average results from peak-shaving at high concentration and also a greater frequency of low concentration days. The observed year-to-year behavior is likely coupled to variations in the frequency distribution of synoptic weather patterns. The 2004 year was characterized as having lower ozone and PM levels throughout most of the U.S. which in a large part was due to being a wetter year than typical.

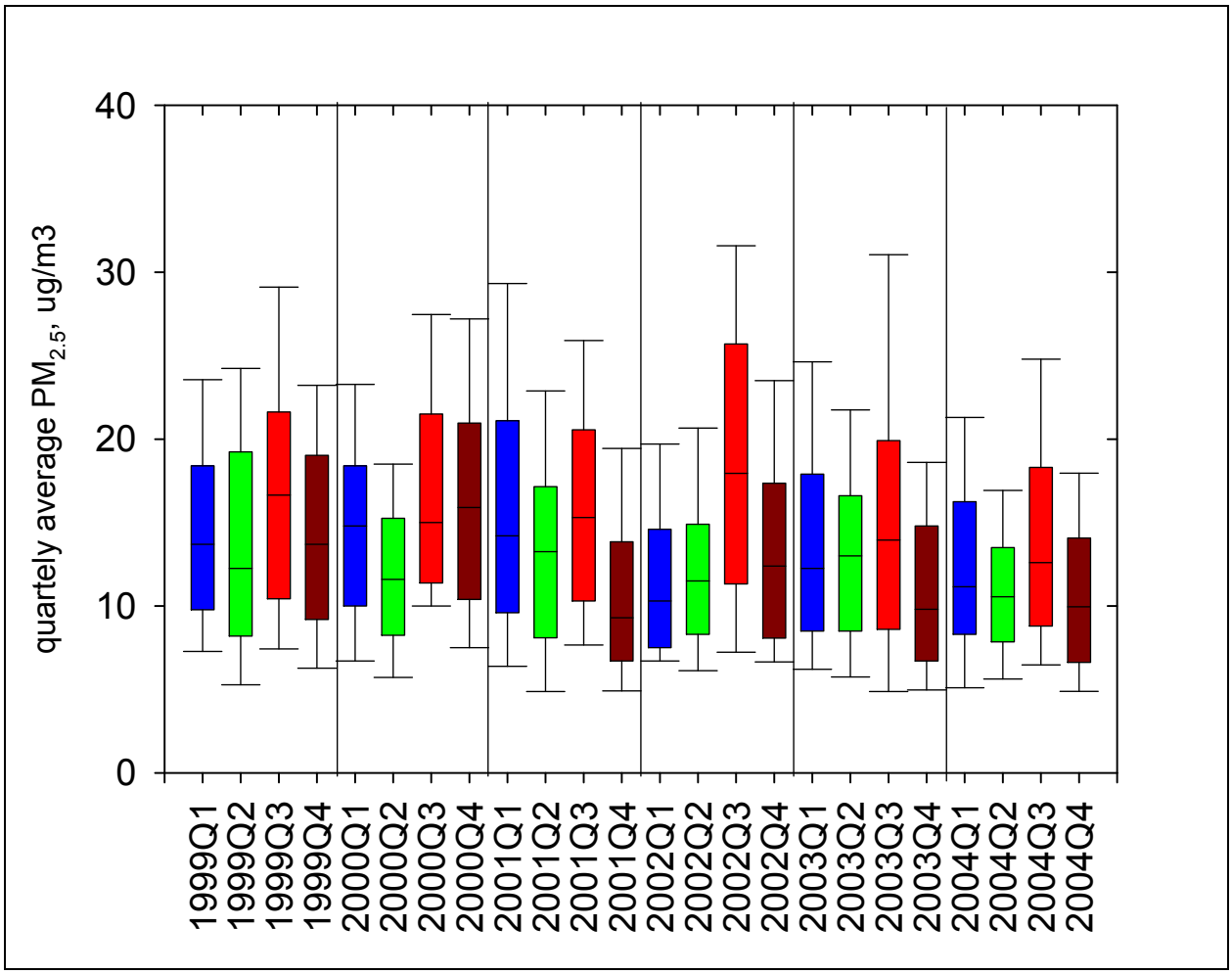

Figure 2-5. Quarterly $PM_{2.5}$ mass concentration distributions at Margaretta (City of St. Louis, MO) monitoring station from 1999 to 2004.

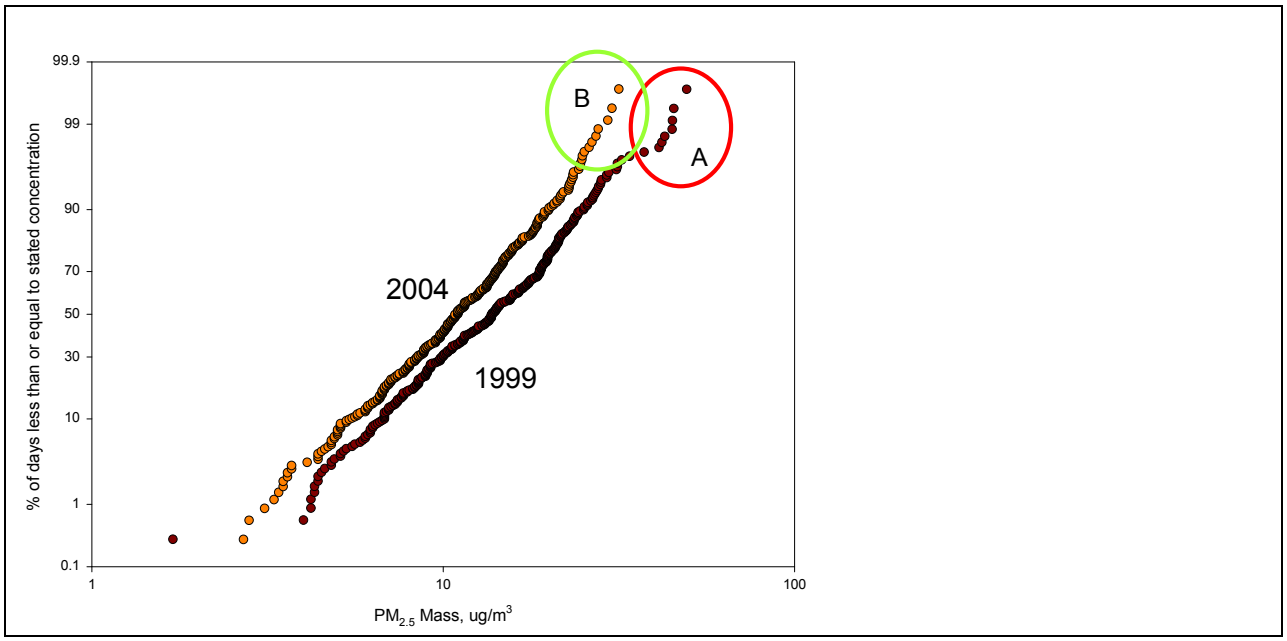

Figure 2-6. Cumulative distribution of daily $PM_{2.5}$ FRM mass concentration for the Margaretta Street (City of St. Louis, MO) monitoring station for 1999 and 2004.

In summary, while only two monitors violated the annual average $PM_{2.5}$ NAAQS (based on 2003-05 design values,, several monitors were close to the standard. NOTE: 2006-08 design value data identify only one site that violates the annual NAAQS (Granite City, IL) Seasonal-average concentrations are typically, but not always, highest in the summertime. There are substantial year-to-year variations in $PM_{2.5}$ concentrations. These differences are driven not only by the frequency of very high concentration days, but also the frequency of very low concentration days and are likely primarily due to meteorological variations.

2.3 COMPOSITIONAL ANALYSIS OF $PM_{2.5}$

Chemical composition or speciation of $PM_{2.5}$ is routinely measured at four Speciation Trends Network (STN) sites in the St. Louis area (see Figure 2-7). The Blair Street site in the City of St. Louis operates on a 1-in-3 day sampling schedule. The Arnold monitor south of the City of St. Louis also operates on 1-in-3 day schedule while the Alton monitor north of St. Louis operates on a 1-in-6 day schedule.[3] STN measurements are also collated at the Capitol site in the city of St. Louis. During the period from June 2001 to May 2003, daily sampling was also performed at the St. Louis – Midwest Supersite core monitoring location in East St. Louis with 24-hour speciated $PM_{2.5}$ samples collected on a 1-in-6 day sampling was conducted for the period from August 2003 to December 2004.

Figure 2-8 displays the 2002 annual average $PM_{2.5}$ composition at East St. Louis Super Site and Blair Street (City of St. Louis) STN site.[4] The inorganic ions (sulfate, nitrate, ammonium) all together account for 47-57% of the $PM_{2.5}$ mass. Organic matter carbon (OMC), estimated as 1.8 times the measured organic carbon (OC) using the OMC/OC ratio from the new IMPROVE equation (Bae *et al.* 2007), is 26-38% of the mass. Elemental carbon (EC) is 5% of the mass at each site. Crustal material was estimated using the IMPROVE equation (Malm et al., 2000) which assumes the dominant oxide forms for Al, Ca, Fe, Si, and Ti in soil. In urban areas, this fraction is contaminated by point source contributions such as iron from steelmaking so is not truly just "soil".

Sulfate and nitrate exhibit seasonal variations with sulfate highest in the summer and lowest in the winter, and nitrate highest in the winter and lowest in the summer (see Figure 2-9). The remaining major components have relatively small seasonal variations. For organic matter, elevated contributions from secondary organic aerosol (SOA) in the summer are balanced by increased woodsmoke / biomass burning contributions in the winter to yield relatively constant monthly OMC concentrations (Bae *et al.* 2004, Bae *et al.* 2007). These combinations of seasonal variations yield a $PM_{2.5}$ mass concentration which typically exhibits a summertime maximum but is still relatively high for all seasons.

[3] The Alton speciation monitor was operated on a 1-in-3 day sampling schedule from January to early April 2002.
[4] 2002 annual average concentration reported in Figure 2-8 are 1.0 to 1.2 $\mu g/m^3$ higher than the values reported in Table 2-1 because: they are based on the mean of the entire year of data whereas Table 1 values are the arithmetic average of quarterly means; and Table 2-1 is based on sampling with Federal Reference Method (FRM) monitors while Figure 2-8 is based on non-FRM measurements of gravimetric mass (Harvard Impactors for East St. Louis, speciation sampler for Blair Street).

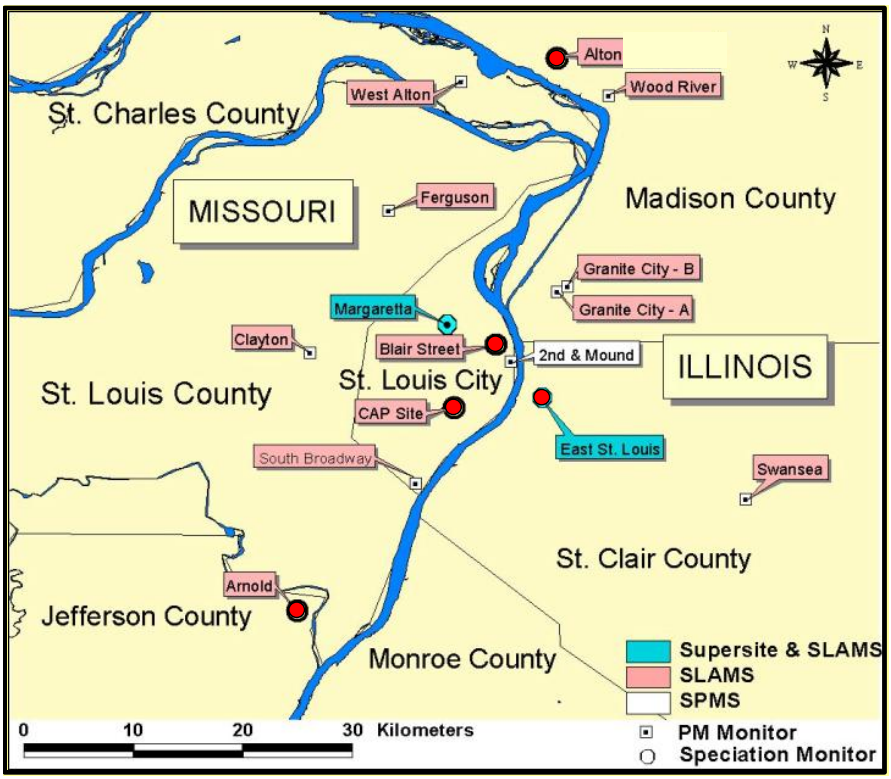

Figure 2-7. St. Louis area $PM_{2.5}$ monitoring network operating in 2002. Red circles denote sites with speciation monitoring.

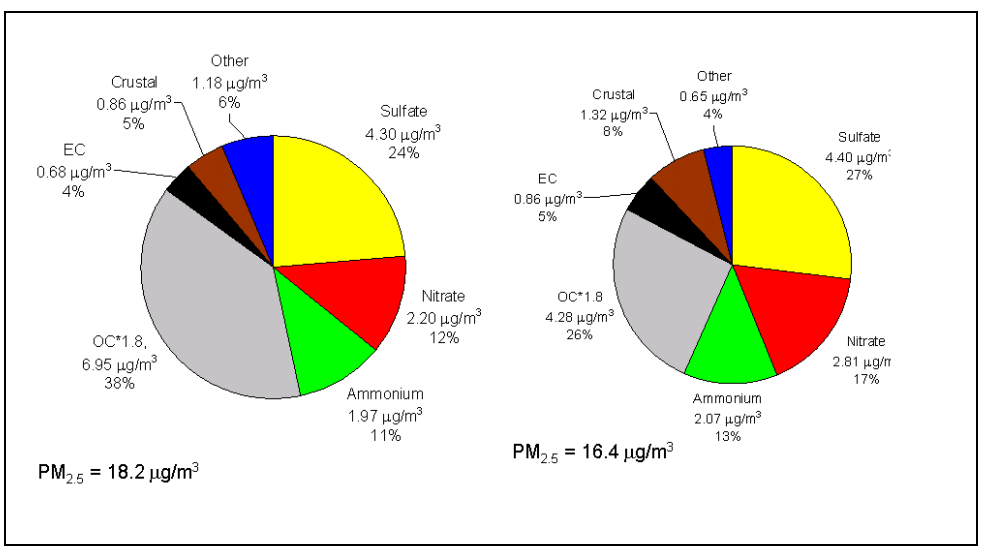

Figure 2-8. Annual average $PM_{2.5}$ composition for 2002 at East St. Louis (left) and Blair Street, City of St. Louis (right). The area of each circle is proportional to the annual average $PM_{2.5}$ mass concentration.

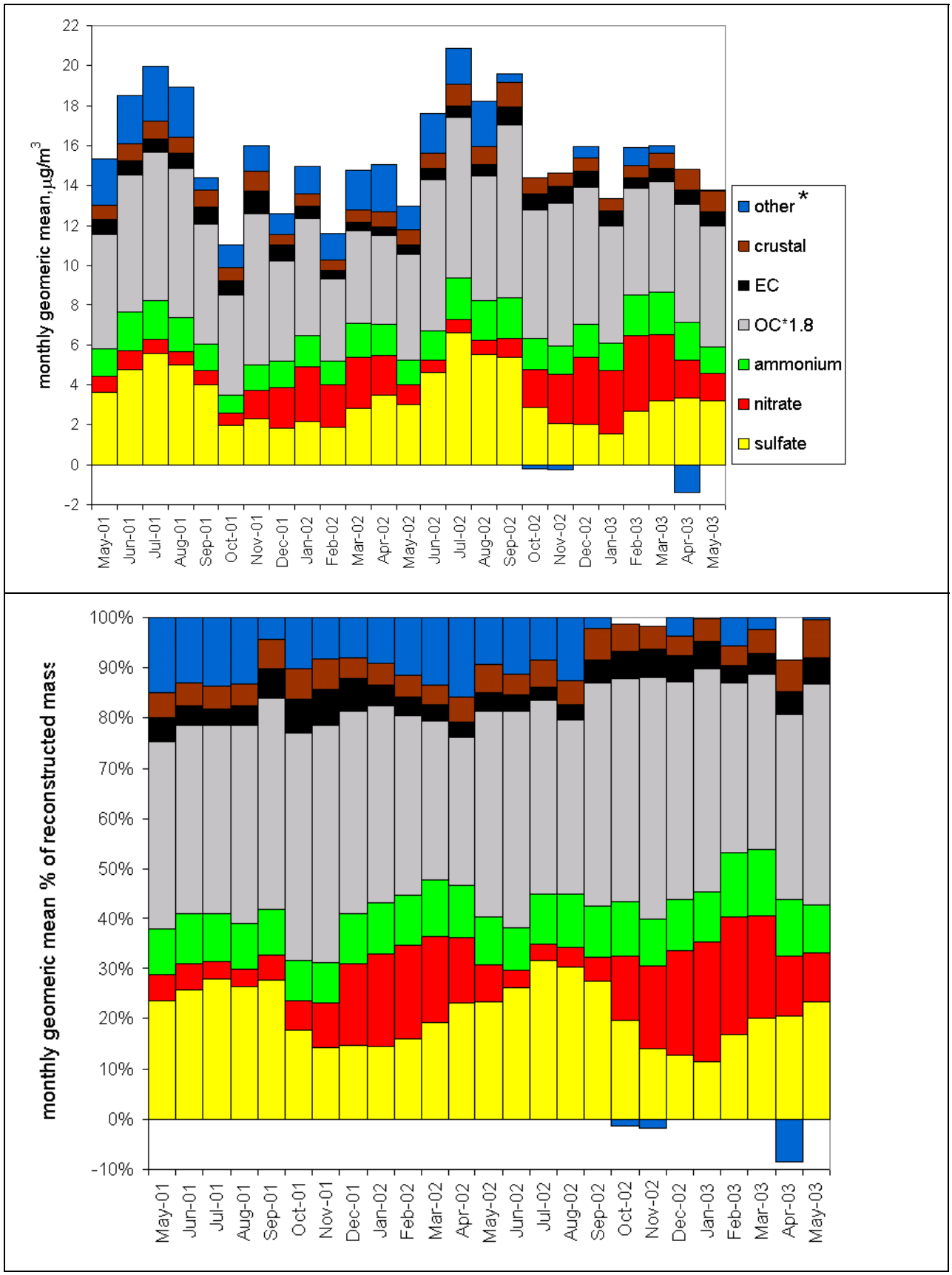

Figure 2-9. Monthly mean $PM_{2.5}$ composition from daily speciation sampling at East St. Louis as absolute concentration (top) and percentage of monthly average concentration (bottom).

Figure 2-10 shows the two-year average concentration for sulfate and nitrate across the three speciation sites with 1-in-3 day or higher measurement frequency (Arnold, Blair Street / City of St. Louis, and East St. Louis). Only those days with valid data at all three sites were used in the analysis. Sulfate (N = 213) is spatially homogeneous with only a 4% variation between the three sites. Nitrate (N = 206), however, exhibits an intra-urban gradient which is highest in the urban core (Blair Street) and decreases with increasing distance outward from the core in either the southern (Arnold) or eastern (East St. Louis) directions. Nitrate is 10% higher at Blair than East St. Louis, which is 12% higher than Arnold yielding a 22% difference across the three sites. Thus, in contrast to sulfate, there is a significant urban increment of nitrate superposed on the dominant regional contribution.

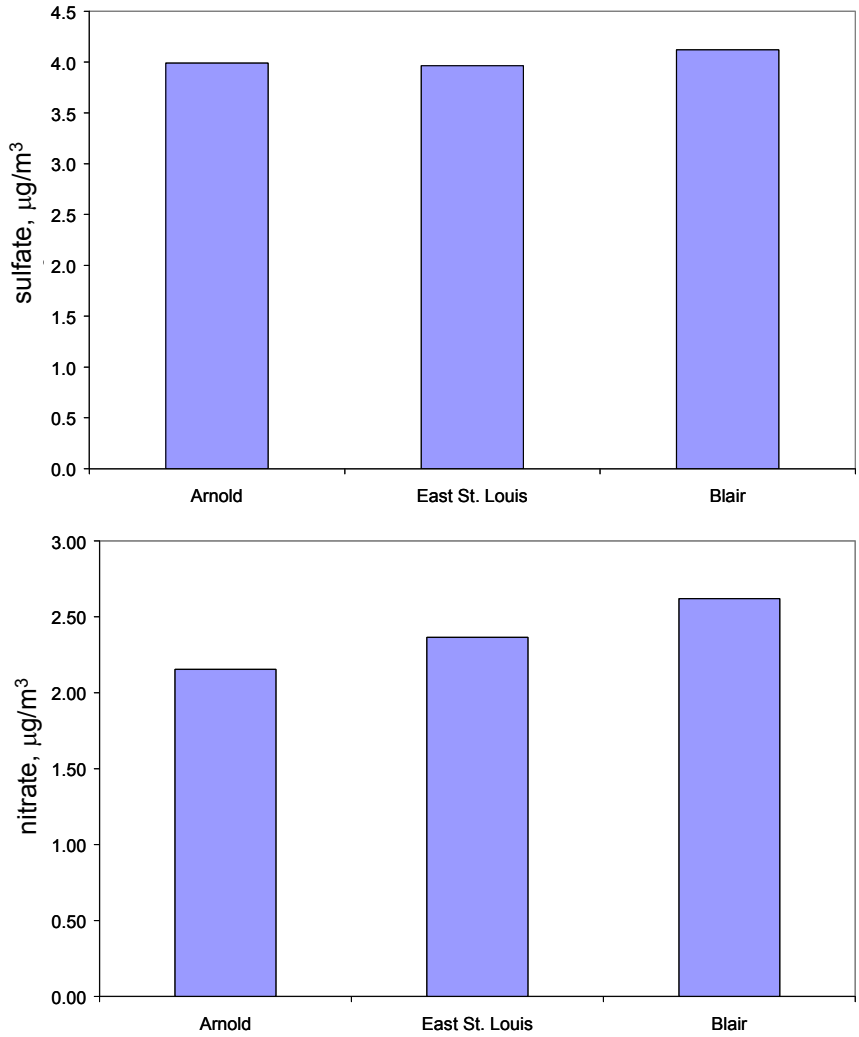

Figure 2-10. Average $PM_{2.5}$ sulfate (top) and nitrate (bottom) from April 2001 to May 2003.

2.4 METEOROLOGICAL INFLUENCES

Both local surface meteorology and synoptic weather modulate $PM_{2.5}$ mass concentrations. Synoptic weather patterns bring air masses into St. Louis from various emission source regions (see discussion of sources of $PM_{2.5}$ below). Surface winds determine the ventilation of emissions generated within the area and also determine whether spatially distributed local sources (e.g. point sources) will impact a monitoring site on a given day. Local surface meteorology is coupled to the synoptic weather. For example, summertime high pressure systems are often centered over the Great Lakes area which not only bring air masses from the SO2 emissions rich regions of the Ohio River Valley and Tennessee Valley into St. Louis, but also create local conditions which are often stagnant or nearly stagnant. Surface meteorology is also augmented by local factors such as terrain.

Figure 2-11 displays two years of seasonal wind roses based on hourly measurements at East St. Louis. On an annual basis, the surface winds are predominantly from the south followed by the north. Surface winds from the west are infrequent and winds from the east are even rarer. There is substantial year-to-year variation in the seasonal wind roses (especially fall and winter) which affects the impact of local sources on specific monitoring sites. Summertime conditions have a relatively high percentage (~20%) of calms with slow advection from the south. Fall conditions also have a relatively high percentage of calms (~20%) with advection from the south and north/northwest. Winter has a relatively low percentage of calms (~10%) and faster wind speeds compared to summertime conditions. Spring conditions also have a relatively low percentage of calms (~10%) with strong winds from the north and south/southeast.

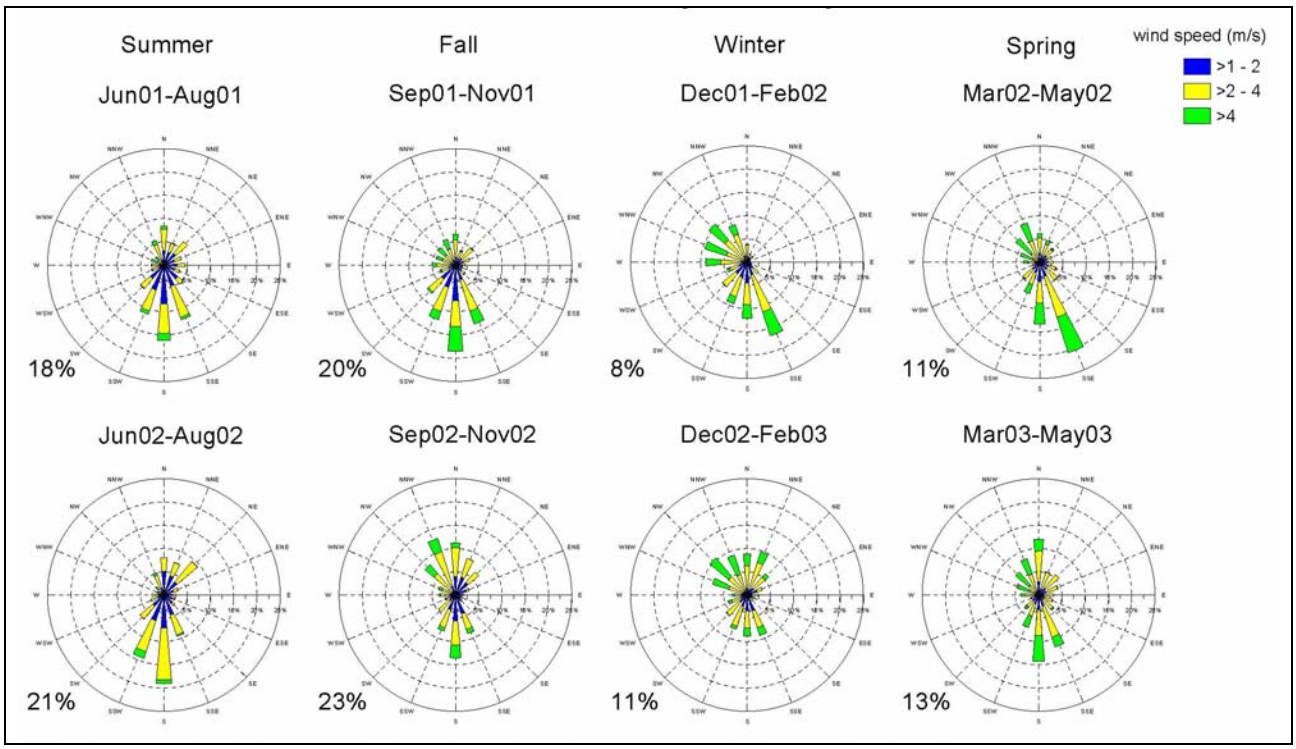

Figure 2-11. Hourly wind roses by season for the East St. Louis site. Wind rose calculations exclude calms (hourly-average wind speed < 1 m/s). Calms as a percentage of total hours is listed in the lower-left of each wind rose.

Weather on a synoptic scale can influence components of $PM_{2.5}$ both by providing favorable conditions for the formation of secondary PM and by transporting both primary and secondary PM and secondary PM precursors. Andersen (2006) analyzed meteorological data for common synoptic patterns and then investigated each regime's relationship to components of $PM_{2.5}$, specifically sulfate and nitrate. Two approaches were used, the first utilizing air mass trajectory analysis and the second utilizing meteorological observations. Both approaches used cluster analysis to determine similarity in synoptic conditions. The trajectory analysis used the NOAA/ARL HYSPLIT model to calculate 5-day back trajectories (air mass history before arrival to St. Louis). Once the trajectories had been run for a two year time period (June 2001 – May 2003) the database was put into a form of cluster analysis called Patterns in Atmospheric Transport History (PATH). This PATH analysis grouped trajectories together given their similarity in space and time. The result was eight clusters of trajectories for this data set. Probability plots in Figure 2-12 show probable areas of influence for a given cluster, where probability is determined as the likelihood that a back trajectory from St. Louis in a given cluster passed over a given area.

The second type of analysis was a two-stage cluster analysis. Input data included both surface meteorology from the St. Louis – Midwest Supersite (East St. Louis, IL) and upper air data from the Springfield, IL National Weather Service upper air station. Principal components analysis (PCA) was used to reduce the original data set of 63 meteorological variables down to five principal components which explain a majority of variance in the data set. The daily time series of these five principal components was put into a two-stage cluster analysis to identify similar patterns based on observed data (as opposed to modeled trajectories).

Relationships between synoptic regimes and $PM_{2.5}$ sulfate and nitrate were examined because these two species are dominated by regionally transported material. The following analyses utilized daily sulfate and nitrate data from the St. Louis – Midwest Supersite in East St. Louis.

Sulfate: Three of the PATH clusters demonstrate elevated sulfate relative to other clusters. PATH1 is the dominant summertime cluster and captures sulfate episodes from April to September. This group of trajectories represents a synoptic situation in which a high pressure (or anticyclonic) system is located to the east or southeast of St. Louis, resulting in weak winds from southerly directions and little subsidence.

While PATH1 is the dominant summertime cluster, it does not capture the highest sulfate concentrations. These days are captured by PATH4 in June and July. PATH4 indicates slow northeasterly flow coming from the Ohio River Valley and upper Midwest regions. This cluster is most frequent in April and September, but when it does occur during summer months it is associated with the highest sulfate concentrations seen in St. Louis. A third cluster, PATH6, is also found to have elevated sulfate. PATH6 does not occur during summer months, as its peak frequency is in April-May and August-October. This cluster shows slow southeasterly flow associated with high pressure systems situated over the east coast, likely a transition period between synoptic systems.

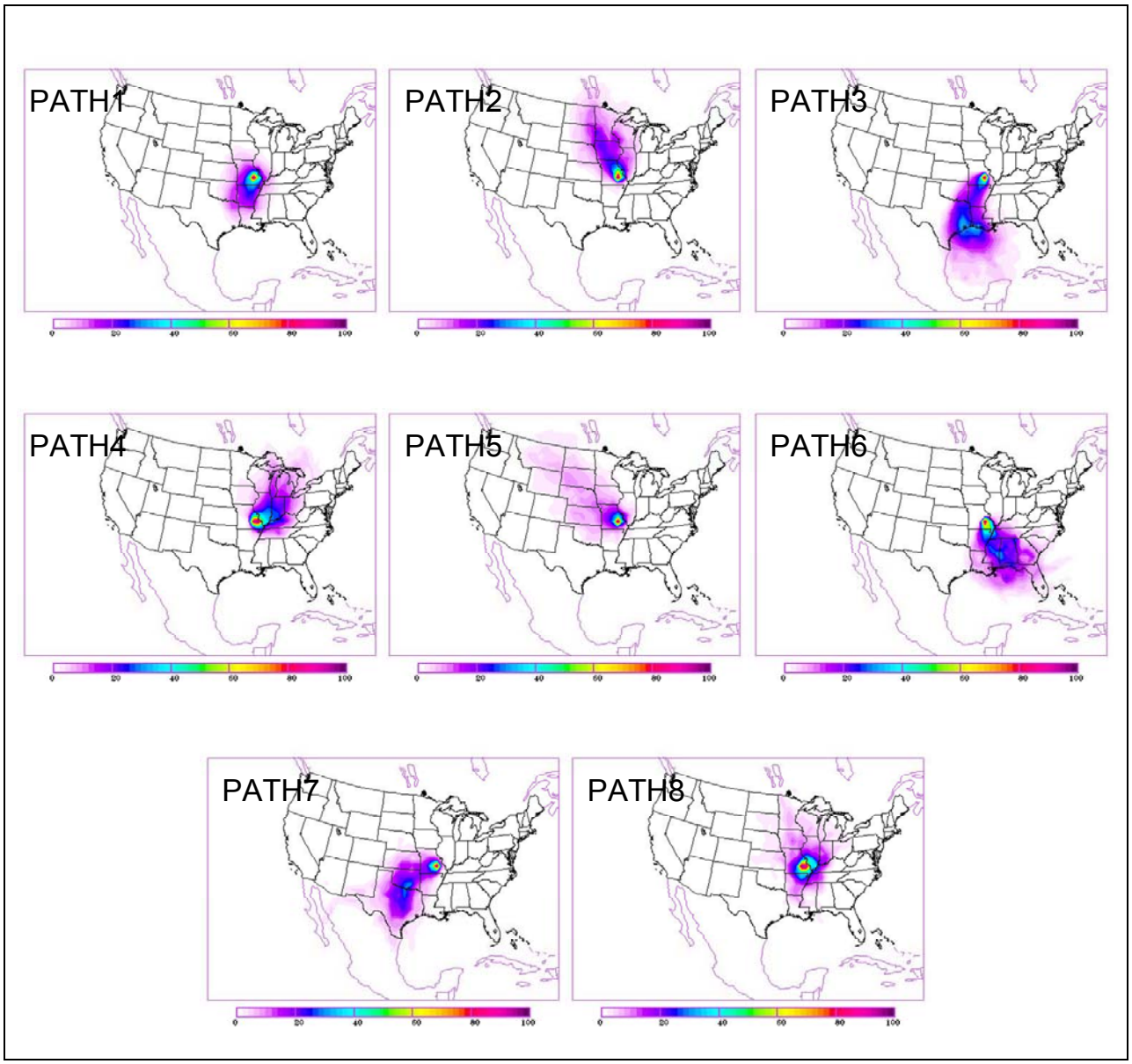

Figure 2-12. Probability fields for each cluster in the St. Louis PATH analysis (source: Anderson 2006).

In the two-stage cluster analysis two clusters showed enhanced sulfate relative to the annual median (Figure 2-13). Cluster 1 (C1) has the highest mean sulfate concentration of all eight clusters. C1 identifies synoptic conditions consistent with a westward extension of the Bermuda High pressure system: light winds, clear skies, and high temperatures. This cluster is most common in May – September and is quite similar to conditions in PATH1. The second cluster showing elevated sulfate is cluster 4 (C4). C4 is identified by the presence of a stationary front to the south of St. Louis. This results in light north winds (varying from northwest to northeast depending on the position of the stationary front), high relative humidity and cloudiness. Local conditions are likely to be semi-stagnant and allow the build-up of pollutants, especially sulfate as this cluster occurs most often in May – July.

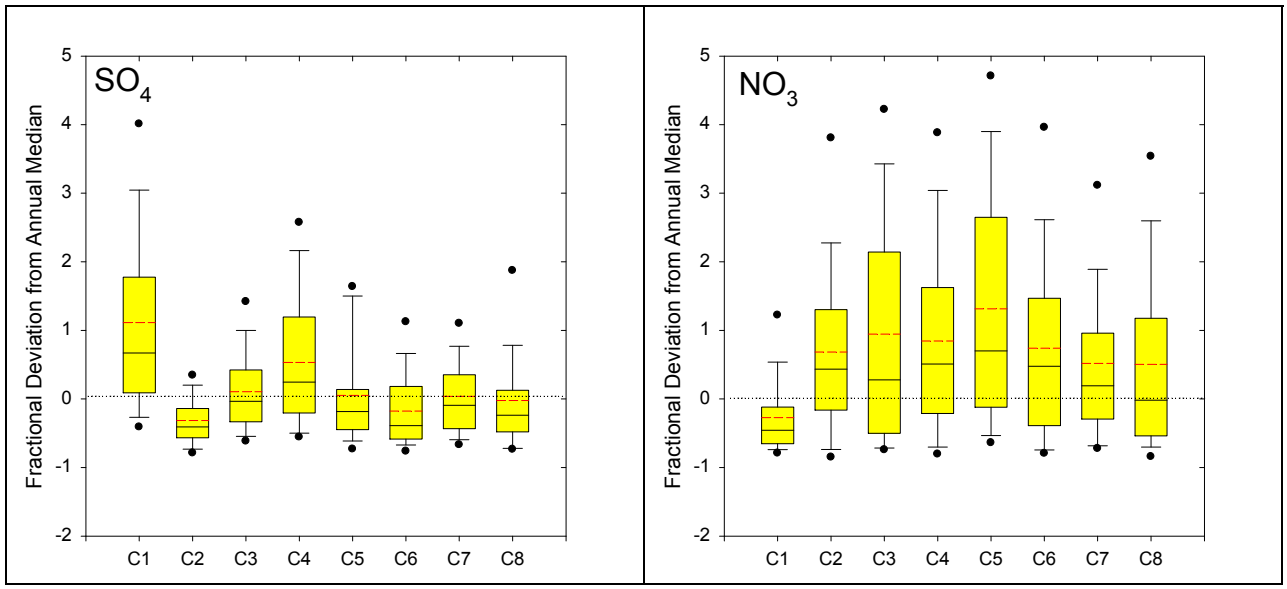

Figure 2-13. Sulfate (left) and nitrate (right) concentration distributions by cluster from the two-stage cluster analysis, relative to the annual median concentration. Closed circles are the 5th/95th percentiles and the dashed red lines are the arithmetic mean deviations. See Table 2-2 for definitions of the cluster assignments. (Source: Anderson 2006)

Table 2-2. Descriptors of the synoptic classes resolved for the two-stage cluster analysis on observed meteorological parameters. (source: Anderson 2006)

Cluster	Description
C1	Summer Anticyclone
C2	Winter Anticyclone
C3	Frontal Approach
C4	Stationary Front
C5	North Central U.S. Transitional Front
C6	Midwest U.S. Cyclogenesis
C7	North Central U.S. Cyclogenesis
C8	Cold Frontal Approach

Nitrate: Regimes influencing high nitrate concentrations are less clearly defined than sulfate in both the PATH analysis and the two-stage cluster analysis. Four different PATH clusters exhibit high nitrate in different months of the year. PATHs 2 and 5 (Figure 2-12) are the only clusters to exhibit a positive deviation from the annual median nitrate concentration. However, when viewing monthly nitrate concentrations, PATHs 3 and 4 exhibit maximum nitrate concentrations in certain months.

PATH2 and PATH5 describe what one would consider the classic flow patterns for high nitrate in St. Louis. PATH2 peaks in nitrate concentration in December and January (though it is not the highest concentration cluster in these months) and indicates slow northerly flow, likely associated with a post-frontal high pressure system to the north. PATH5 peaks in December – March, and has the highest nitrate concentration of all clusters in December. This cluster indicates fast northerly and northwesterly flow associated with high pressure systems moving quickly out of Canada.

PATH3 contains the highest nitrate concentrations in January and February. The typical flow pattern is moderate south or southwesterly winds, typically associated with the passage of low pressure systems and fronts from the Rockies eastward. PATH4 has the highest nitrate in March and April, and it should be noted is also one of the high sulfate clusters of trajectories. This PATH produces slow northeasterly flow in the St. Louis area, likely from a high pressure system moving slowly out of Canada and crossing the Great Lakes.

The two-stage cluster analysis also identifies multiple clusters influencing elevated nitrate in St. Louis. Clusters 2 (C2), 4 (C4), 5 (C5), and 6 (C6) show the most significant positive deviation from annual median nitrate concentrations, though it should be noted that clusters 3 and 7 also show positive deviations (Figure 2-13). C2 occurs after a recent cold frontal passage, characterized by a high pressure system moving into the US from Canada bringing northerly winds, clear skies, and the coldest temperatures and dew points of all clusters. C4 is characterized by a stationary front to the south of St. Louis, and is discussed in the sulfate section. This cluster is most common in May – July, but perhaps captures late season nitrate events, or possibly early season nitrate events in October. C5 shows the greatest positive deviation from annual median nitrate concentrations, and is most common in autumn months (peak in November) with a secondary maximum in March and April. It is characterized by moderate southerly flow usually in association with a low pressure system moving through the upper plains to the north of St. Louis. C6 occurs in the spring (peaking in May) and the late autumn/early winter (peaking in December). It is characterized by light northwesterly winds typically following the passage of a cold front.

Summary: Clustering techniques, using both modeled trajectory data and observed meteorological data, provide insights into the typical synoptic scale meteorology affecting concentrations of sulfate and nitrate in the St. Louis area. Trajectory analysis, utilizing the PATH algorithm for clustering, groups days based on flow pattern. Two-stage cluster analysis of meteorological data groups days based on similarity of observed local conditions.

In each type of analysis elevated sulfate concentrations were identified by synoptic conditions leading to transport from regions to the northeast, east, and southeast of St. Louis. These areas include the Ohio River Valley and Tennessee Valley where there are numerous coal-fired power plants with substantial SO_2 emissions. The transport patterns identified in this analysis also show summertime peaks in occurrence, which is the favorable season for ammonium sulfate formation.

There are no distinct transport regimes leading to high elevated nitrate concentrations. Both the trajectory and two-stage cluster analysis identified transport patterns with influence from the north, northeast, southeast and south. All of these regimes have occurrences in November – March, when ammonium nitrate formation is favorable due to cooler temperatures and lower sulfate concentrations. Flows from the north can become rich in ammonia after crossing the agricultural regions of the Upper Midwest, while flows from an easterly direction can pick up ammonia emissions from agricultural activity in Illinois and Indiana. There are likely NO_x sources within these areas as well, which can react to form nitric acid and drive ammonium nitrate formation. While there are several different transport regimes associated with elevated nitrate, they have two things in common: occurrences in relatively cold weather, and flow over regions emitting ammonia and likely also nitrogen oxides. Based on chemical life times, the transport distance of nitrate is shorter than sulfate which may also help explain the weaker specific transport signature of nitrate compared to sulfate.

2.5 ATMOSPHERIC PROCESSES CONTRIBUTING TO PM2.5

The major $PM_{2.5}$ chemical components over St. Louis are ammonium sulfate [$(NH_4)_2SO_4$], ammonium nitrate [NH_4NO_3] and carbonaceous matter that is primarily organic matter carbon (OMC). Each of these components can be directly emitted by sources (primary emissions) and formed by gas-to-particle conversion (secondary processes) in the atmosphere. Although ammonium sulfate and ammonium nitrate are primarily secondary in origin.

Sulfate: Intraurban homogeneity for sulfate (Figure 2-10) together with a small urban excess for sulfate on a daily basis suggests that sulfate is overwhelmingly of regional origin. Figure 2-14 shows three months of daily 24-hour integrated sulfate measurements at East St. Louis and Park Hills (MO). The latter is a rural location near the Bonne Terre monitoring site, about 100 km south of the St. Louis urban core. There is good agreement for sulfate between the urban and rural sites on a daily basis with only a 4% urban excess for the three-month period. September 5-6 corresponds to a high intensity, short duration sulfate episode that impacted the two sites on different days. Assuming the rural site is representative of the regional contributions to the urban site, there might be a significant local contribution on certain high sulfate days (greater than ~5 $\mu g/m^3$). This pattern was also observed for sulfate comparisons between the Blair Street (City of St. Louis) urban site and Bonne Terre rural site, and needs further examination.

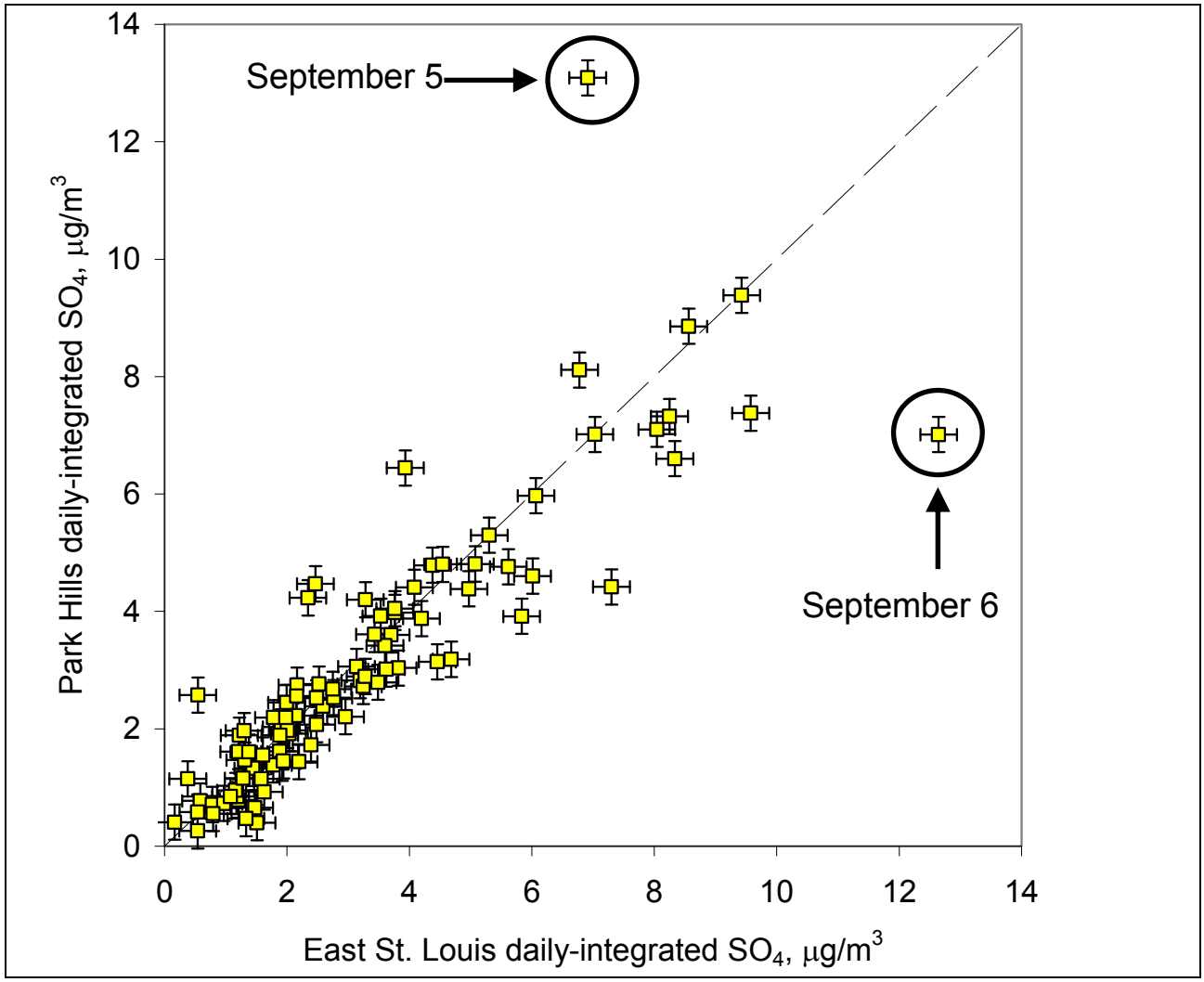

Figure 2-14. Daily 24-hour integrated fine PM sulfate at the rural Park Hills site (near Bonne Terre, MO) and the urban East St. Louis site from August 17 to November 20, 2001.

Potential source contribution function (PSCF) maps, based on incremental probabilities for transport patterns on high sulfate days compared to average climatology, show source regions to the east and southeast of St. Louis (Figure 2-15). The urban/rural contrast patterns and PSCF maps are consistent with sulfate arising from secondary processing of SO_2 emissions, particularly from the Ohio River Valley and Tennessee Valley regions which have numerous coal-fired utility boilers. The weather conditions on regional high sulfate days (relatively high temperature and humidity) are also conducive to secondary formation of sulfate from local emissions.

Nitrate: Ammonium nitrate formation depends on the thermodynamic details of the ammonium-sulfate-nitrate-water system (Seinfeld and Pandis, 1998). There is an equilibrium between sulfate-nitrate-ammonium in which nitrate may take the form of either gaseous nitric acid [HNO_3] and for particulate ammonium nitrate [NH_3NO_3]. Cooler temperatures and higher relative humidity favor particulate ammonium nitrate, whereas under higher temperatures the particulate ammonium nitrate will volatilize into gaseous nitric acid. Sulfate has lower volatility than nitrate so will readily condense into a particle under most conditions. Nitrate, on the other hand, has higher volatility and needs a basic compound to bond with to form a particle. Ammonium is the most frequent basic compound found bonded to particulate nitrate, although in coastal areas sodium may also bind with nitrate and calcium is another basic compound that has been associated with particulate nitrate. Wintertime conditions over the Midwest favor ammonium nitrate formation because temperatures are cooler and there is still relatively high humidity. Synoptic weather patterns bring ammonia-rich air masses from the northwest through northeast with highest nitrate corresponding to transport from Illinois and the Ohio River Valley where large NO_x sources are located (Figure 2-16). The combination of high total ammonia and relatively low sulfate establishes conditions conducive to ammonium nitrate formation. Note that since SO_4 is a stronger acid available ammonia will be bound to SO_4 over NO_3. Intraurban variability in nitrate (Figure 2-10) suggests significant local contributions to the reactant limiting ammonium nitrate formation (either ammonia or nitric acid) and this is supported by day-of-week patterns. Figure 2-17 shows the day-of-week distributions for sulfate and nitrate in East St. Louis. The distributions are constructed from the daily concentration data scaled to centered seven-day average concentration. This scaling approach dampens the effect of seasonal concentration variations on the distributions (Millstein *et al.* 2006). Sulfate shows no significant day-of-week variation while nitrate is lowest on Mondays followed by Sundays and Tuesdays, consistent with lower NO_x emissions on weekends and a time lag for the atmospheric processing of NO_x into nitric acid (Millstein *et al.* 2006).

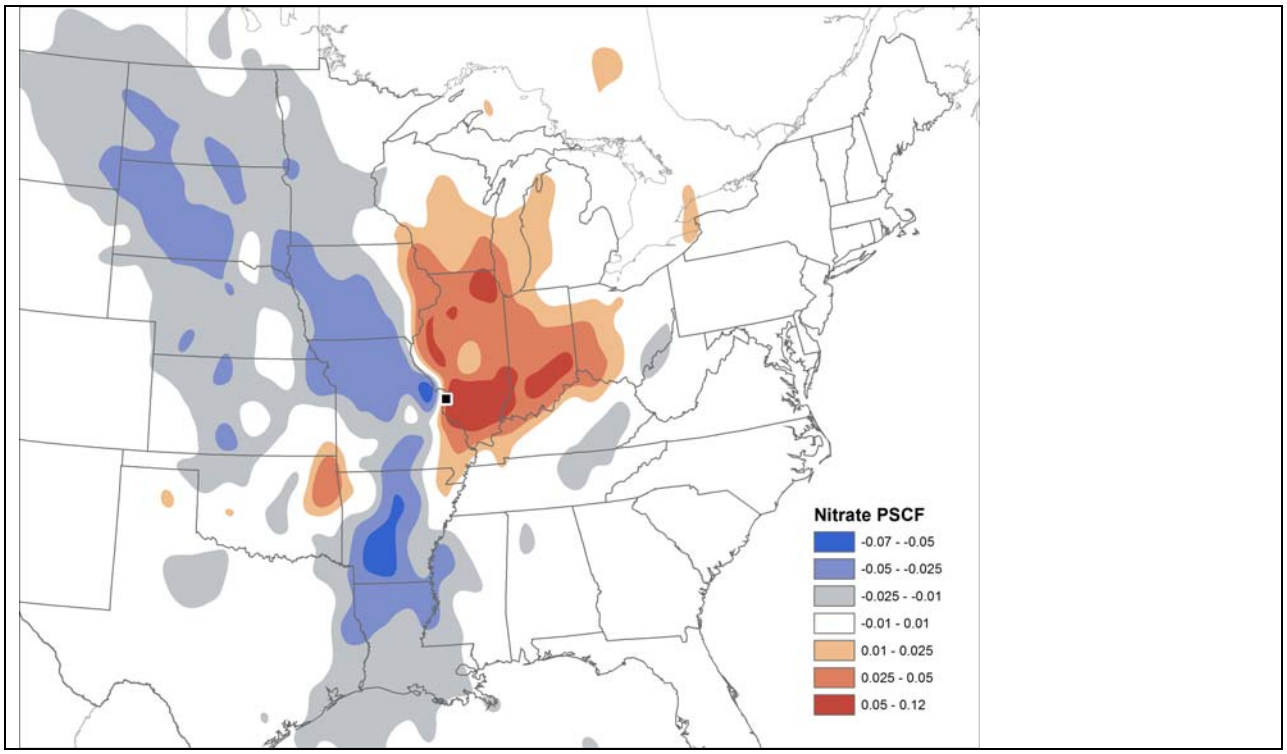

Figure 2-15. Incremental probability, compared to average seasonal climatology, of trajectories passing over a given point leading to high (red) or low (blue) sulfate in St. Louis (Analysis performed by Sonoma Technology, Inc.).

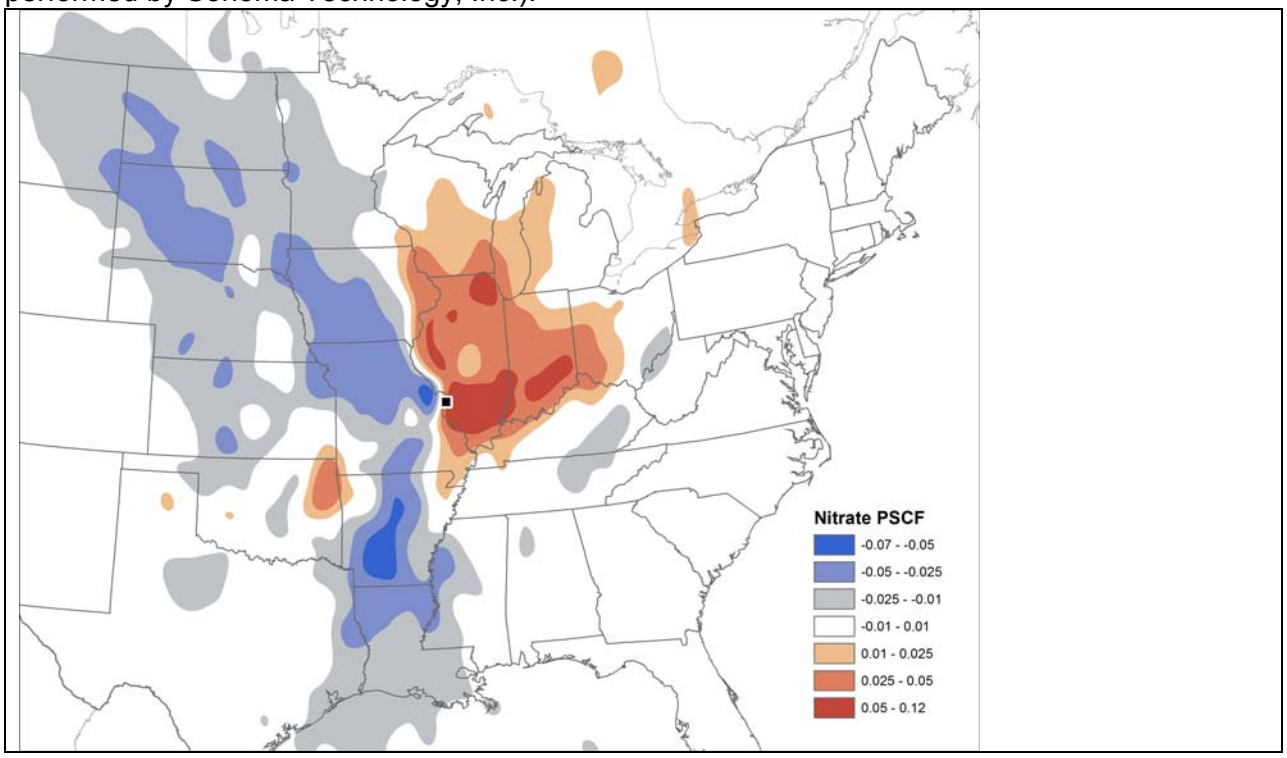

Figure 2-16. Incremental probability, compared to average seasonal climatology, of trajectories passing over a given point leading to high (red) or low (blue) nitrate in St. Louis (Analysis performed by Sonoma Technology, Inc.).

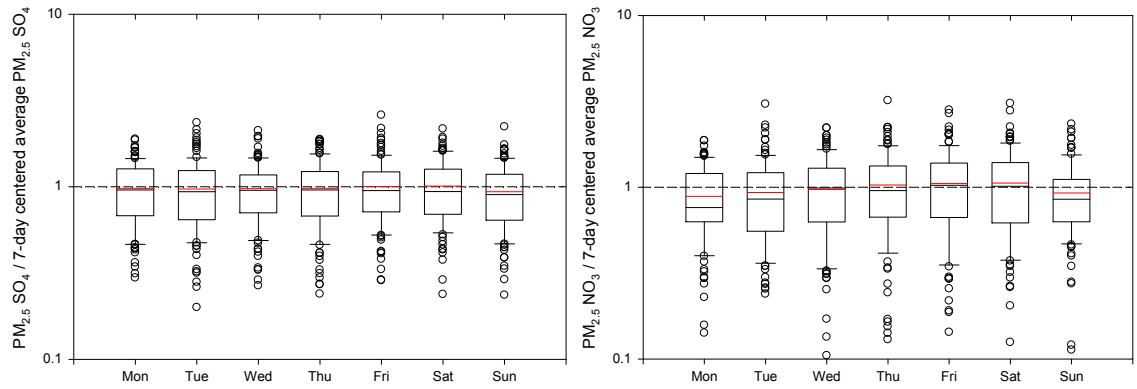

Figure 2-17. Day-of-week distributions for sulfate (left) and nitrate (right) for East St. Louis from June 2001 to May 2003. The red line is the arithmetic mean scaled concentration.

Organic Matter Carbon: In contrast to sulfate and nitrate, which are overwhelmingly formed from atmospheric processing of precursor gas emissions (i.e., SO2 and NOx), organic matter carbon (OMC) arises from both primary emissions and secondary formation. Secondary organic aerosol (SOA) can be transported into the area from regional sources and can be formed over the St. Louis area by both locally generated and regionally transported gaseous organic compounds that are processed by the reactive conditions in an urban environment. In addition to chemical processing of precursor gases, semivolatile organic compounds (SVOC) can condense onto pre-existing aerosol. The complexity of carbonaceous particulate matter, both in terms of the spectrum of organic compounds and the various pathways for their atmospheric reaction, makes this PM component particularly challenging to characterize within a conceptual framework.

Figure 2-18 displays $PM_{2.5}$ organic carbon measured at the rural Bonne Terre site and urban Blair Street (City of St. Louis) site from February 2003 to May 2005 (N = 178). It has not been blank-corrected but as a first approximation the blank corrections for both sites should be similar. The urban excess (urban minus rural) is positive for 89% of the days, and the difference is more negative than -1 $\mu g/m^3$ for only one day. Assuming the St. Louis urban plume does not significantly impact the rural site, the average $PM_{2.5}$ OC excess is 1.4 $\mu g/m^3$, which is 32% of the non-blank corrected urban OC and 41% of the blank corrected OC for this comparison data set. Figure 2-19 shows a time series for the urban excess; there is no discernible seasonal pattern.

The current best estimate is that approximately 60% of the annual average $PM_{2.5}$ organic matter carbon over the St. Louis urban core is regionally transported material and about 40% is locally generated (through local primary emissions and secondary formation of locally emitted and regionally transported precursors). The significant urban excess for elemental carbon brings the total carbonaceous matter (OMC + EC) urban excess to about 50%. This agrees well with the estimate of ~50% observed between East St. Louis and Park Hills for the fall 2001 season using a similar methodology. Chemical transport modeling and receptor modeling are needed to further inform our understanding of this important contributor to $PM_{2.5}$ mass concentrations.

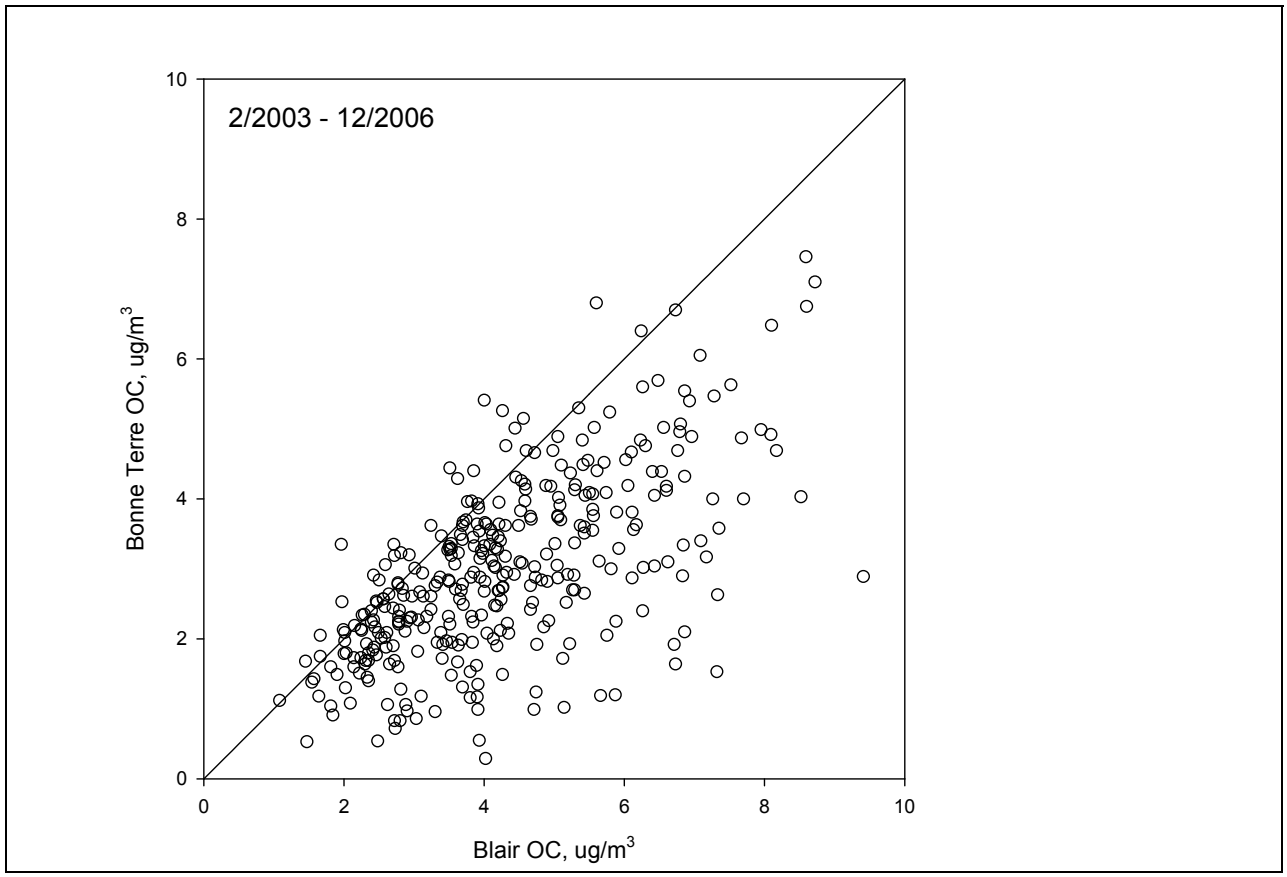

Figure 2-18. $PM_{2.5}$ organic carbon at Bonne Terre (rural site) and Blair Street (urban site in City of St. Louis) speciation sites, without blank correction.

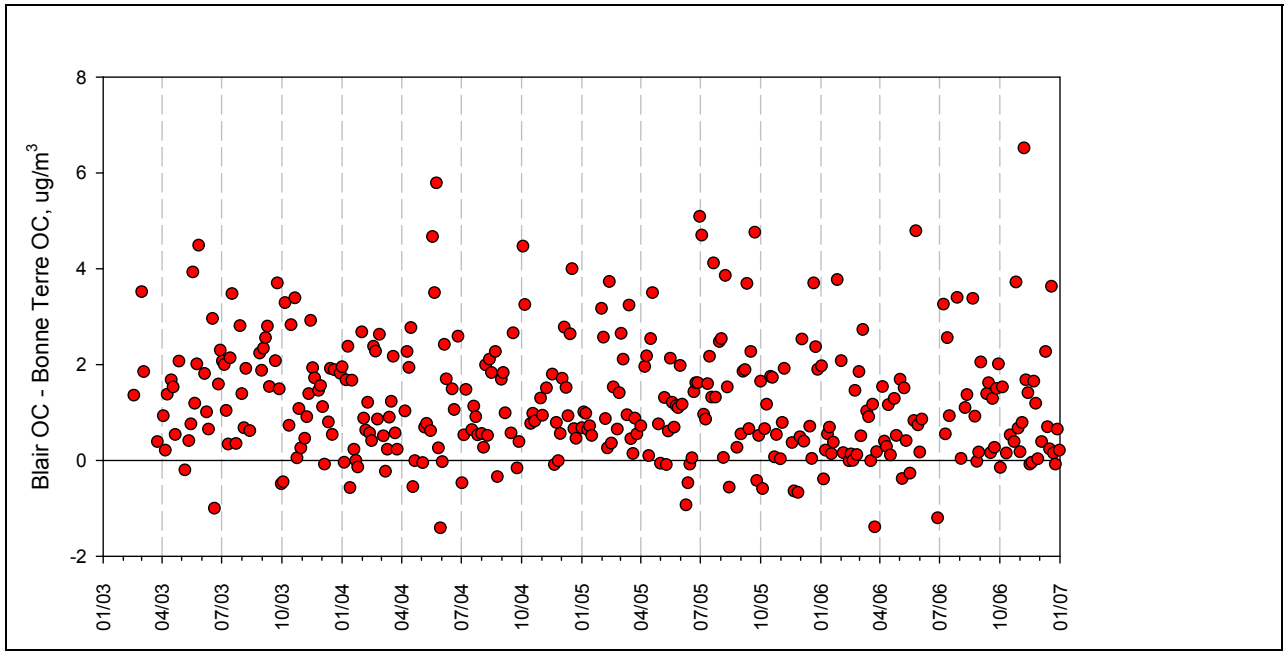

Figure 2-19. $PM_{2.5}$ organic carbon urban excess for Blair Street (urban in City of St. Louis) compared to Bonne Terre (rural site).

2.6 SOURCES AND SOURCE REGIONS CONTRIBUTING TO PRINCIPAL CHEMICALS OF CONCERN

The major chemical components of $PM_{2.5}$ over St. Louis are ammonium sulfate, ammonium nitrate, and carbonaceous matter. Elements of the conceptual model covered in the previous sections have shed light into the general nature of these components, such as the relative roles of regional transport and local emissions. This understanding informs the development and implementation of chemical transport and receptor models for St. Louis, which in turn provide additional insights for the conceptual model. This section summarizes our understanding of sources and source regions contributing to the $PM_{2.5}$ burden over St. Louis. It focuses primarily on results from receptor modeling and allied data analyses but also uses insights gleaned from chemical transport modeling.

Source apportionment of St. Louis $PM_{2.5}$ data has been performed by numerous groups. This section focuses on insights obtained from refinements to the preliminary source apportionment of East St. Louis data published by Lee *et al.* (2006). Garlock (2006) presents the details for most of this work, although subsequent refinements have been made. Figure 2-20 shows the current best-estimate source apportionment of $PM_{2.5}$ mass at East St. Louis using the Positive Matrix Factorization (PMF) receptor model. Chemical species retained for this study, signal noise (S/N) ratio, Q-robust and Q-true scores, and residual analysis of each species are included in Appendix E. For the purpose of this discussion, we adopt the source category assignments of Lee *et al.* (2006) although, as will be shown, there is still ambiguity in the sources represented by certain factors. Note that PMF uses observed PM concentrations and identifies "factors" of PM contributions that are associated with common PM compounds, trace elements and compounds. Based on the composition of the PM, trace elements and compounds, the factors may be interpreted as associated with specific sources. However, there are numerous uncertainties in such associations and many factors are likely composed of several different source categories. However, even with these uncertainties the PMF "source apportionment" is a useful tool for helping to identify the potential sources that contribute to PM concentrations at a given monitor.

The secondary sulfate factor makes up 33% of the study-average $PM_{2.5}$ mass concentration and is dominated by sulfate and ammonium. A secondary nitrate factor was resolved which is dominated by nitrate and ammonium, and accounts for 17% of the $PM_{2.5}$ mass. The carbon rich sulfate factor (CRS), so-named by Lee *et al*. (2006) although it contains much more carbon than sulfate, accounts for 9% of the $PM_{2.5}$ mass. It has a relatively high ratio of EC to OC and its origin is unclear. A refinement to the preliminary apportionment was the reconciliation of the modeled regional and urban contributions to total carbon for the East St. Louis mass apportionment using urban and rural data (East St. Louis, IL and Park Hills, MO). The best agreement was obtained by assigning CRS as a regional source rather than a local source. Furthermore, apportionments performed using less-detailed information for the carbon components (two lumps, EC and OC, rather than the eight lumps used in the best estimate apportionment) redistributed the CRS carbon to the sulfate and nitrate factors which are clearly dominated by regional transport. A wood smoke / biomass burning factor was resolved which accounts for 10% of the $PM_{2.5}$ mass. For the period August 2001 to November 2001, when there were daily measurements at the Park Hills rural site, the urban/rural contrast and modeled source contributions were best reconciled by attributing the wood smoke factor to regionally transported material. It is possible that some $PM_{2.5}$ mass contributions from this factor are local sources, particularly in the wintertime when enhanced residential burning is expected. Aggregating these four factors (sulfate, nitrate, CRS and wood smoke/biomass burning), it appears that regionally

transported material can account for up to 70% of the average $PM_{2.5}$ mass at the East St. Louis site.

The wood smoke / biomass burning factor has a relatively high daily baseline (0.3 $\mu g/m^3$ for the 25th percentile). This factor might be contaminated by other emission sources and the actual biomass burning contributions might be closer to 5% of the $PM_{2.5}$ mass. Efforts to allocate the factor contributions to local and regional source contributions were unsuccessful. However, there is compelling evidence that a significant portion of the biomass burning contributions are regional in origin. Figure 2-21 shows satellite-detected fire locations stratified by season for the period from May 2001 to May 2005. This dataset is a compilation of "hot spot" pixels detected by the MODIS sensors onboard NASA's Terra and Aqua satellites. Terra passes over in the morning and Aqua in the afternoon. The sensor is able to reliably detect fires of 500 acre area, but also detects smaller fires if they are hot enough. Fires cannot be detected during periods of cloud cover and some hot spots are improperly classified as fires (e.g., Chicago and Detroit). High fire densities are observed to the southwest of St. Louis in the spring due to the grasslands fires in Kansas and Oklahoma, and south of St. Louis in the fall with possibly contributions from agricultural burning in the Missouri "boot heel" and eastern Arkansas. Figure 2-22 is a spatial map of the transport pattern for the PMF-resolved biomass burning factor obtained from a Quantitative Transport Bias Analysis (QTBA). This analysis identifies regional transport from a broad area south and southeast of St. Louis as a source of high biomass burning contributions. The emissions hot spot is centered over the Lower Mississippi River Valley, possibly corresponding to agricultural burning. Results from the QTBA are consistent with the spatial density of satellite-detected fires (Figure 2-21). There appears to be a secondary zone of contributions from the Idaho area, and again this is consistent with the map of satellite-detected fires. This analysis provides evidence that the PMF-resolved biomass burning factor is indeed capturing some fire impacts including regionally transported smoke.

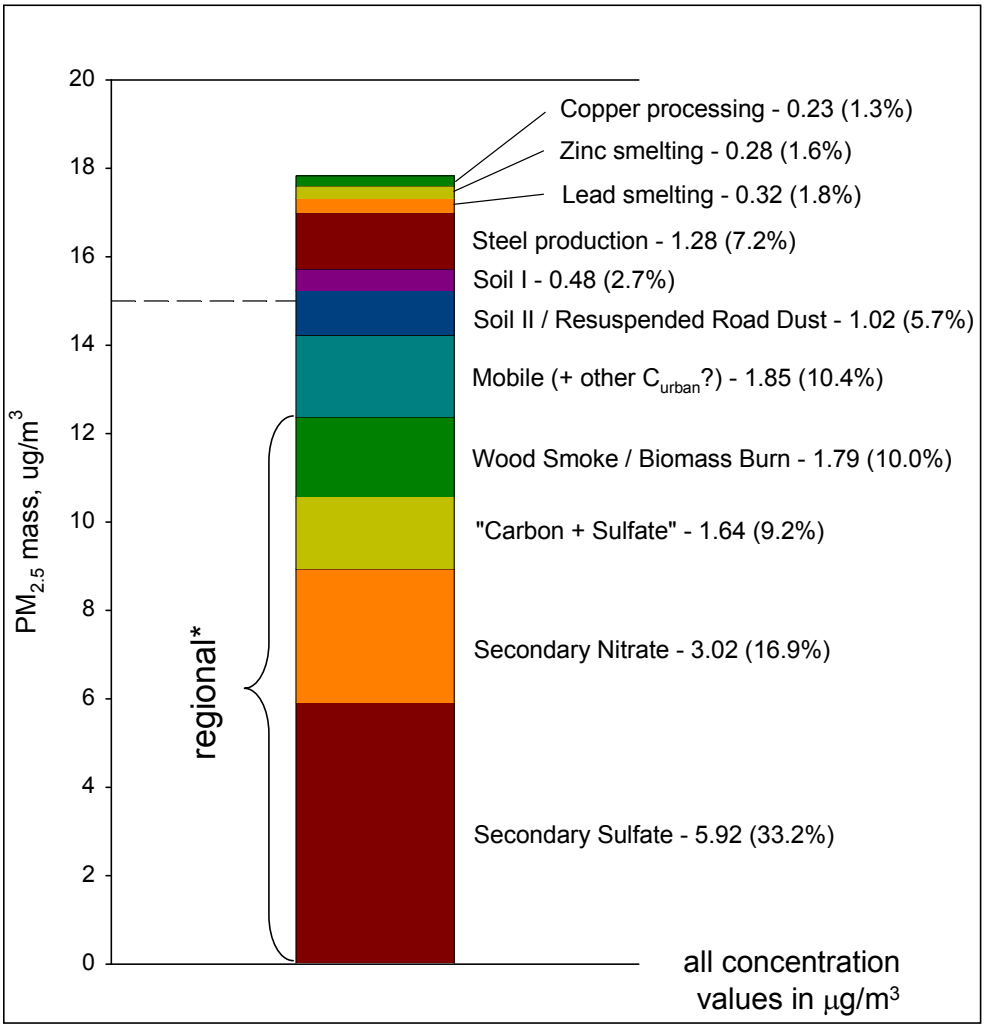

Figure 2-20. Apportionment of $PM_{2.5}$ mass at East St. Louis by Positive Matrix Factorization (EPA PMF). Data from June 2001 to May 2003.

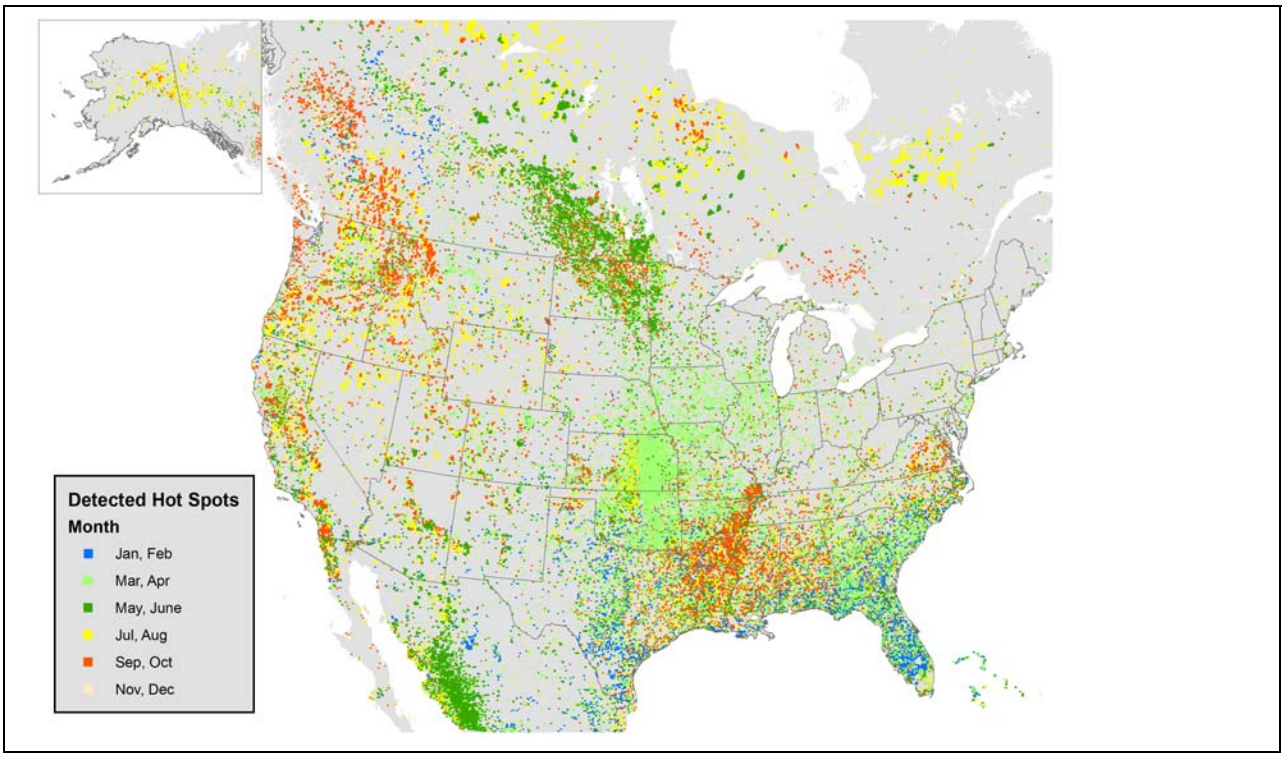

Figure 2-21. Spatial map of satellite detected fire sensitivity.

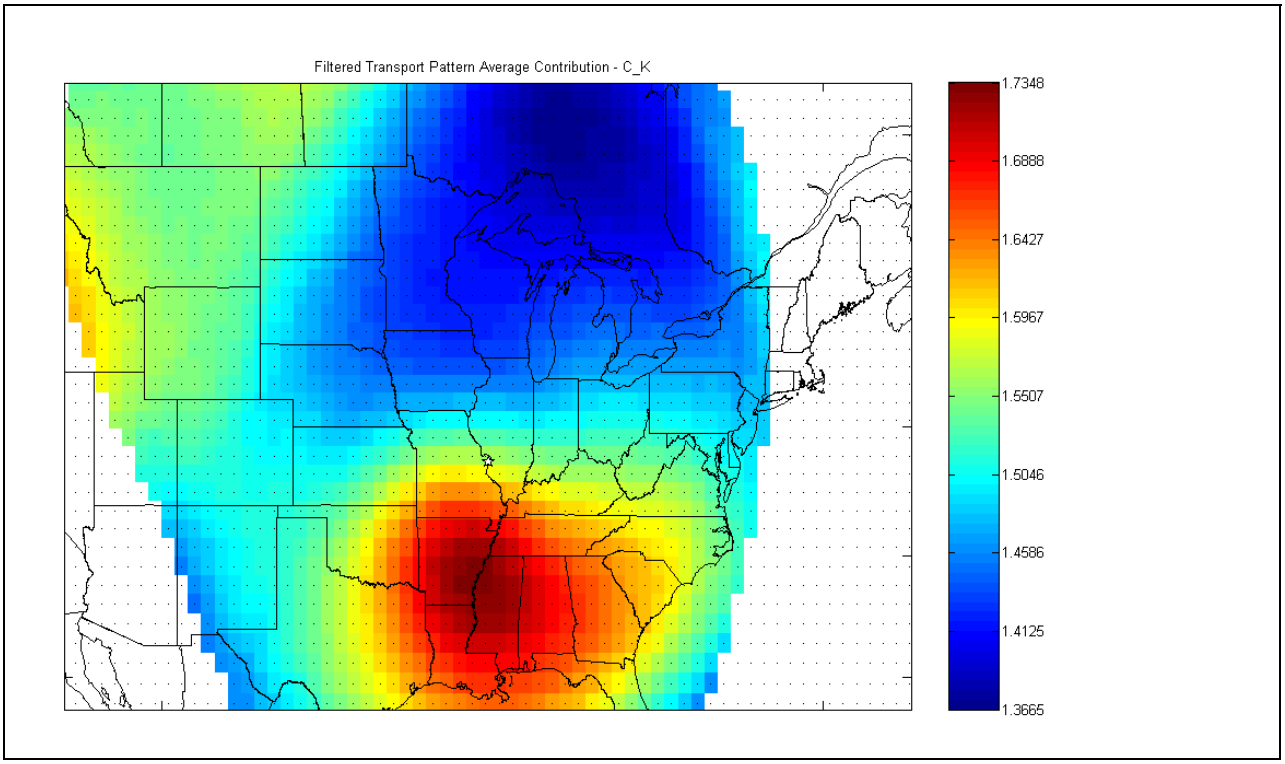

Figure 2-22. Quantitative Transport Bias Analysis (QTBA) filtered transport pattern average contributions to the PMF-resolved biomass burning factor at East St. Louis. (Analysis performed by Dr. Gary Norris of USEPA/ORD).

A carbon-rich factor was resolved which was attributed by Lee *et al.* (2006) to gasoline vehicle sources. It represents 11% of the $PM_{2.5}$ mass and might include contributions from diesel vehicles and other carbon sources, such as industrial point sources located in the urban area. An organic carbon source apportionment is currently being conducted to refine the interpretation of this factor (renamed as a "mobile source" factor). Lee *et al*. (2006) resolved a factor attributed to suspended crustal material ("soil I" factor in Figure 2-20) which accounted for 7% of the mass in the preliminary apportionment and less than 3% of the mass in the refined apportionment. This factor is distinguished by silicon, aluminum, and iron but contains no calcium which we would expect to be present in soil, especially in the St. Louis area which is rich in karst.

A diesel / railroad factor was resolved by Lee *et al*. (2006) which accounted for 3.5% of the $PM_{2.5}$ mass. In addition to EC and OC, this factor contains most of the calcium. In the refined apportionment, this factor is 5.7% of the $PM_{2.5}$ mass and has been renamed the "soil II / resuspended road dust" factor (Figure 2-20). It contains a high loading of calcium and an apportionment which included PMC mass (PM coarse, determined by PM10- $PM_{2.5}$ mass) loaded most of the PMC onto this factor and none of the PMC onto the soil I factor (which has most of the Al and Si). It is possible that this factor does include the diesel emissions contributions but more work is needed to refine the interpretation of this factor. One possibility is that local diesel vehicle activities resuspend road dust and thus the diesel emissions and road dust covary. Both PMC and EC exhibit significantly lower concentrations on weekends and especially Sundays (Figure 2-23). PMC is highest for stagnant surface winds rather than conditions conducive to transport (we would expect windblown dust to increase on windy days). Both these features – lower PMC on weekends and higher PMC for calm winds – suggest a relationship to local industrial activities (which might include the use of diesels).

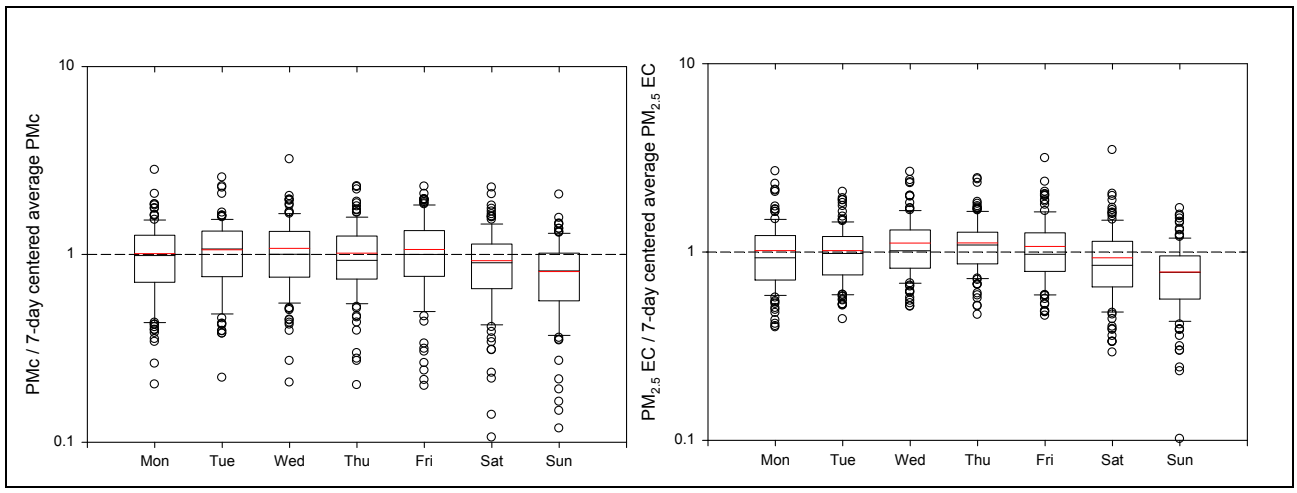

Figure 2-23. Day-of-week distributions for PMC mass (left) and $PM_{2.5}$ elemental carbon (right) for East St. Louis from June 2001 to May 2003. The red line is the arithmetic mean scaled concentration.

A conditional probability function (CPF) plot[5] for the soil II/resuspended road dust factor (Figure 2-24) does not isolate a narrow dominant wind sector for enhanced contributions, but is a fan of wind directions pointing towards the riverfront. However, the wind sector with the strongest relationship points towards an area in Sauget (IL) along the Mississippi River with barge unloading operations (including significant diesel vehicle activity) and a large coal pile. These sources are consistent with the diesel and resuspended road dust signatures of this factor.

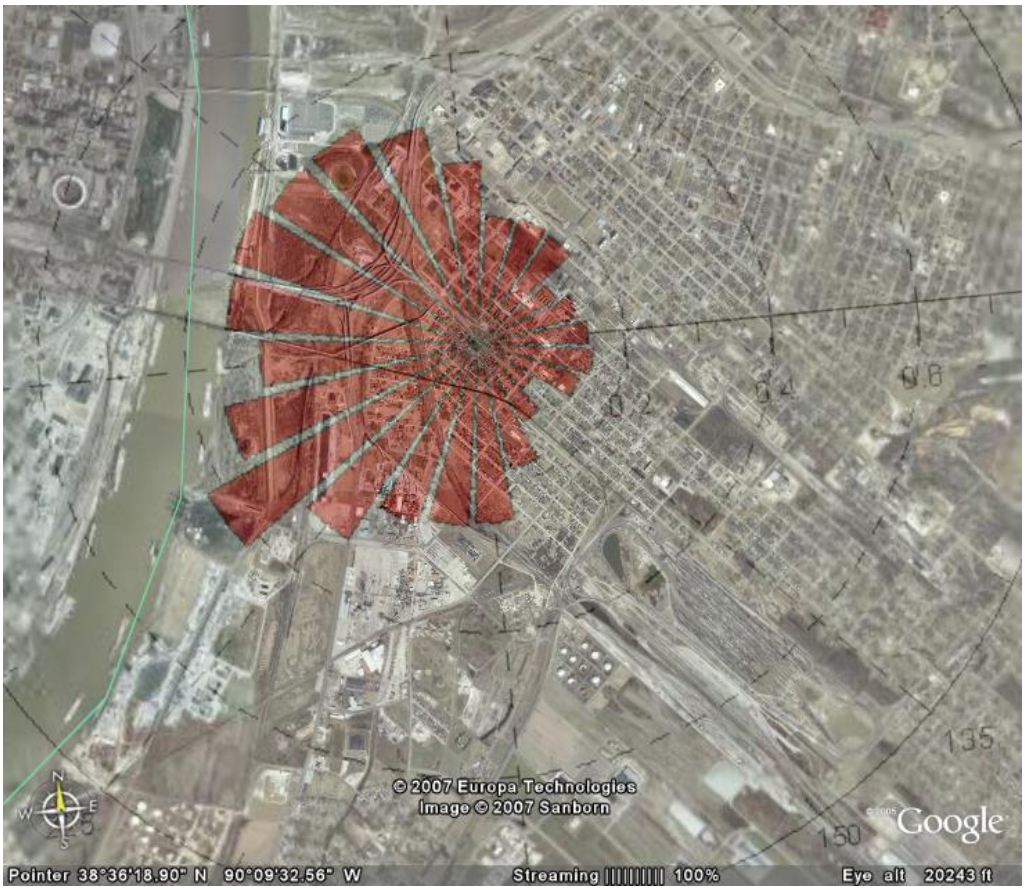

Figure 2-24. Conditional probability function plot for the diesel factor (Soil II / Resuspended Dust in Figure 21) resolved for the East St. Louis site.

[5] The CPF plot was constructed using the days representing the top quartile of the diesel factor contributions to modeled $PM_{2.5}$ mass. The bars on the CPF plot represent the fraction of hours for each wind sector that correspond to a day with one of the top quartile diesel factor contributions. This approach removes, or at least significantly dampens, the wind direction bias observed in the wind rose (Figure 11) to better resolve the bearing of sources with respect to the monitoring site. It does not resolve source strength, but rather it answers the question 'do winds from a given direction more often coincide with elevated concentrations (in this case, the diesel factor) than winds from other directions?' CPF plots are 1-D in space (wind angle only) with the radius representing the relative frequency of observing high contributions for each wind sector; they indicate the bearing of possible sources but not the distance from the receptor.

An iron-rich factor was resolved at East St. Louis which also had significant sulfate, nitrate and carbon. This factor accounts for 7.2% of the $PM_{2.5}$ mass and, based on both the factor profile and a wind direction analysis showing a dominant contribution from due north, is dominated by steelmaking and possibly other industrial operations in the Granite City (IL) area. An additional three factors were resolved which, based on their high loadings of lead, zinc and copper and surface winds analysis indicated contributions from primary lead smelting (Herculaneum, MO), primary zinc smelting (Sauget, IL), and copper products processing (Sauget, IL). In aggregate, these three factors account for 4.7% of the $PM_{2.5}$ mass and might represent admixtures with other emission sources. For example, the copper processing factor has high phosphorus loading which is consistent with contributions from a synthetic organic chemical manufacturing facility located in the same area of Sauget which makes organophosphate compounds (Lee *et al.* 2006).

Contributions from the factors assigned to industrial point sources deserve additional scrutiny to understand the extent to which the factors that were assigned mass contribution from these sources might actually arise from a specific facility. This work is currently in progress and we only briefly describe our initial analysis methodology through an example. Figure 2-25 shows the daily steel factor contributions stratified by daily-average wind direction. The highest concentrations are observed when winds are from the north, consistent with Granite City steelmaking operations being upwind of the East St. Louis receptor on such days. However, there are numerous days with elevated steel factor contributions and daily average winds from the south. Given this is the dominant wind direction these days significantly contribute to the overall mass contribution assigned to the steel factor. The colored markers in Figure 2-25 represent those days with relatively few calm periods (less than 12 five-minute periods with winds below 1 m/s) and relatively narrow standard deviations of the wind direction. There are numerous days with stable winds from the south and small but significant contributions from the steel factor (especially when summing over the frequency of such days). It is unlikely that the steel making operations to the north actually contribute to the steel factor contributions on these days. Open markers represent days that do not meet the designated criteria for frequency of calm winds or stable wind direction. For these days, even though the daily-average winds are from the south the steel making operations still might be impacting the East St. Louis site. High time resolution iron measurements have revealed high concentration plumes of short duration (a few hours) that can lead to relatively high daily averages. Hourly wind direction data for high concentration steel factor days are currently being examined for evidence of at least some periods where the winds are from the north (on either the sampling day or the preceding day) even though the daily-average wind direction is from the south.

In summary, a $PM_{2.5}$ mass apportionment for East St. Louis has provided substantial insights into the sources and source regions significantly contributing to the measured $PM_{2.5}$ concentrations. The analysis suggests that a majority (~70%) of the $PM_{2.5}$ is due to transport, but that there are significant local contributions including contributions from steel production facilities in Granite City. More work is needed to clarify the sources actually contributing to certain factors, especially the factors currently assigned to mobile sources and road dust.

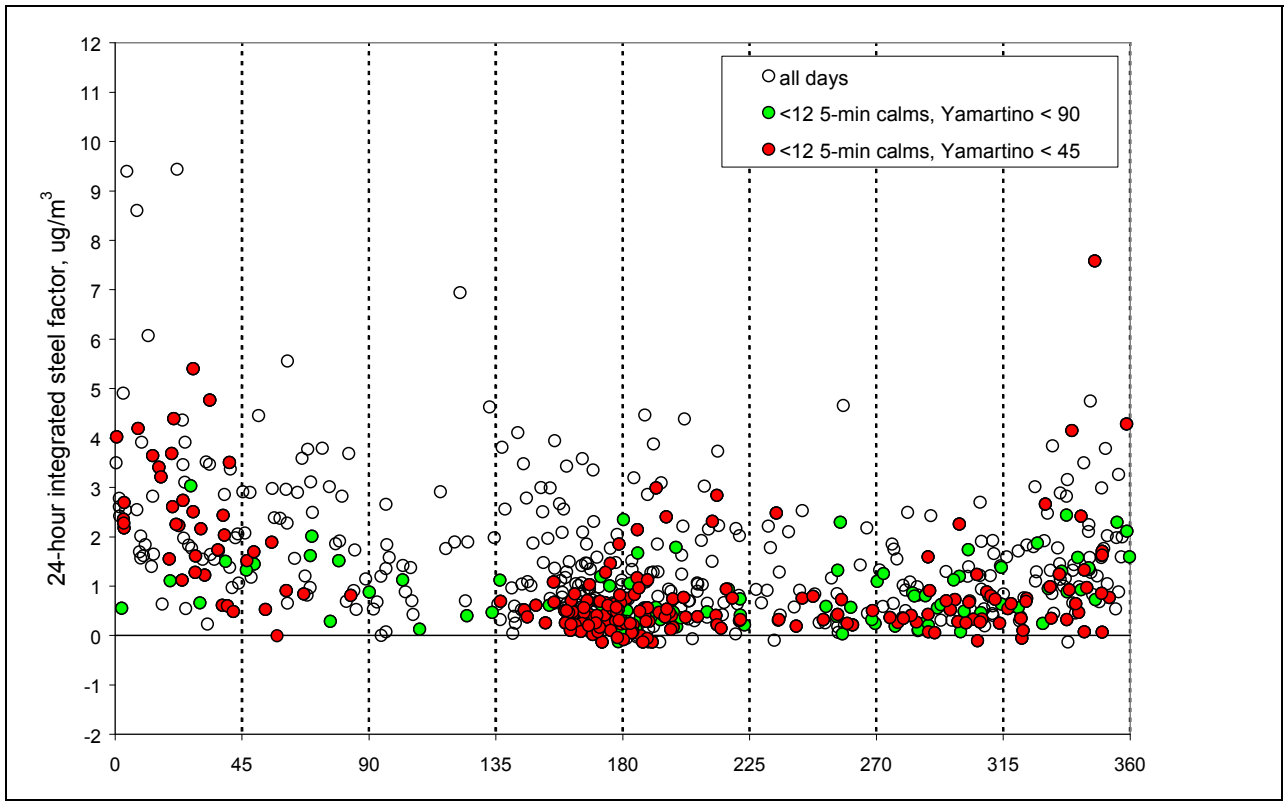

Figure 2-25. PMF-apportioned steelmaking factor contributions stratified by daily-average wind direction. Colored markers represent days dominated by advective conditions and relatively stable wind directions.

Ambient Particulate Matter Burdens at the Current Design Value Site: While the above discussion focused on insights obtained from the routine speciation monitoring network and the St. Louis – Midwest Supersite data sets, another data analysis effort focused on the current FRM monitoring site with the highest $PM_{2.5}$ Design Value site located at 23rd & Madison in Granite City, Illinois (Granite City monitor). While this is not a speciation sampling site, filters from January 2002 to December 2004 collected at the Granite City FRM site were analyzed by XRF for elemental composition and then extracted and analyzed by IC for major ions. This chemical analysis, and a preliminary data analysis performed by Sonoma Technology, Inc., was funded by LADCO. We are currently refining the analysis and interpretation of this data set.

Figure 2-26 displays the 2002 annual average $PM_{2.5}$ mass concentrations for the FRM network deployed in the greater St. Louis region. A gradient of nearly 2 $\mu g/m^3$ exists between two monitors in Granite City (A and B in Figure 2-26) which are separated by only 600 m. The higher value is at a middle-scale site (A) adjacent to a steelmaking facility (Washington Ave.). The other monitor (B), which is the Granite City Design Value site for the St. Louis (MO-IL) nonattainment area for the annual-average $PM_{2.5}$ NAAQS, is also impacted by near-field sources including the steelmaking facility. Note that the middle-scale site (A) on Washington Avenue is not a compliance site for the annual average $PM_{2.5}$ NAAQS that is being addressed in this SIP.

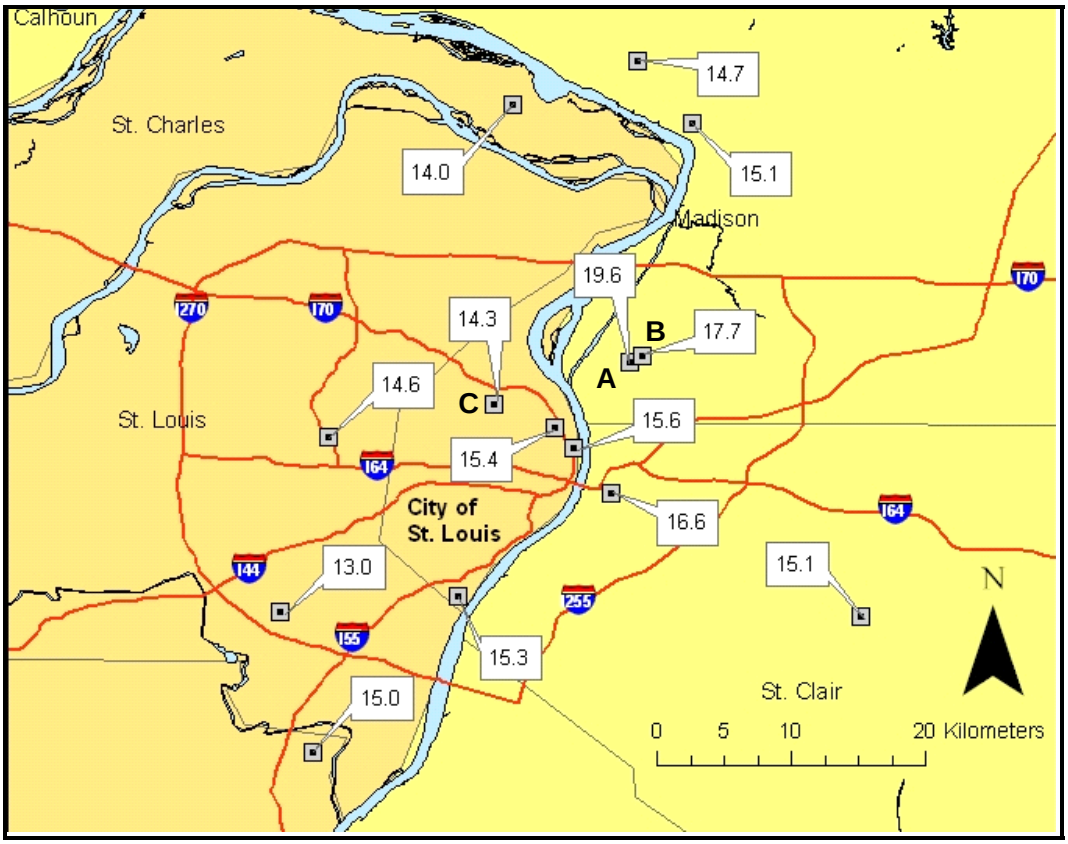

Figure 2-26. $PM_{2.5}$ mass concentrations at the FRM network sites in the St. Louis area, calendar year 2002.

Figure 2-27 is the CPF plot for the $PM_{2.5}$ excess mass concentration measured at the Granite City site compared to the Margaretta Street station (City of St. Louis, MO; "C" in Figure 2-26). The plot was constructed using the top quartile of the concentration difference distribution for FRM data from June 2001 to December 2004. The Margaretta Street station was used as the reference urban background site because it is impacted to some extent by St. Louis urban core activities but is relatively distant from major point sources, industrial activities along the riverfront, and major highways. Mean and median values of the $PM_{2.5}$ daily mass difference distribution (period 2002-2004) were 3.2 and 2.2 $\mu g/m^3$, respectively. Hours with winds from the southeast through southwest have the greatest frequency of days with the top quartile $PM_{2.5}$ excess at Granite City. These wind directions are consistent with the physical footprint for the steelmaking facility (green boundary in Figure 2-27 with coke ovens and blast furnaces in the eastern sector and a basic oxygen furnace, casting, alloying and finishing operations in the western sector). Furthermore, the wind sector with the greatest relative frequency of excess $PM_{2.5}$ observed at the Granite City monitoring site is aligned with the basic oxygen furnace (BOF) portion of the Granite City Steelworks footprint. While CPF plots are powerful tools for identifying the bearing of important emissions sources impacting a receptor, more information is needed to determine the actual sources and their quantitative impacts. However, these results are strong evidence of local contributions to $PM_{2.5}$ at the Granite City FRM monitor due to the local steel production facility.

Figure 2-27. Conditional probability function plot for $PM_{2.5}$ excess mass at Granite City site "B" compared to $PM_{2.5}$ mass at the Margaretta Street station (City of St. Louis, MO). This analysis used FRM data from June 2001 to December 2004 (N = 392) with the top quartile of the excess mass concentration distribution (N = 98) used to define elevated concentrations at the Granite City site. The green line defines the footprint of an integrated steelmaking facility.

Chemical speciation was performed on the FRM filters at the Granite City monitoring site (B). Species concentrations were stratified by the quartiles for the distribution of the daily $PM_{2.5}$ excess at Granite City compared to Margaretta. Figure 2-28 shows box plots for $PM_{2.5}$ iron (Fe) and manganese (Mn) mass concentrations, two signature species of steel production operations. Both Fe and Mn concentrations increase with increasing $PM_{2.5}$ excess mass at Granite City, consistent with steelmaking operations having an influence on days with high excess mass. The mean $PM_{2.5}$ iron concentration was 2.0 $\mu g/m^3$ (3.1 $\mu g/m^3$ assuming the iron has composition FeO_2) for the top quartile of the excess $PM_{2.5}$ mass distribution. Assuming iron in the bottom quartile represents the urban baseline (mean 0.2 $\mu g/m^3$, which is identical to the $PM_{2.5}$ iron concentration at the Blair Street STN site near the St. Louis urban core) and subtracting this value out from the Granite City B site iron concentrations, the 2002-2004 study-average FeO_2 from local (Granite City area) sources would be about 0.8-0.9 $\mu g/m^3$ which is 25-30% of the excess $PM_{2.5}$ mass at Granite City for the same time period. While this analysis does not mean the integrated steelmaking facility is responsible for all of the excess $PM_{2.5}$ mass observed at this site, it is likely a significant contributor with fine PM iron a large component of the excess mass. Additional analysis is underway to further quantify local source contributions to the $PM_{2.5}$ mass concentration excess at the Granite City site.

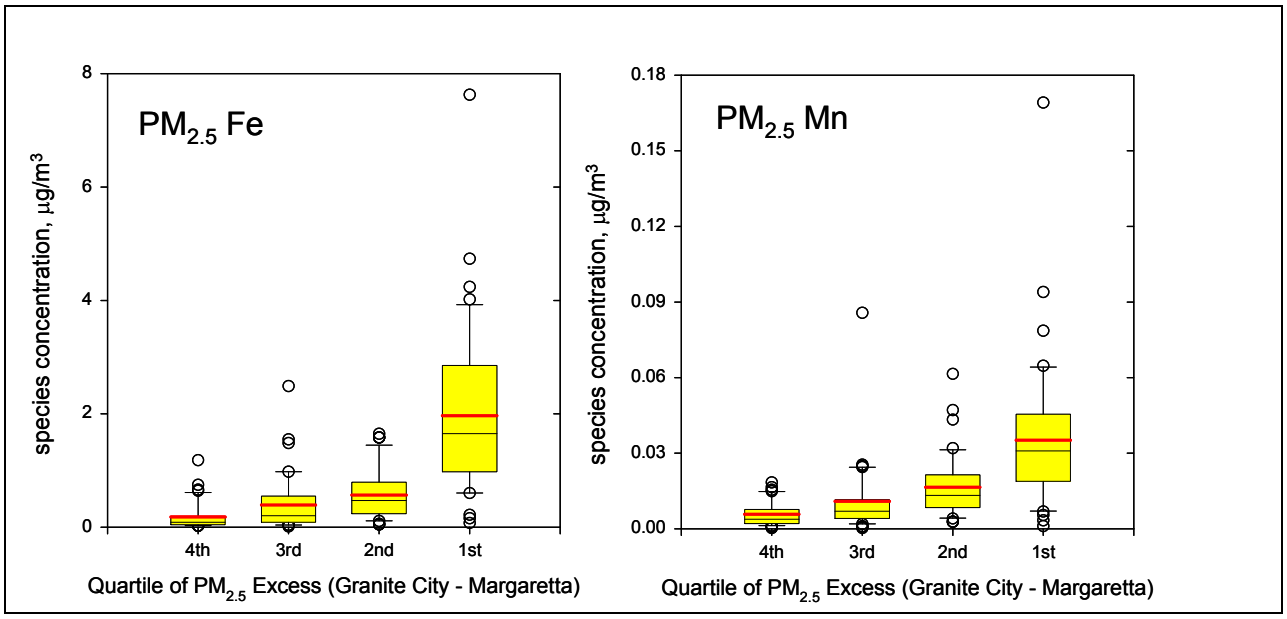

Figure 2-28. $PM_{2.5}$ Fe and Mn concentrations stratified by quartiles for the distribution of excess $PM_{2.5}$ mass at the Granite City site compared to the Margaretta site (City of St. Louis, MO). XRF analysis performed on the Granite City FRM samples for 1-in-6 day data from January 2002 to December 2004 (N = 167).

2.7 DETERMINISTIC SOURCE APPORTIONMENT MODELING

The PM Source Apportionment Technology (PSAT) in the Comprehensive Air-quality Model with extensions (CAMx) was used to estimate the source categories, regions and species that contribute to annual $PM_{2.5}$ concentrations in the St. Louis area. CAMx/PSAT was applied for the 2002 annual period using the 36/12 km grid structure as described elsewhere in this document. The 2009 Base D (Base 4) emissions were used in the CAMx/PSAT analysis; Base D/4 emissions were preliminary emission estimates that have been updated several times during the course of the study. Most notably is the fact that the Base D/4 emissions overstated fugitive dust emissions in Missouri by approximately a factor of 4, which needs to be accounted for in the interpretation of the results. More details of the CAMx/PSAT PM source apportionment modeling is presented in Chapter 6. Below we just present a summary of results for the Granite City monitor that corroborate the receptor model based source apportionment modeling results presented above.

The St. Louis CAMx PSAT modeling was conducted for the 2002 annual period. The modeling domain was split into source regions consisting of the St. Louis NAA, remainder of Missouri, remainder of southern Illinois, northern Illinois, states near St. Louis and groups of states, etc. The emission inventory was divided into six source categories for the PSAT source apportionment modeling: (1) biogenic sources; (2) on-road mobile sources; (3) non-road mobile sources; (4) electrical generating units (EGU's) point sources; (5) non-EGU point sources; and (6) remainder anthropogenic or area sources. Source apportionment is also obtained for initial concentrations (IC) and boundary conditions (BC). The sulfate (SO_4), nitrate (NO3) and primary particulate matter (PM) PSAT families of source apportionment were modeled. PSAT was not used to apportion secondary organic aerosol (SOA) to source regions and categories. However, the CAMx model separately tracks SOA due to biogenic and anthropogenic VOC emissions so those distinctions are retained in the interpretation of the source apportionment modeling results. Version 4.4 of the CAMx model was used.

Figure 2-29 presents the PSAT annual $PM_{2.5}$ source apportionment by source categories and PM species. The largest source category contribution is "area" sources. As noted above, Missouri fugitive dust emissions in the 2009 Base D/4 emissions are overstated by approximately a factor of 4 which if included would result in area sources being the largest source category contribution. Accounting for the overstated fugitive dust emissions, the area sources and EGU point sources contribute a little over 3 $\mu g/m^3$ each to the annual $PM_{2.5}$ concentrations at Granite City monitor. The EGU contribution is dominated by sulfate, whereas the area source contributions are several species including soil, primary organic aerosol (POA), nitrate and sulfate. Non-EGU points is the next most important source category contributing a little over 2 $\mu g/m^3$ that is composed of sulfate, nitrate and other $PM_{2.5}$ (soil). On-road mobile and non-road mobile sources contribute a little over and a little less than 1 $\mu g/m^3$, respectively, that is composed mainly of nitrate with a little POA and elemental carbon (EC). BCs also contribute approximately 1 $\mu g/m^3$ that is mainly sulfate. The biogenic contribution listed in the furthest left bar in Figure 2-29 refers to just the biogenic contribution due to biogenic NOx emissions and is very small. The PM contributions due to biogenic VOC emissions is listed under secondary organic aerosol biogenic (SOAB) that is the farthest bar to the right in Figure 2-29 that is approximately 0.5 $\mu g/m^3$. Note that Lewandowski and co-workers (2007) estimate SOAB in the St. Louis area due to isoprene alone is approximately 2.5 $\mu g/m^3$. However, CAMx Versions 4.4 used in the PSAT analysis does not include SOA from isoprene. Any future CAMx modeling should be performed using CAMx Version 4.5 that includes the isoprene SOA formation pathway.

Figure 2-30 displays the CAMx/PSAT annual $PM_{2.5}$ source apportionment by source region and source category. Even accounting for the overstated fugitive dust emissions, by far the largest source region contributing to annual $PM_{2.5}$ concentrations at Granite City are area sources within the St. Louis NAA. The next most important source regions are southern Illinois and Missouri.

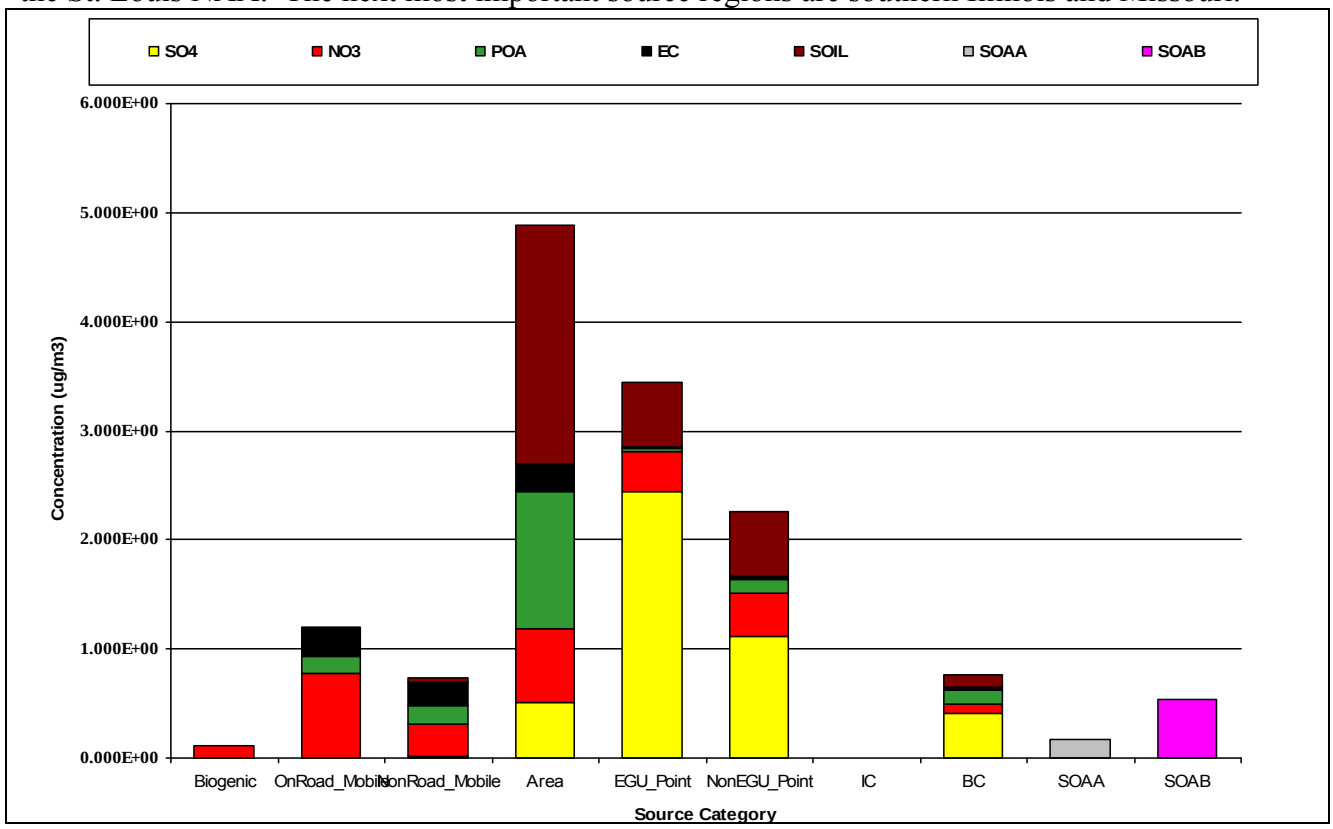

Figure 2-29. CAMx/PSAT estimated contributions to 2002 annual $PM_{2.5}$ concentrations at the Granite City FRM monitoring site by source category and PM component.

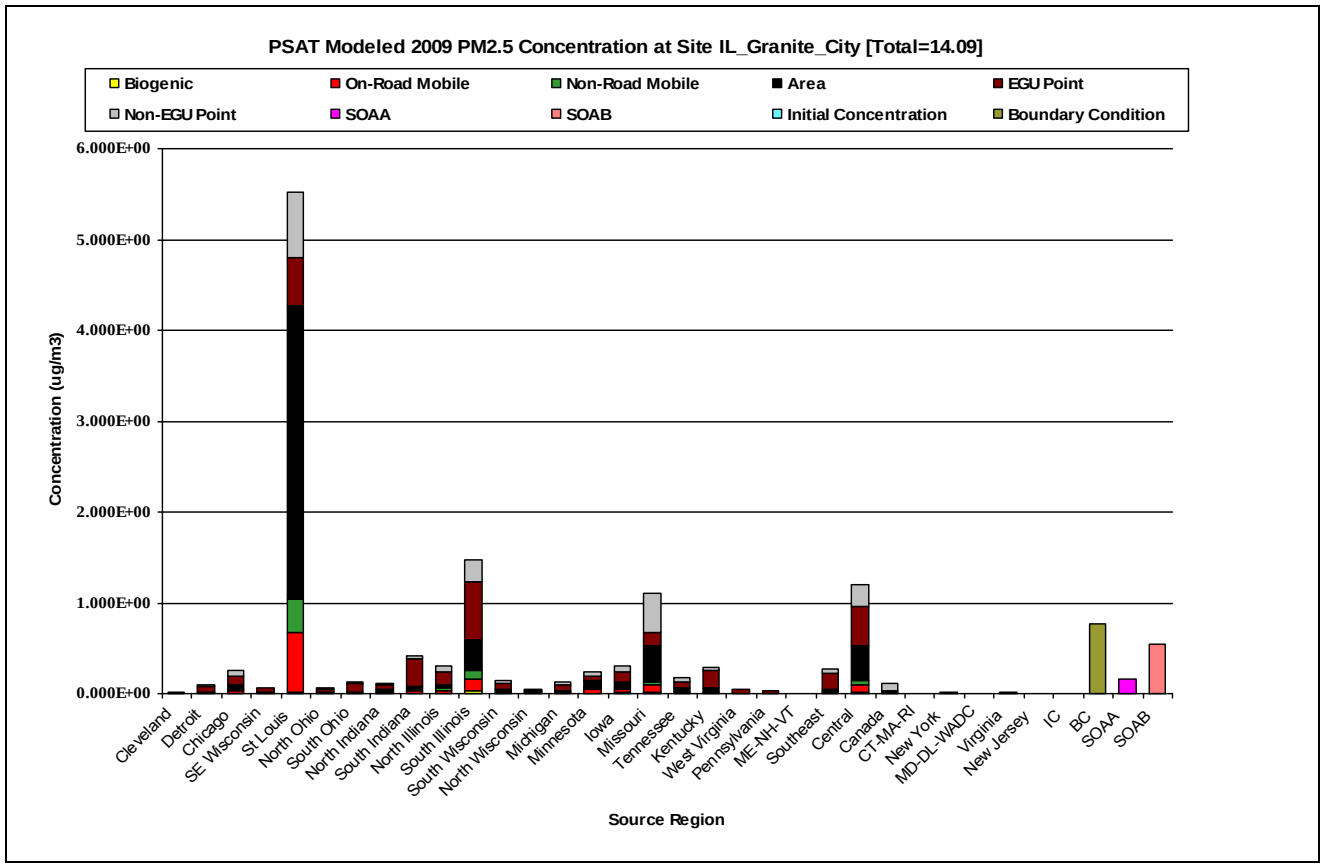

Figure 2-30. CAMx/PSAT estimated contributions to 2002 annual $PM_{2.5}$ concentrations at the Granite City FRM monitoring site by source region and source category.

2.8 IMPLICATIONS FOR THE ST. LOUIS $PM_{2.5}$ SIP

Strategies to reduce the ambient fine particulate matter burden over St. Louis considered the complex array of emission sources that exert influence on different spatial and temporal scales. Analyses underlying the conceptual model demonstrate that regionally transported particulate matter is largely sulfate, nitrate, ammonium and carbon. Regional transport is the dominant source of sulfate over St. Louis, although there might be some local contributions on the highest sulfate days. Regional transport is also the dominant source of nitrate, although local emission sources appear to account for about 20% of the annual average nitrate at the urban core. Fine particulate matter mass concentration reductions to be gained from regional control strategies for SO_2 and NO_x will depend on whether the airshed is HNO_3- or NH_3-limited for ammonium nitrate production. The limiting reactant might vary by time and space, even within the airshed. If the system is NH_3-limited, then sulfate ambient concentration reductions from SO_2 emission controls might be partially offset by increased ammonium nitrate concentrations (a phenomenon referred to as "nitrate replacement"). On the other hand, SO_2 emission reductions will be most effective (in terms of total fine PM ambient mass concentration reductions) if the system is HNO_3-limited. Analyses for other Midwest sites suggest this region of the country is HNO_3-limited. The conceptual model provides a description of the synoptic weather patterns and air mass transport regimes associated high sulfate and nitrate.

Regionally transported particulate organic matter carbon (OMC) is likely primarily secondary organic aerosol (SOA). Gaseous hydrocarbon emissions arise from both anthropogenic and biogenic sources upwind of St. Louis. Isoprene can react to form particulate matter upon mixing with NO_x from rural point source plumes or within the urban area. If the isoprene pathway is

found to be a major contributor to SOA over St. Louis, there might be opportunities to reduce its impact through reductions in the reactants driving its conversion. Regionally transported material should be spatially homogeneous across the nonattainment area but is subject to significant year-to-year variations from changes in synoptic scale weather patterns. This behavior makes virtually all sites in the metropolitan St. Louis area susceptible to exceedances of the annual average NAAQS. Sites in downtown St. Louis and the Metro East area are particularly vulnerable because there are local point and area source contributions which can be significant contributors to $PM_{2.5}$ mass.

The current design value monitor for the St. Louis nonattainment area (annual average $PM_{2.5}$ NAAQS) is located in Granite City, Illinois. This site certainly has significant impacts from local point sources, including but not necessarily limited to the US Steel Granite City Steelworks. The compliance monitor in East St. Louis, 10 km south of Granite City, also has exceeded the annual average $PM_{2.5}$ NAAQS in the recent past. Source apportionment for this site for data collected from June 2001 to May 2003 suggests 60-70% of the $PM_{2.5}$ mass is regionally transported material from outside the nonattainment area. Wood smoke (biomass burning) was a significant contributor to $PM_{2.5}$ measured at East St. Louis from June 2001 to May 2003. While there are some contributions from regionally transported wood smoke (such as distinct forest and grasslands fires) it is quite possible that significant contributions arise from local burning activities such as residential fireplaces and wood stoves, and possibly outdoor waste burning ("burn barrels", including yard waste). The relative contribution of local and regional sources to total wood smoke burden is being investigated. USEPA is currently examining methodologies for analyzing routine samples from the compliance monitoring network for wood smoke, including chemical analysis for soluble potassium ion and levoglucosan. It is possible that more data on the temporal and spatial structure of such markers would provide insights into the local versus regional split for wood smoke contributions.

Nearly 19% of the $PM_{2.5}$ mass at East St. Louis from June 2001 to May 2003 was apportioned to mobile sources and suspended soil. However, this estimate likely also includes other, non-mobile source urban scale primary emissions which cannot be adequately resolved in a conventional $PM_{2.5}$ mass apportionment. Most of the mass apportioned to these sources is carbon, and an organic carbon source apportionment is currently in progress to refine the contributions estimates for carbonaceous particulate matter. There is a strong coupling between $PM_{2.5}$ EC and coarse particulate matter (PMC) mass. One hypothesis is PMC at the East St. Louis site is significantly influenced by activities also emitting EC such as diesel vehicle traffic (i.e., road dust PMC co-varies with tailpipe EC).

About 12% of the $PM_{2.5}$ mass at East St. Louis from June 2001 to May 2003 was attributed to primary point sources. Separate contribution estimates were obtained for steelmaking, lead smelting, zinc smelting and copper processing and in each case the wind direction of enhanced impacts was consistent with known point source locations. However, more work is needed to understand the extent to which the highlighted facilities actually contribute to the resolved contributions. In some cases, there is clearly admixing of the source plume with other, nearby sources. In other cases, there are positive concentration contributions on days with stable winds that should carry the plumes from these sources away from the monitoring site.

While the East St. Louis observational data analysis and source apportionment provides substantial insights into ambient fine particulate matter in St. Louis, impacts from local emission sources are quite possibly not representative of the entire St. Louis area. For example, when modeling each site individually the steel processing impacts at Blair Street (City of St. Louis) are

much lower than the impacts at East St. Louis although the Blair Street site is closer to Granite City. Perhaps this pattern emerges because surface wind frequencies favor material being transported from Granite City to East St. Louis than to the City of St. Louis (northerly surface winds are much more common than northeasterly/easterly surface winds). The $PM_{2.5}$ mass apportionment of Lee and Hopke (2006) for Arnold (MO) resolved a motor vehicle factor which exhibited enhanced contributions on days with surface winds from the southeast through southwest. This is inconsistent with conventional wisdom that motor vehicle contributions should be greatest in the urban core. Such inconsistencies present a barrier in using receptor modeling results in a control strategy development context.

Ultimately, the conceptual model for elevated PM concentrations in the St. Louis reveals impacts from upwind sources (outside the nonattainment area) for sulfate and nitrate along with some local impact that vary by season. In addition, there are indications of both regional and local components to carbonaceous mass at many urban monitors. At the Granite City (IL) design value site, there are indications of regional, metropolitan, and local source impacts with a strong indication of direct PM impacts from the U.S. Steel Granite City Works.