# St. Louis – Midwest Fine Particulate Matter Supersite

## REVISED FINAL REPORT

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between the United States Environmental Protection Agency and Washington University in St. Louis

# Submitted by:

Jay R. Turner
Washington University
Campus Box 1180, One Brookings Drive
St. Louis, MO 63130-4899
(jrturner@wustl.edu)
314-935-5480

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# St. Louis – Midwest Particulate Matter (PM) Supersite Final Report

Washington University in St. Louis Jay R. Turner, Principal Investigator

#### 1. Introduction

The overall goal of the St. Louis - Midwest Supersite was conduct aerosol physical and chemical measurements needed by the health effects community, the atmospheric science community and the regulatory community to properly assess the impact of particulate matter exposure on human health and to develop control strategies to mitigate these effects. Metropolitan St. Louis is a major population center (2.5 million) well isolated from other urban centers of even moderate size, and is impacted by both distant and local sources. Local industry includes manufacturing, refining, and chemical plants. St. Louis is climatologically representative of the country's eastern interior, affected by a wide range of synoptic weather patterns and free of localized influences from the Great Lakes, Ocean, Gulf, and mountains. It accordingly provides an ideal environment for studying the sources, transport, and properties of ambient particles.

The St. Louis - Midwest Supersite commenced detailed measurements of ambient particulate matter (PM) in the St. Louis area in April 2001 with some measurements sustained through March 2005. This four-year measurement program was funded by various organizations. A cooperative agreement between USEPA OAQPS/ORD and Washington University established the foundation for the program (including infrastructure) and supported one year of measurements (April 2001 – May 2002). A grant through USEPA Region VII, with contributions from USEPA, Missouri DNR, CENRAP and LADCO/MRPO, permitted a majority of the initial measurement platform to be sustained through at least May 2003. Subsequently, LADCO/MPRO funded a skeletal suite of measurements through March 2005. Portions of the measurement program were also funded by the Electric Power Research Institute (EPRI).

The lead institution for the St. Louis Supersite was Washington University in St. Louis (Jay Turner, PI). The following groups were formally involved in the measurement program.

- Washington University in St. Louis (Jay Turner group)
- Desert Research Institute (Judith Chow and John Watson group)
- Georgia Institute of Technology (Rodney Weber group)
- Harvard School of Public Health (Petros Koutrakis group)
- University of Maryland College Park (John Ondov group)
- University of Minnesota (Peter McMurry group)
- University of Wisconsin Madison (James Schauer group)

Additional collaborators in the St. Louis – Midwest Supersite Consortium included (affiliations at the time of their core involvement with the consortium):

- George Allen, Harvard School of Public Health
- Alan Hansen and Tina Bahadori, EPRI
- Rudolf Husar, Bret Schichtel and Warren White, Washington University

There were three primary objectives for this monitoring program:

- 1. Implement and evaluate highly time-resolved particle measurement techniques.
- 2. Characterize spatial and temporal (from minutes up to 24 hours) patterns of a large spectrum of particle physical and chemical properties in the St. Louis metropolitan area.
- 3. Investigate particle health effects through integration with allied epidemiological and toxicological studies.

Table 1 summarizes hypotheses linked to each of these objectives.

## Table 1. Hypotheses examined through the St. Louis – Midwest Supersite project.

- 1. Implement and evaluate highly time-resolved particle measurement techniques.
  - 1.1. Continuous methods can now be used to conduct sustained measurements of aerosol number, size and surface area; mass; sulfate, nitrate, elemental carbon and organic carbon composition.
  - 1.2. Experience gained through the field deployment and evaluation of continuous methods can be used by the scientific and instrument manufacturing communities to further the development and evolution of these monitors.
  - 1.3. Comparisons between measurements for related parameters (e.g., Aethalometer black carbon versus thermo-optical elemental carbon) provide insights into their functional differences which in turn influences data interpretation.
- 2. Characterize spatial and temporal (from minutes up to 24 hours) patterns of a large spectrum of particle physical and chemical properties in the St. Louis metropolitan area.
  - 2.1. Data sets collected using an exhaustive platform of continuous monitors and integrated samplers will be suitable for future investigations to develop source/receptor models.
  - 2.2. These data sets can be used to identify and examine the sources, formation processes and physical-chemical properties of ambient particles.
  - 2.3. These data sets, integrated the compliance network and speciation network data, will also be suitable for future investigations to support State Implementation Plan (SIP) development (the St. Louis metropolitan area violates the annual average  $PM_{2.5}$  NAAQS).
- 3. Investigate particle health effects through integration with allied epidemiological and toxicological studies.
  - No hypotheses this Supersite project was the environmental data collection component needed for the health effects studies.

# 2. Scientific Findings

The St. Louis Supersite program has generated numerous scientific findings with several studies currently underway or programmed that will further capitalize on the collected data set. This section summarizes the key findings in the context of the objectives and hypotheses presented in Table 1.

#### 2.1. Data and Samples to Support Exposure and Health Effects Studies

The St. Louis Supersite data are being used to investigate relationships between air quality parameters and various health and toxicological endpoints. These projects are funded separate from the Supersites program but draw upon the St. Louis Supersite data (and in some cases the operations infrastructure) and thereby represent significant leveraging of investment in the St. Louis Supersite project. (Objective 3)

- Helen Suh and colleagues (Harvard School of Public Health) conducted a panel study of seniors (> 60 years old) which included field trips into the City of St. Louis urban core. An extensive suite of health endpoints and air quality parameters were measured. Dubowsky et al. (2006) reported that increases in air pollution may be associated with increases in systemic inflammation in older adults. Associations between pollution and short-term changes in inflammatory markers were the strongest for individuals with diabetes, obesity, concurrent diabetes, obesity, and hypertension, and elevated mean inflammatory markers. Dubowsky Adar et al. (in press) examined relationships between particle exposures and exhaled nitric oxide. Fine particle exposures were positively associated with exhaled nitric oxide, suggesting increased airway inflammation from increased particle exposures. Relationships of exhaled nitric oxide to both microenvironmental measures of air quality and central monitoring site measures of air quality (the East St. Louis site) were examined.
- Douglas Dockery and colleagues (Harvard School of Public Health) investigated relationships between ambient air pollutants and ventricular arrhythmias (VA) detected by implantable cardioverter defibrillators. Rich *et al.* (2006) reported that for 24 hour (lags 0-23) moving average pollutant concentration data, there was a statistically significant increased risk of VA with SO<sub>2</sub> and no increased risk of VA associated with PM<sub>2.5</sub> mass, EC, OC, NO<sub>x</sub>, CO, and O<sub>3</sub>. For SO<sub>2</sub>, increased risk of VA was also statistically significant for 12- and 48-hour lags (albeit not at strong as the 24-hour lag). Sulfur dioxide may be the specific toxic agent, or it may be a marker for other pollutants that may be responsible for the associations with ventricular arrhythmias observed in this study. This project capitalized on the high time resolution data which was used to construct moving averages for various air quality parameters. It was limited in its statistical power due to the small sample size for the health effects data and the non-differential misclassification of exposure (i.e. concentrations at central monitor used as proxies for personal exposures).
- Weekly-integrated PM samples in two size fractions (PM<sub>2.5-10</sub> and PM<sub>0.1-2.5</sub>) were collected using a prototype to the ChemVol High Volume Cascade Impactor (Thermo Electron Corporation Model 2400). One year of weekly-integrated samples (mass loadings ~150 mg/sample) were provided to Kevin Dreher (USEPA) for toxicological

studies. A duplicate set of samples was collected and has been archived for use in future studies.

## **2.2 Ambient Particulate Matter Measurement Methods**

This study provided numerous opportunities to evaluate emerging and recently-commercialized methods for measuring ambient aerosol chemical and physical properties. [Objective 1]

Evaluation of emerging on-line methods for the major chemical components of  $PM_{2.5}$  mass

- Semicontinuous aerosol carbon measurements by a first generation commercial Sunset Labs ECOC Field Analyzer (Serial Numbers 1 and 2) exhibited good agreement with 24-hour integrated filter measurements of elemental carbon (EC) and organic carbon (OC). Field robustness and relatively modest operational and maintenance requirements make this instrument suitable for deployment in routine networks. [Bae *et al.* 2004a] (supports hypothesis 1.1)
- Semicontinuous aerosol sulfate measurements by the HSPH thermal/catalytic sulfate monitor (prototype to the Thermo 5020SPA) were highly correlated with 24-hour integrated and 6-hour integrated substrate sulfate and hourly-average PILS-IC sulfate. A pre-production unit operated for one year showed excellent recovery compared to filter sulfate. A short-term intensive with two 5020SPA commercial instruments demonstrated the monitor is suitable for deployment in routine networks. [Allen *et al.* 2004; Deardorff 2004; Goodwin 2005] (supports hypotheses 1.1 and 1.2)
- Semicontinuous aerosol nitrate measurements by the R&P 8400N were typically biased low with respect to both 24-hour integrated filter nitrate and hourly-average PILS-IC nitrate. This negative bias can be explained, at least in part, by a matrix effect. 8400N nitrate recoveries improved in the presence of increasing aerosol carbon, suggesting there can be an electron donor deficiency in chemically reducing nitrate to gaseous NO/NO<sub>2</sub> (a reduction reaction). This effect was experimentally confirmed under field conditions by doping the carrier gas to the instrument with a carbon source (carbon monoxide) which incrementally increased the nitrate recovery. The 8400N shows promise for deployment in routine networks subject to improvements in the instrument design and/or operation to minimize the observed negative bias. [Reid 2005; Reid *et al.* 2005] (in part supports hypothesis 1.1; the instrument is suitable for elucidating qualitative trends but presents challenges for obtaining quantitative data)
- Semicontinuous aerosol sulfate measurements by the Georgia Tech / BNL Particle-into-Liquid Sampler (PILS-IC) during the first year of measurements showed excellent agreement with filter sulfate after screening the data for periods when gaseous SO<sub>2</sub> plumes break through the denuder and cause a positive bias in the sulfate data. PILS nitrate showed excellent agreement with filter nitrate for the first year measurement data. In subsequent years, sustained measurements with modest field staff support presented additional challenges to obtaining high data quality. Using July 2004 June 2005 data, a methodology was developed for adjusting PILS-IC hourly sulfate to match the hourly Thermo 5020SPA sulfate. These sulfate data adjustments were applied to the nitrate data resulting in excellent agreement between PILS-IC nitrate and filter nitrate. [Yu 2005; Ryszkiewicz 2006] (in part

- supports hypothesis 1.1; this work did not determine whether the contemporary version of the PILS-IC unit is suitable for routine monitoring deployments)
- The Weber group (Georgia Tech) developed a PILS system coupled to a total organic carbon (TOC) analyzer. The sample is filtered prior to reaching the TOC analyzer and thus the instrument measured the water-soluble organic carbon (WSOC) fraction of ambient particulate matter. A PILS-WSOC was deployed at the St. Louis Supersite for nearly six months. This was the first sustained field deployment of this instrument which has subsequently been used in several field campaigns. [Sullivan *et al.* 2004] (supports hypothesis 1.1 that sustained measurements could be conducted with no intent to determine suitability of this prototype instrument for routine deployments)

Data analysis advances for accepted semicontinuous measurement methods

- The Magee Scientific Aethalometer has been deployed in routine networks including the National Air Toxics Trends Sites (NATTS). An Aethalometer operated continuously at the East St. Louis site for five years. Several insights were obtained into the black carbon concentration data. (supports hypothesis 1.3)
  - O The Aethalometer response is subject to "optical saturation" as the collection media loads with light-absorbing particles. This is manifested as a step increase in the reported BC concentration across a filter tape advance. The nature of the artifact can be robustly quantified using collocated Aethalometers. Data from a single instrument can be used to quantify the artifact (for averaging times of at least a month) if care is taken to minimize measurement noise. The optical saturation artifact exhibited a distinct seasonal structure with highest artifact in the winter and lowest artifact in the summer. One hypothesis is that sulfate aerosol increases the effective mass absorption efficiency of the aerosol either internally mixed or as an external mixture on the filer tape and this effect partially offsets optical saturation. [Goodwin 2005]
  - o Based on the St. Louis Supersite data, Aethalometer black carbon (BC) exhibits a stronger correlation with EC from the IMPROVE TOR method than the NIOSH TOT method, suggesting the former is a better surrogate for light absorbing carbon than the latter. Variations in the relationship between BC and NIOSH EC can be explained by variations in sulfate concentrations, consistent with the optical saturation measurement artifact being sensitive to the single scattering albedo. [Goodwin 2005]
  - o The Aethalometer response can be deconvoluted into low- and high-frequency contributions if care is taken to minimize measurement noise. These components likely indicate the relative contributions from near-field (middle- and finer-scale) and far-field (neighborhood- and coarser-scale) black carbon emission sources. [Turner and Allen, *submitted*]

Advances in aerosol physical property measurement methods

• Ambient particle size distributions (range 3 nm – 10 μm) were measured at 5-minute resolution for 25 months. With periodic site visits by the lead researchers (5-6 week intervals), the instruments ran with very modest on-site operator assistance. Robust data validation protocols were developed. While widespread deployment of these instruments is not anticipated, sustained measurements at a network of several sites is strongly encouraged. This would be most effectively implemented through a formal collaboration between

researchers with experience in such measurements and the organizations conducting the onsite monitoring. [Shi 2003] (supports hypothesis 1.1)

- Relative humidity (RH) conditioning worked well to bring the aerosol physical properties to a controlled state. Otherwise, the particle size distribution measurements may have been overwhelmed by variability in aerosol water content. Such RH conditioning also helped to protect the DMA and CPC instrumentation which can be adversely affected by extremely high water content.
- Calibration of the DMA-OPC combination was performed each hour by delivering a stream of ambient aerosol with constant mobility diameter to the OPC. This approach provided a method to reconcile the overlapping portion of the size distribution measured by the DMA and OPC. Furthermore, these measurements provided insights into the mixing state of particles with different optical properties.
- In collaboration with TSI, we evaluated the Electrical Aerosol Detector (Model 3070A). From a field operations perspective, the EAD was robust with high data completeness and low maintenance requirements over a three year measurement period. The EAD response showed good agreement with the corresponding moment derived from detailed size distribution measurements. The EAD response appears to be a good indicator of aerosol surface area deposited in the lung and would be suitable for use in epidemiological studies. [Wilson *et al.* 2007] (supports hypotheses 1.1, 1.2, and 1.3)
- In collaboration with Thermo Scientific, we evaluated the Synchronized Hybrid Ambient Real-Time Particulate (SHARP) monitor (Model 5030) through one year of beta testing followed by a one-year field deployment of two SHARP units with daily FRM gravimetric mass measurements. From a field operations perspective, the SHARP monitors were robust with high data completeness and low maintenance requirements. Collocated precision for daily-average SHARP PM<sub>2.5</sub> mass concentrations was 0.7 μg/m³ (4%). SHARP and FRM PM<sub>2.5</sub> mass concentrations were highly correlated. A regression of the SHARP PM<sub>2.5</sub> concentration on the FRM PM<sub>2.5</sub> concentration had a statistically insignificant intercept and a slope of 1.15. There was no discernible seasonal variation in the SHARP versus FRM relationship. [Hill *et al.* 2006] (supports hypotheses 1.1 and 1.2)

## Comparisons across measurement platforms

• A three month measurement intensive was conducted at the Reserve, KS IMPROVE protocol site (SAFO1). Substrate-based aerosol sampling and analysis methods showed good agreement between the measurements of this deployment and the IMPROVE data. PM<sub>2.1</sub> sulfate and nitrate from the Harvard-EPA Annular Denuder System (HEADS) showed excellent agreement with IMPROVE PM<sub>2.5</sub> sulfate and nitrate. PM<sub>2.5</sub> mass and PM<sub>10</sub> mass using Harvard Impactors were highly correlated – and biased about 10% high – to the respective IMPROVE mass measurements. PM<sub>2.5</sub> total carbon using the University of Wisconsin sampler / ACE-ASIA thermo-optical analysis was about 10% high with respect the IMPROVE data, with greater differences for elemental carbon (EC) and organic carbon (OC) arising from differences in the thermo-optical analysis methods used to obtain the EC/OC splits. [Deardorff 2004]

## 2.3 Aerosol Climatology and Source-Receptor Relationships

The Supersite data set and allied data sets for the St. Louis metropolitan area have been used to elucidate spatial and temporal variability for several aerosol chemical and physical properties. These data are being used to: develop source/receptor models and determine source/receptor relationships for St. Louis; identify and examine the sources, formation processes and physical-chemical properties of ambient particles; and support State Implementation Plan (SIP) development. (Objective 2 and associated hypotheses)

Washington University is currently funded by Missouri DNR to perform observational data analysis and provide technical support for the development of the control strategy SIP for the St. Louis PM<sub>2.5</sub> nonattainment area (annual average NAAQS). Supersite data is being used for chemical transport model validation and diagnostics evaluation. A conceptual model has been developed for ambient fine particulate matter over St. Louis (Turner and Garlock, 2007). USEPA/ORD has funded projects under its Advanced Monitoring Initiative (AMI) which focus on development of source/receptor modeling tools and use the Supersite data as the primary test cases. (supports hypotheses 2.1 and 2.3)

This section summarizes key scientific findings to date for aerosol climatology and source/receptor relationships. The subsequent section summarizes ongoing studies which capitalize on the Supersite data and therefore address Objective 2 and associated hypotheses.

- Annual average PM<sub>2.5</sub> mass concentrations across the metropolitan St. Louis area are spatially heterogeneous. There is a strong influence of regionally transported fine particulate matter into the airshed, leading to a relatively high areawide baseline concentration. However, there exist small but important spatial gradients and/or hot spots with higher concentrations in areas with greater mobile/area source activities (the urban core and riverfront activities) and downwind of major industrial source areas (Sauget / East St. Louis and Granite City). These patterns have important implications to control strategies to meet the annual average PM<sub>2.5</sub> NAAQS (15 μg/m³). Furthermore, based on 2003-2005 data there are monitoring sites in the St. Louis area which violate the recently-promulgated 24-hour PM2.5 NAAQS (35 μg/m³). [Turner and Garlock, 2007; Turner and Allen, *submitted*]
- There exists significant day-to-day variation in ambient PM<sub>2.5</sub> burdens with synoptic scale weather patterns dictating the regionally transported pollutant levels and surface weather dictating the contributions from local emission sources. Calm conditions greatly exacerbate ambient PM<sub>2.5</sub> concentrations at the East St. Louis site, in part due to the close proximity of several significant point sources but also through poor ventilation of the urban mix. High time resolution speciation data has been quite valuable in elucidating the nature of such events. [Turner and Garlock, 2007]
- Annual-average diurnal profiles for most of the measured PM<sub>2.5</sub> physical and chemical properties exhibit a maximum in the nighttime or early morning hours and minimum at midday, demonstrating the significant role of atmospheric ventilation on ground-level concentrations. An exception is sulfate which exhibits a flat annual-average diurnal profile. The sulfate is overwhelmingly regional in nature and has a large dynamic range with

multiday episodes which build over several days and wash out rather dramatically due to synoptic weather transitions. This behavior tends to smear out any underlying diurnal structure upon time averaging. The sulfate diurnal profile constructed by conditioning the data to include only high-sulfate days exhibits a midday maximum which tracks the solar radiation profile, consistent with local sulfate generation superposed on a high regional baseline. However, this midday maximum could also be explained by entrainment from aloft and more work is needed to resolve this observed behavior.

- The annual-average PM<sub>2.5</sub> burden in East St. Louis (as measured by Harvard Impactors) was 18.2 μg/m³ (year 2002) consisting of 24% sulfate, 12% nitrate, and 11% ammonium; 38% organic matter and 4% elemental carbon; 5% metal oxides (mostly crustal material); and 6% other. Sulfate was high in the summer and low in the winter, while nitrate was high in the winter/spring and low in the summer. Carbonaceous particulate matter concentrations were nearly constant across all seasons. [Turner and Garlock, 2007]
- Sulfate is spatially homogeneous across the urban area on a day-to-day basis. Nitrate exhibits greater spatial variability on a day-to-day basis and an intraurban gradient on an annual basis with concentrations highest in the urban core. The annual average nitrate gradient across the metropolitan area is ~20-25%. Organic carbon and especially elemental carbon exhibit significant day-to-day intersite variability. [Turner and Garlock, 2007]
- PM<sub>2.5</sub> mass and sulfate exhibited no discernible day-of-week differences. Nitrate was lowest
  on Mondays and next-lowest on Sundays and Tuesdays, consistent with reduced precursor
  emissions on weekends and a time lag in the atmospheric processing of nitrogen oxides to
  nitric acid. Organic carbon exhibited no discernible day-of-week differences, while
  elemental carbon was lowest on weekends, especially on Sundays. [Bae et al. 2004b; Turner
  and Garlock, 2007]
- Episodes of high sulfate typically corresponded to air masses from the east/southeast including the Ohio River Valley and the Tennessee Valley areas. Synoptic behaviors corresponding to high sulfate were summer anticyclones and stationary fronts. Episodes of high nitrate were observed for a range of synoptic weather patterns, and in some cases nitrate episodes transitioned into sulfate episodes. [Anderson, 2006; Turner and Garlock, 2007]
- Apportionment of PM<sub>2.5</sub> mass by positive matrix factorization (PMF) yielded eleven factors including two factors consistent with secondary processes (factors dominated by sulfate and nitrate), separate gasoline and diesel factors, a soil factor, a biomass burning factor, four point source factors, and one additional factor that was predominantly carbon with some sulfate. Wind directions associated with high contributions from each point source factor were consistent with known emission source locations. [Lee et al. 2006; Garlock 2006; Turner and Garlock, 2007]
  - O Data collected at the Park Hills regional background site demonstrated the sulfate observed in St. Louis is overwhelmingly regionally transported material. Also, comparisons between the East St. Louis apportionment and the East St. Louis and Park Hills measurement data shows that carbon is best reconciled if the aforementioned carbon/sulfate factor is treated as regionally transported material. [Allen and Turner, submitted]

- O Consistent PM<sub>2.5</sub> mass apportionments were obtained using IMPROVE thermal fractions, IMPROVE OC/EC, and NIOSH OC/EC. The carbon/sulfate factor was not resolved when using IMPROVE OC/EC instead of the IMPROVE thermal fractions and the mass from the carbon/sulfate factor loaded onto the sulfate and nitrate factors.
- Over the two-year period June 2001 May 2003, the average source contributions were approximately 60% from secondary sulfate and nitrate (with associated carbon), 18% from mobile sources and airborne soil, 10% from wood combustion, and 12% from industrial point sources.
- O There appears to be significant admixing of sources within the resolved factors and quite possibly misclassification of factors to emission source categories. For example, the biomass factor is consistently above 0.5-1.0  $\mu g/m^3$  and is poorly correlated with PM<sub>2.5</sub> levoglucosan.
- Apportionment of the PM<sub>2.5</sub> primary organic matter by molecular marker CMB for East St. Louis was performed for nominally 1-in-6 day samples over the two-year period June 2001 May 2003. Study-average arithmetic mean contributions (μg/m³) were: meat cooking (1.8); wood smoke (1.4); gasoline vehicles (1.3); diesel vehicles (0.7); road dust (0.2); tire wear (0.1); vegetative detritus (0.1); and natural gas combustion (0.1). While certain portions of the apportionment were deemed representative (e.g. wood smoke), others have raised concern (e.g. meat cooking). [Bae 2005]
- Apportionment of the PM<sub>2.5</sub> organic carbon by PMF for East St. Louis yielded eight factors. Study-average contributions (μg/m³) were: resuspended soil (0.86); mobile sources (0.80); secondary organic aerosol (0.42); wood combustion (0.51); two wintertime combustion factors (0.26, 0.09); and two point sources (0.28, 0.27). The modeled residual was 0.36 μg/m³. Meat cooking was the largest source strength in the CMB apportionment but was not resolved in the PMF apportionment with cholesterol loading onto the resuspended soil factor. [Jaeckels *et al.*, submitted]
- Chemical Mass Balance (CMB) methods require that all relevant emission sources be
  identified and have well-characterized emission profiles. Unidentified and poorlycharacterized emission sources can bias CMB results including the organic molecular marker
  CMB described in the previous bullet. Screening tools have been developed to identify when
  point sources are impacting measurements used in CMB molecular marker source
  apportionment models and applied to the St. Louis Supersite organic molecular marker data
  set. [Bae 2005]
- The ratio of organic matter (OM) to organic carbon (OC) was estimated using two independent methods: (1) a top-down approach which determined the OM/OC ratio needed to reconcile PM<sub>2.5</sub> mass measured gravimetrically and reconstructed measurements of the major chemical components; and (2) a bottom-up approach using organic speciation and molecular marker source apportionment with assumed source-specific OM/OC ratios. Both methods yielded an annual average OM/OC ratio of ~1.8 with relatively little seasonal variation. [Bae 2005; Bae *et al.* 2006]
- PILS-IC measurements included not only sulfate and nitrate but also several additional inorganic ions and three organic acids (formate, acetate, and oxalate). Diurnal profiles with midday maximums for acetate and oxalate were observed in January and November 2002.

These profiles were not observed in warmer seasons, and at least for oxalate are positively correlated with solar radiation and negatively correlated with temperature. One explanation is that these conditions can drive atmospheric formation of the organic acids yet with temperatures cool enough to promote partitioning into the particle phase. Additional work is needed, however, to verify the measured profiles are indeed PM organic acids and not gas phase organic acids breaking through the upstream denuder.

- Black carbon data collected at five-minute time resolution was deconvoluted into high- and low-frequency components. The low frequency component accounted for ~85% of the black carbon mass concentration and exhibited an annual average diurnal profile that mimicked the total black carbon concentration with a morning rush hour maximum and a broad midday minimum. The high-frequency component accounted for ~15% of the annual average black carbon mass concentration and did not exhibit a midday minimum. This pattern occurs because the emission sources responsible for the high frequency component are too close to the receptor to be vertically mixed throughout the mixing layer depth. Weekend diurnal profiles, especially Sundays, exhibited markedly less high frequency contributions than weekdays. [Turner and Allen, *submitted*]
- PM<sub>2.5</sub> mercury concentrations were highly variable over the two year period from June 2001 to May 2003. Daily 24-hour integrated sampling with analysis by XRF revealed extended periods of time (months) with low PM<sub>2.5</sub> mercury but other extended periods with high PM<sub>2.5</sub> mercury. Measurement intensives with semi-continuous monitors for gaseous elemental mercury (Hg<sup>0</sup>), gaseous reactive organic mercury (RGM) and particulate matter mercury (PHG) revealed a series of distinct plumes of duration one-to-several hours. Surface wind directions during these plume events were consistent with bearings for industrial point sources with TRI-reported mercury emissions to the atmosphere. The plumes were not coupled to emissions from the coal-fired utility boilers in the St. Louis area. [Manolopoulos *et al.*, submitted]
- Industrial point source plumes were observed to impact the East St. Louis site. Hourly metals data from the University of Maryland SEAS sampler revealed plumes of one-to-several hours in duration for certain measured metals including iron and zinc, consistent with known sources including an integrated steelmaking facility and a secondary zinc smelter. Plumes for metals such as arsenic were also observed, although the specific emission sources were not conclusively identified. Hourly OC data together with 24-hour integrated organic speciation data identified two distinct PM<sub>2.5</sub> primary OC point sources. PM<sub>2.5</sub> Pb at East St. Louis decreased by ~50% during the measurement study. The timing and extent of this decrease was consistent with the implementation of additional emission controls at a nearby primary lead smelter.
- Lead isotope analysis was performed on 116 filter samples collected at both the urban East St. Louis site and the rural Park Hills site. Relationships between <sup>207</sup>Pb/<sup>206</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb isotope abundance ratios fell along a mixing line between Missouri ores used for lead smelting and contemporary urban lead ratios. In virtually all cases in the urban area, PM<sub>10</sub> samples exhibited isotope abundance ratios closer to the Missouri ores than PM<sub>2.5</sub> samples. This finding suggests that historical lead emissions, perhaps deposited from smelting operations in the metropolitan area several decades ago, might be a significant contributor to contemporary coarse PM lead in the urban area.

#### Aerosol physical properties

- The geometric mean of the PM<sub>1</sub>/PM<sub>2.5</sub> mass ratio was 0.80 and highly correlated (0.97). The geometric mean of the PM<sub>2.5</sub>/PM<sub>10</sub> mass ratio was 0.56 and with moderate correlation (0.82). For comparison, the geometric mean of the PM<sub>2.5</sub> mass ratio for the City of St. Louis Margaretta site (urban residential) to the East St. Louis site was 0.77 and highly correlated (0.96). [Turner and Garlock, 2007]
- Coarse PM mass concentrations (PMc, by difference from PM<sub>2.5</sub> and PM<sub>10</sub> gravimetric mass measurements) exhibited 3-5 day cycles. PMc concentrations were lowest on weekends and especially on Sundays. They were highly correlated with PM<sub>2.5</sub> calcium mass concentrations and typically highest during stagnant conditions. These patterns suggest local (perhaps urban- or finer-scale) fugitive dust emissions might be significant contributors to PMc measured at the East St. Louis site. While the precise sources have not been determined, analyses for the Supersite and St. Louis area speciation sites suggest the emissions might be related to riverfront activities (e.g., barge loading/unloading, materials hauling). [Turner and Garlock, 2007]
- Over two years of sustained measurements, the average particle number concentration was  $4.0 \times 10^4$  #/cm³ (3 nm 2 µm). About 50% of these particles were in the size range 3-10 nm. [Shi 2003]
- Particle number concentration measurements revealed three distinct types of ultrafine (sub-100 μm) events: regional nucleation events; 3-40 nm events strongly associated with SO<sub>2</sub> plumes; and 10-300 nm events strongly correlated with NO<sub>x</sub> and CO. One distinct type of accumulation mode (0.1 1 μm) event was periodically observed and these events were typically coincident with organic carbon plumes. During the first year of measurements, one-or-more of these four classes of events occurred on 95% of the days. Thus, the particle size distribution has a rich texture that can be exploited for insights into aerosol dynamics, climatology and emission source characteristics. [Shi 2003; Shi *et al.* 2007]
- Nucleation events were regionwide as evidenced by the distinct temporal patterns in the size distribution following a nucleation event. Freshly nucleated particles typically appeared shortly after sunrise (although there were cases where nucleation bursts occurred later in the morning). Particle production was not constrained to a simple burst in the morning, however, but rather it typically persisted for a few hours and sometimes throughout the morning. The particle growth rate (dD<sub>p</sub>/dt) following a nucleation event was constant in many cases. [Shi 2003; Shi et al. 2007]
- Nucleation dynamics were coupled with solar radiation, suggesting that photochemical processes played a role in these events. No nucleation events were observed for conditions with solar radiation below 200 W/m<sup>2</sup>. [Shi 2003; Shi *et al.* 2007]
- In contrast to results obtained for Atlanta, nucleation events in St. Louis are not correlated with elevated SO<sub>2</sub> concentrations. However, the particle size distributions for such regional nucleation events are similar to those measured in Atlanta during summer 2002. [Shi 2003; Shi *et al.* 2007]

- Nucleation events were most frequent in the spring, summer and fall (observed on about 1/3 of such days) and rare in the winter. Particle growth rates following nucleation bursts were higher in the summer than the winter. [Shi 2003; Shi *et al.* 2007]
- Ultrafine events in the 3-40 nm size range that were strongly associated with SO<sub>2</sub> plumes also exhibited very high maximum number concentrations (on average about four times higher than the maximum number concentration observed during nucleation events). These events were observed on about 1/2 of days and exhibited no seasonal dependence. [Shi 2003]
- Ultrafine events in the 10-300 nm size range were strongly associated with NO<sub>x</sub> and CO and likely originate from motor vehicles or other combustion sources. These events were observed on about 2/3 of days and exhibited no seasonal dependence. [Shi 2003]
- Accumulation mode events were strongly associated with PM-2.5 mass measured by independent methods. They typically occurred at night under conditions with poor atmospheric ventilation and were associated with organic particulate matter plumes. Their origin is likely emissions from a local point source. These events were observed on about 10% of days and exhibited no seasonal dependence. [Shi 2003]
- Aerosol physical properties exhibited seasonal, weekly and diurnal variability. Summer months featured high volume concentrations and low number concentrations. Annual-average diurnal profiles for aerosol volume, surface area and accumulation mode number concentration a maximum in the nighttime or early morning hours and minimum at midday, demonstrating the significant role of atmospheric ventilation on ground-level concentrations. There was a transition in diurnal behavior at about 30 nm with smaller particles exhibiting an annual-average diurnal profile which peaked in the early-to-mid morning and did not exhibit a midday minimum due to the frequent occurrence of morning nucleation events. Day-of-week differences in aerosol physical properties were weak. [Shi 2003]

## 2.4 Other Leveraging and Data Analysis Activities

Objective 2 was to collect data sets suitable for future investigations. Key scientific findings to date are summarized in sections 2.3 and 2.4. This section summarizes ongoing, funded work which capitalizes on the St. Louis Supersite data set and will provide additional scientific findings. (Objective 2)

• James Schauer (University of Wisconsin – Madison) and colleagues have an EPA STAR grant "Application of Thermal Desorption GC-MS (TD-GC-MS) for the Analysis of Polar and Non-Polar Semi-Volatile and Particle-Phase Molecular Markers" to fully develop, validate, and employ a cost-effective thermal desorption gas chromatography mass spectrometry (TD-GCMS) technique for the analysis of semi-volatile and particle-phase organic compounds, which can be applied to both atmospheric and source samples. In addition to the solvent extraction-GCMS data that has been collected and analyzed (Bae 2005; Bae *et al.* 2005; Jaeckels *et al.*, submitted), organic speciation by TD-GCMS was performed on daily 24-hour integrated samples collected over a two-year period. Analysis of this data is in progress, including source apportionment of the daily time series. Additional funding for this project was provided by EPRI and the Illinois Department of Commerce and Economic Opportunity.

- Michael Kleeman (UC Davis) and colleagues have an EPA STAR grant "Source-Oriented Chemical Transport Model (CTM) for Primary and Secondary Organic Aerosol" to construct a source-oriented Chemical Transport Model that can identify source contributions to Primary Organic Aerosol (POA) and Secondary Organic Aerosol (SOA) with improved accuracy and resolution relative to receptor-oriented techniques. The new source-oriented CTM with improved SOA calculations is being used to predict concentrations of elemental carbon (EC), POA, and SOA at St. Louis for two multi-week periods in 2002.
- William Christensen and Shane Reese (BYU) have been awarded an EPA STAR grant "Addressing Temporal Correlation, Incomplete Source Profile Information, and Varying Source Profiles in the Source Apportionment of Particulate Matter". Two of the three stated project objectives are: (1) to address both the challenges and advantages presented by temporally correlated ambient data, and address the opportunity for improved source contribution estimates when the temporal resolution of ambient measures is improved; and (2) to develop the iterated confirmatory factor analysis (ICFA) approach, which can utilize partial source profile information and take on aspects of CMB analysis, confirmatory factor analysis (CFA), and exploratory factor analysis (EFA) by assigning varying degrees of constraint to each element of the estimated source profile matrix during the estimation process. Data from the St. Louis Supersite is being used extensively in this work. [excerpted from STAR Grant Abstract]
- USEPA/ORD has funded two projects under its St. Louis Advanced Monitoring Initiative (AMI), with the intent to fund a third project, which all capitalize on the St. Louis Supersite data set to develop and refine source apportionment methodologies. Ronald Henry (USC) has been developing and applying nonparametric source apportionment to identify and quantify local emission sources of PM<sub>2.5</sub> in St. Louis. Philip Hopke (Clarkson) is performing advanced data analyses including source apportionment on highly time resolved data. The pending project would use the pseudo deterministic regression model (PDRM) to estimate point source contributions to observed PM<sub>2.5</sub> burdens.
- David Sterling and colleagues (St. Louis University School of Public Health) are currently funded by EPRI to investigate relationships between ambient particulate matter physical and chemical properties and hospital visits for certain classes of respiratory and cardiac effects (using hospital discharge records).
- Rebecca Klemm and colleagues (Klemm Analysis Group) were recently funded by EPRI to investigate the relationships between daily mortality by broad causes of death (cardiovascular, respiratory, deaths among those >65 years of age, etc.) and components of air pollution and particulate matter. The analyses will initially consider broad categories of pollutants (e.g., metals, EC, OC); later analyses will focus upon subcategories of these major groupings. The air quality data will be obtained from measurements made at the St. Louis Supersite. A similar analysis is planned to examine the relationship between daily emergency department visits and pollution components

## 2.5 Key Citations

Allen, D.T. and J.R. Turner, Transport of Atmospheric Fine Particulate Matter: Part 1. Findings from Recent Field Programs on the Extent of Regional Transport within North America, *submitted*.

Allen G.A., B.P. Goodwin, and J.R. Turner (2004) Real-Time Carbon and Sulfate Measurements from the MANE-VU Rural Aerosol Intensive Network (RAIN): Design, Methods, and Early Data, Paper #18, *Proceedings of the A&WMA Visibility Specialty Conference: "Regional and Global Perspectives on Haze: Causes, Consequences and Controversies"* (October 2004, Asheville, NC).

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# 3. Knowledge Gaps

- The Supersites program has provided unprecedented insights into aerosol climatology through deployments of typically one year duration. There can be year-to-year variations in the frequency and intensity of synoptic and surface weather patterns and data from the St. Louis Midwest Supersite demonstrates that such variations are also expressed in the *multiyear* time series. For example, seasonal BC/EC ratios exhibited significant variation from year-to-year. Sustained measurements are needed to elucidate aerosol climatology over long time scales and clarify the underlying drivers for its variability.
- Substantial advances have been made into understanding the sources and nature of artifacts in both substrate-based integrated sampling and semicontinuous monitoring. Allied data streams have been quite valuable in this effort. For example, differences in EC measured by different thermo-optical methods can be traced back to variations in emission source contributions and/or differences in the analytical methodologies. Negative bias in flash volatilization nitrate measurements can be explained, at least in part, by a matrix effect. Comprehensive, multi-parameter monitoring platforms are critical to such assessments. Lessons learned from the Supersites and related programs can be used in the rational design of such platforms. Continued efforts are needed to assess the consistency between instruments and between platforms to understand compatibly between data sets.
- No single source apportionment tool/analysis can adequately characterize the source-receptor relationships. A battery of tools should be used to support a weight-of-evidence approach. For example, day-specific source apportionment of the organic aerosol by the molecular marker chemical mass balance method was affected by the presence of a significant point source with an unknown source profile and a series of largely ill-characterized special events. Annual-average source apportionment yielded the typical suite of key sources but meat cooking contributions were surprisingly high. PM-2.5 mass source apportionment by PMF yielded factors which in some cases were admixtures of multiple sources. Source apportionment tools need refinement, and we also need a strategy for their consistent application and harmonization.

# 4. Technical and Economic Feasibility

#### Measurements

• Several semicontinuous instruments show promise for achieving high data quality in long-term deployments including routine monitoring networks. Compared to gaseous criteria pollutant monitoring, these instruments typically require more effort to ensure proper instrument performance (i.e. ongoing review of a suite of diagnostic parameters) and more effort to post-process and validate the data. Operating procedures and data analysis tools are needed to improve the consistency and efficiency of such tasks. The Supersites program has dramatically improved our understanding of how these instruments perform in the field and provided valuable insights for the development of operating procedures and data analysis tools. This effort must be continued as the measurement technologies continue to evolve.

#### Control Strategies

• Development and implementation of effective control strategies relies upon a sound understanding of the source/receptor relationships operating in the airshed of concern. Source apportionment and other analyses on the St. Louis – Midwest Supersite data has advanced our understanding of the key emission sources and their potential impact, but their actual impact cannot be discerned solely from the ambient data. Chemical transport modeling for the St. Louis airshed is currently very good for sulfate, good for nitrate and elemental carbon, and poor for geologic material and organic carbon. A better understating of organic carbon sources and their impacts is particularly important because organic carbon is a significant contributor to the annual-average PM<sub>2.5</sub> mass with contributions from local sources comparable to concentrations from regionally transported material (as determined by urban/rural contrast studies). Organic carbon emission inventories and atmospheric chemistry mechanisms used in the chemical transport models need improvement before the observed organic carbon mass concentrations can be fully reconciled with modeling results.

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Allen, D.T. and J.R. Turner, Transport of Atmospheric Fine Particulate Matter: Part 1. Findings from Recent Field Programs on the Extent of Regional Transport within North America, *submitted*.

**Abstract**. Air quality field data, collected as part of the fine particulate matter Supersites program and other field measurements programs, have been used to assess the role of aerosol transport, over length scales of approximately 100-1000 km, on fine particulate matter concentrations. Assessment of data from New York, Baltimore, Pittsburgh, Atlanta, Houston, St. Louis and Fresno indicate that in virtually all of the regions, transport of aerosol over distances of 100-1000 km has a significant impact on urban particulate matter concentrations and a dominant role in determining rural particulate matter concentrations. This assessment is generally consistent with previous conceptual models of fine particulate matter formation and accumulation in these regions. The nature of the transported aerosol is largely sulfate in eastern and Midwestern cities and nitrate in the Central Valley of California. In addition to physical transport of aerosol over distances of 100-1000 km, regional transport of aerosol precursors may lead to conditions conducive to large scale nucleation events. Regional nucleation events have been reported in the east, Midwest and in California. The events occurred in the morning soon after surface layers coupled with layers aloft and the events generate ultra-fine particles. In some cases, these nucleation events have been correlated with availability of sulfur dioxide, and therefore may be sulfate formation events.

Bae M.S., J.J. Schauer, J.T. DeMinter and J.R. Turner (2004a) Hourly and Daily Patterns of Particle-Phase Organic and Elemental Carbon Concentrations in the Urban Atmosphere, *Journal of the Air & Waste Management Association*, **54**, 823-833.

Abstract. Two semicontinuous elemental and organic carbon analyzers along with daily integrated samplers, which were used for laboratory elemental and organic carbon analysis, were operated to measure PM2.5 organic carbon (OC) and elemental carbon (EC) for the entire year of 2002 at the St. Louis Midwest Supersite. The annual-average denuded OC and EC concentrations were 3.88 and 0.7  $\mu g/m^3$ , respectively. A comparison of the 24-hr average denuded and undenuded OC measurements showed a positive bias for the undenuded OC measurement that was best represented by a positive intercept of 0.34  $\pm$  0.1  $\mu g/m^3$  and a slope of 1.06  $\pm$  0.02, with an  $R^2$  of 0.91. The full year of daily EC and OC measurements was used to demonstrate that a one-in-six-day sampling strategy at this site accurately represents the annual average concentrations. Although fine particle OC concentrations did not correlate with day of the week, EC concentrations showed a significant weekly pattern, with the highest concentration during the middle of the workweek and the lowest concentration on Sundays. Hourly EC and OC measurements yielded average diurnal patterns for the EC to OC ratio that peaked during morning rush hour traffic on weekdays but not on weekends.

Bae M.S., J.J. Schauer, J.T. DeMinter, J. R. Turner, D. Smith and R.A. Cary (2004) Validation of a Semi-Continuous Instrument for Elemental Carbon and Organic Carbon Using a Thermal-Optical Method, *Atmospheric Environment*, **38**, 2885-2893.

**Abstract**. A commercial semi-continuous elemental and organic carbon (ECOC) analyzer has been developed by Sunset Laboratory Inc. for the analysis of atmospheric particulate matter. The field deployable instrument is an alternative to off-line laboratory-based analysis of samples collected in the field. Although the Sunset Laboratory analyzer provides time-resolved particulate ECOC measurements using a methodology comparable to the laboratory-based NIOSH 5040 ECOC measurement, the performance of the semi-continuous ECOC analyzer has not been fully validated in the past.

As part of the St. Louis-Midwest Supersite, two semi-continuous Sunset Labs ECOC field analyzers were operated to measure fine particle organic and elemental carbon for the entire year of 2002. The dual instrument operation provided a means to have a true continuous ECOC measurement, which would not be possible with only one instrument since the instrument cannot continue sample collection during the sample analysis period. In parallel with the semicontinuous ECOC analyzers, daily 24-h integrated PM2.5 samples were collected for ECOC analysis in the laboratory. Both the 24-h integrated filter samplers and the semi-continuous ECOC instruments were operated downstream of an organics denuder to remove positive adsorption artifacts associated with semi-volatile organic compounds. Comparison of 24-h averaged semi-continuous fine particle total carbon (TC), organic carbon (OC) and elemental carbon (EC) showed good agreement with the daily integrated off-line measurements. The linear regression of the averaged semi-continuous TC on the integrated off-line TC had a coefficient of regression ( $R^2$ ) of 0.89 and a regression slope of 0.97  $\pm$  0.02 when at least 20 h of the day were measured. The OC measurements had a  $R^2$  equal to 0.90 and a regression slope of 0.93  $\pm$  0.02. The EC measurements had a poorer R<sup>2</sup> due to the very low levels of EC at the sampling site but a regression slope of  $0.95 \pm 0.05$ . The accuracy of using a single semi-continuous ECOC instrument,

Bae M.S., J.J. Schauer and J.R. Turner, Estimation of Monthly-Average Ratios of Organic Mass to Organic Carbon for Fine Particulate Matter at an Urban Site, *Aerosol Science and Technology*, **40**, 1123-1139.

**Abstract**. Two independent methods are used to estimate the seasonality of the ratio of fine particulate organic matter (OM) to fine particulate organic carbon (OC) for atmospheric particulate matter collected at the St. Louis—Midwest Supersite. The first method assumes that all of the fine particulate matter mass that cannot be attributed to sulfate ion, nitrate ion, ammonium ion, elemental carbon and metal oxides is organic matter. Using this method, 98 daily samples were used to estimate the annual average fine particulate matter OM/OC ratio to be  $1.81 \pm 0.07$  with a summer average of  $1.95 \pm 0.17$  and a winter average of  $1.77 \pm 0.13$ . The second approach to estimating fine particle OM/OC employed OC source apportionment results and estimates of source specific OM/OC, including primary sources and secondary organic aerosol. The OM/OC estimate that was based on 98 daily source apportionment calculations over

a two year period yielded an annual average ratio of  $1.96 \pm 0.03$ . Methods used in the study yielded a relatively stable annual average estimate of the OM/OC ratio for fine particulate matter in the St. Louis area. The source apportionment results indicate that the similar OM/OC ratio for St. Louis in the summer and winter results from an increased relative contribution of secondary organic aerosol in the summer months that is balanced by the higher woodsmoke in the winter. Although the estimated OM/OC ratios that were determined for St. Louis cannot be directly applied to other locations, the methodologies used to estimate OM/OC can be broadly applied given the necessary data for these calculations.

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**Abstract**. Daily 24-hour integrated PM<sub>2.5</sub> (particulate matter <2.5  $\mu$ m aerodynamic diameter) mass and species concentrations were measured at the St. Louis-Midwest Supersite East St. Louis, Illinois, during the sampling period from June 2001 to May 2003. PM<sub>2.5</sub> speciation data were analyzed using a receptor model, positive matrix factorization (PMF), to identify sources contributing to the observed PM<sub>2.5</sub> burdens. Species profiles the identified sources and their contributions to the observed mass concentration at receptor were derived from the PMF modeling. These source-specific contributions then coupled with on-site wind data to identify the directionality of the identified sources which are compared to known point source locations. Overall, ten source categories were resolved (study average contribution to the PM<sub>2.5</sub> mass in parentheses): secondary sulfate (33%), carbon-rich sulfate (20%), gasoline exhaust (16%), secondary nitrate (15%), steel processing (7%), airborne soil (4%), diesel emissions/railroad traffic (zinc smelting (1.3%), lead smelting (1.3%), and copper production (0.5%). Temperature resolved organic and elemental carbon fractions enhanced the source separation between secondary sulfate and carbon-rich sulfate and between gasoline exhaust and diesel emissions/railroad traffic. A major Saharan dust plume observed throughout the Midwestern U.S. in July 2002 was also observed in this study. Overall, about half of PM<sub>2.5</sub> mass concentration measured at this site was distinctly apportioned to secondary sulfate and secondary nitrate. Contributions from distinct primary emissions included local industrial sources (9%), transportation (gasoline/diesel/railroad, 19%), and airborne dust (4%). The remaining 20% of the PM<sub>2.5</sub> mass was apportioned to a carbon-rich sulfate factor which is likely an admixture of primary emissions and secondary formation. More work is needed to identify the distinct sources contributing to this factor.

Majestic, B.J., M.M. Shafer, J.J. Schauer, J.R. Turner, C. Sioutas and P.M. Fine (2006) Development of a Wet Chemical Method for the Speciation of Iron in Atmospheric Aerosols, *Environmental Science and Technology*, **40**, 2346-2351.

**Abstract.** The ability to quantify the chemical and physical forms of transition metals in atmospheric particulate matter (PM) is essential in determining potential human health and ecological effects. A method for the speciation of iron in atmospheric PM has been adapted which involves extraction in a well-defined solution followed by oxidation state specific detection. The method was applied to a suite of environmental aerosols. Ambient atmospheric aerosols in an urban area of St. Louis (the St. Louis-Midwest Supersite) were collected on Teflon substrates and were leached in one of four different solutions: (1) >18.0 M  $\Omega$  water; (2) 140  $\mu$ M NaCl solution; (3) pH = 7.4 NaHCO<sub>3</sub> solution; and (4) pH = 4.3 acetate buffering system. Fe(II) was determined directly using the Ferrozine method as adapted to liquid waveguide spectrophotometry using a 1 m path-length cell. Fe(III) was determined similarly after reduction to Fe(II). It was found that, at low ionic strength, pH exerted a major influence on Fe(II) solubility with the greatest Fe(II) concentration consistently found in the pH = 4.3 acetate buffer. Soluble Fe(III) (as defined by a 0.2 µM filter) varied little with extractant, which implies that most of the Fe(III) detected was colloidal. To characterize well-defined materials for future reference, NIST standard reference materials were also analyzed for soluble Fe(II) and Fe(III). For all SRMs tested, a maximum of 2.4% of the total iron (Urban Dust 1649a) was soluble in pH = 4.3 acetate buffer. For calibration curves covering the ranges of  $0.5-20 \mu g/L$  Fe(II), excellent linearity was observed in all leaching solutions with  $R^2$  values of >0.999. Co-located filters were used to test the effect of storage time on iron oxidation state in the ambient particles as a function of time. On two samples, an average Fe(II) decay rate of 0.89 and 0.57 ng Fe(II) g<sup>-1</sup> PM day<sup>-1</sup> was determined from the slope of the regression, however this decrease was determined not to be significant over 3 months (95% confidence). As an application of this method to mobile source emissions, size-resolved PM10 samples were collected at the inlet and outlet of the Caldecott Motor Vehicle Tunnel in northern California. These samples indicate that the coarse fraction (PM10-PM2.5) contains almost 50% of the total soluble Fe(II) in the aerosol.

Qian, S., H. Sakurai, P. H. McMurry (2007) "Climatology of Regional Nucleation Events in Urban East St. Louis" *Atmospheric Environment*, doi:10.1016/j.atmosenv.2007.01.011.

Abstract. Continuous measurements of aerosol size distributions (3 nm–2 μm) were carried out over a 26 month period (1 April 2001–31 May 2003; 650 days with valid data) in urban East St. Louis, IL, as a part of the US Environmental Protection Agency's Supersite program. This paper analyzes data for the 155 days on which "regional nucleation events" were observed during this study. Such events were observed during every month of the study except January 2003. We observed some differences; however, between events in the summer (defined here as April–September) and winter (December–February). Regional nucleation events were observed more frequently in summer months (36 ±13% of days) than in winter (8 ± 7%), and nucleated particles grew faster in the summer (6.7 ± 4.8 nm ± 1.9 nm h<sup>-1</sup>). The daily maximum in the number

concentration of nanoparticles formed by nucleation  $(4.8 \pm 3.5 \times 10^4 \text{ cm}^{-3})$  was highly variable and showed no clear seasonal dependence. Particle formation increased particle concentrations by an average factor of 3.172.8. Maximum daily rates of 3 nm particle production  $(17 \pm 20 \text{ cm}^{-3} \text{ s}^{-1})$  were also highly variable and without a clear seasonal dependence. During these events, particle formation rates were typically near their maxima at 08:00-09:00 a.m., but particle production sometimes persisted at diminishing rates until late in the afternoon (15:00-16:00 p.m.).

Rich, D.Q., M.H. Kim, J.R. Turner, M.A. Mittleman, J. Schwartz, P.J. Catalano and D.W. Dockery (2006) Association of Ventricular Arrhythmias Detected by Implantable Cardioverter Defibrillator and Ambient Air Pollutants in Saint Louis, Missouri, *Occupational and*. *Environmental Medicine*, **63**, 591-596.

**Abstract**. Background: It has previously been reported that the risk of ventricular arrhythmias is positively associated with ambient air pollution among patients with implantable cardioverter defibrillators (ICD) in Boston. Aims: To assess the association of community exposures to air pollution with ventricular arrhythmias in a cohort of ICD patients in metropolitan St Louis, Missouri. Methods: ICD detected episodes reported during clinical follow up were abstracted and reviewed by an electrophysiologist to identify ventricular arrhythmias. A total of 139 ventricular arrhythmias were identified among 56 patients. A case-crossover design was used with control periods matched on weekday and hour of the day within the same calendar month. Conditional logistic regression models were adjusted for temperature, barometric pressure, and relative humidity in the 24 hours preceding the event. **Results:** There was a significant (24%, 95% CI 7% to 44%) increase in risk of ventricular arrhythmias associated with each 5 ppb increase in mean sulphur dioxide and non-significantly increased risk (22%, 95% CI -6% to 60%; and 18%, 95% CI –7% to 50%) associated with increases in nitrogen dioxide (6 ppb) and elemental carbon (0.5 µg/m<sup>3</sup>), respectively in the 24 hours before the arrhythmia. **Conclusions:** These results provide evidence of an association between ventricular arrhythmias and ambient air pollutants in St Louis. This is consistent with previous results from Boston, although the pollutants responsible for the increased risk are different.

Sullivan A.P., R.P. Weber, A.L. Clements, J.R. Turner, M.S. Bae and J.J. Schauer (2004) A Method for On-Line Measurement of Water-Soluble Organic Carbon in Ambient Particles: Results from an Urban Site, *Geophysical Research Letters*, **31**, L13105.

Abstract. An instrument for on-line continuous measurement of the water-soluble organic carbon (WSOC) component of aerosol particles is described and results from an urban site in St. Louis are presented. A Particle-into-Liquid Sampler impacts ambient particles, grown to large water droplets, onto a plate and then washes them into a flow of purified water. The resulting liquid is filtered and the carbon content quantified by a Total Organic Carbon analyzer providing continuous six-minute integral measurements with a detection limit of 0.1 μgC/m³. Summer and fall measurements of WSOC and organic carbon (OC) indicated WSOC/OC ratio typically ranged from 0.40 to 0.80. Adiurnal variation in WSOC/OC that correlated with ozone was

observed over extended periods in June; however, other periods in August had no correlation. The results suggested that WSOC was composed of a complex mixture of compounds that may contain a significant fraction from secondary organic aerosol formation.

Turner, J.R. and D.T. Allen, Transport of Atmospheric Fine Particulate Matter: Part 2. Findings from Recent Field Programs on the Intraurban Variability in Fine Particulate Matter, *submitted*.

Abstract. Air quality field data, collected as part of the fine particulate matter Supersites Program and other field measurements programs, have been used to assess the degree of intraurban variability for various physical and chemical properties of ambient fine particulate matter. Spatial patterns vary from nearly homogeneous to quite heterogeneous, depending on the city, parameter of interest, and the approach or method used to define spatial variability. Secondary formation, which is often regional in nature, drives fine particulate matter mass and the relevant chemical components towards high intraurban spatial homogeneity. Those particulate matter components which are dominated by primary emissions within the urban area, such as black carbon and several trace elements, tend to exhibit greater spatial heterogeneity. A variety of study designs and data analysis approaches have been used to characterize intraurban variability. High temporal correlation does not imply spatial homogeneity. For example, there can be high temporal correlation but with spatial heterogeneity manifested as smooth spatial gradients, often emanating from areas of high emissions such as the urban core or industrial zones.

Wilson, W.E., J. Stanek, H.S. Han, T. Johnson, H. Sakurai, D.Y.H. Pui, J.R. Turner, D.R. Chen, and S.A. Duthie (2007) Use of the Electrical Aerosol Detector as an Indicator for the Total Particle Surface Area Deposited in the Lung *Journal of the Air & Waste Management Association*, **57**, 211-220.

**Abstract**. Because of recent concerns about the health effects of ultrafine particles and the indication that particle toxicity is related to surface area, we have been examining techniques for measuring parameters related to the surface area of fine particles, especially in the 0.003- to 0.5µm size range. In an earlier study, we suggested that the charge attached to particles, as measured by a prototype of the Electrical Aerosol Detector (EAD, TSI Inc., Model 3070), was related to the 1.16 power of the mobility diameter. An inspection of the pattern of particle deposition in the lung as a function of particle size suggested that the EAD measurement might be a useful indicator of the surface area of particles deposited in the lung. In this study, we calculate the particle surface area (micrometer squared) deposited in the lung per cubic centimeter of air inhaled as a function of particle size using atmospheric particle size distributions measured in Minneapolis, MN, and East St. Louis, IL. The correlations of powers of the mobility diameter,  $D^X$ , were highest for X = 1.1-1.6 for the deposited surface area and for X = 1.25 with the EAD signal. This overlap suggested a correspondence between the EAD signal and the deposited surface area. The correlation coefficients of the EAD signal and particle surface area deposited in the alveolar and tracheobronchial regions of the lung for three breathing patterns are in the range of Pearson's r = 0.91-0.95 (coefficient of determination,  $R^2 = 0.82-$  0.90). These statistical relationships suggest that the EAD could serve as a useful indicator of particle surface area deposited in the lung in exposure and epidemiologic studies of the human health effects of atmospheric particles and as a measure of the potential surface area dose for the characterization of occupational environments.

#### **PRESENTATIONS**

- Allen G.A., B.P. Goodwin, and J.R. Turner "Field Validation of the Thermo Model 5020 Continuous Sulfate Analyzer", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Allen G.A., B.P. Goodwin, and J.R. Turner, "Real-Time Carbon and Sulfate Measurements from the MANE-VU Rural Aerosol Intensive Network (RAIN): Design, Methods, and Early Data", A&WMA Visibility Specialty Conference: "Regional and Global Perspectives on Haze: Causes, Consequences and Controversies" (October 2004, Asheville, NC).
- Allen G.A., B.P. Goodwin, and J.R. Turner "Method Validation and Field Deployment of the Thermo Model 5020 Continuous Sulfate Analyzer", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).
- Anderson B., J.R. Turner and J.L. Garlock, "Application of Source and Receptor Models to Analyze Selected Episodes from the St. Louis Midwest Supersite", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Bae M.S., J.J. Schauer and J.R. Turner, "Understanding the Impact of 'Unknown' Point Sources on Molecular Marker Chemical Mass Balance Models", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Bae M.S., J.J. Schauer and J.R. Turner, "Estimation of Organic Mass to Organic Carbon Ratios using Source Apportionment Data", 2005 Annual Meeting of the American Association for Aerosol Research (October 2005, Austin, TX).
- Bae M.S., J.J. Schauer, J.R. Turner, J.C. Chow and P.K. Hopke, "Seasonal Correlation between NIOSH and IMPROVE Carbon Measurements", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Clements A.L., M.N.S. Yu, J.R. Turner and R. Weber "Particulate Matter Ion Measurements by the Particle-Into-Liquid Sampler (PILS) at the St. Louis Midwest Supersite", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Clements A.L., J.R. Turner and R.J. Weber, "Particulate Matter Organic Acid Measurements by the Particle-Into-Liquid Sampler (PILS) at the St. Louis Midwest Supersite", International State of the Science Workshop on Organic Speciation in Atmospheric Aerosols Research (April 2004, Las Vegas, NV).
- Deardorff N.D., S.A. Duthie, J.R. Turner and J.D. Reifschneider", "PM-2.5 Monitoring at a Rural Midwest Site to Support Regional Haze Planning", 2003 Annual Meeting of the Air & Waste Management Association (June 2003, San Diego, CA).
- Deardorff N.D. and J.R. Turner "Ambient Particulate Matter Measurements at Two Rural Sites in the Midwestern United States", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).

- Deardorff N.D. and J.R. Turner, "An Investigation of PM-2.5 Climatology at a Rural Midwest Site", A&WMA Visibility Specialty Conference: "Regional and Global Perspectives on Haze: Causes, Consequences and Controversies" (October 2004, Asheville, NC).
- Deardorff N.D., J.R. Turner, M.S. Bae, J.J. Schauer, and W.H. White, "Urban / Rural Contrast for Ambient Fine Particulate Matter in the St. Louis Area", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).
- Duthie S.A., S.R> Falke, R.B. Husar, W.H> White and J.R. Turner, "A Spatio-Temporal Aerosol Climatologic Context for the Saint Louis – Midwest Supersite", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Goodwin B.P. and J.R. Turner, "Optical Saturation Effects on Aethalometer Response", 2005 Annual Meeting of the American Association for Aerosol Research (October 2005, Austin, TX).
- Goodwin B.P., J.R. Turner, and G.A. Allen, "Characterization and Performance Evaluation for the Magee Scientific Aethalometer TM for Ambient Black Carbon Concentration Measurements", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).
- Goodwin B.P., N.D. Deardorff, J.S. Hill, J.R. Turner, J.J. Schauer and M.S. Bae, "Interpreting Aerosol Black Carbon Measurements from a Magee Scientific Aethalometer", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Hall B., H. Manolopoulos, J. Schauer, D. Krabbenhoft, M. Olson, D. Gross, M. Yuen, A. Ault, R. Frontiera, A. Schmitt and J. Turner, "Atmospheric Mercury Measurements at the St. Louis - Midwest Supersite", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Han H.S., S. Kaufman, J.R. Turner, W.E. Wilson, D.Y.H. Pui, "Electrical Aerosol Detector (EAD) Measurements at the St. Louis Supersite", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Heinzerling D., N.D. Deardorff and J.R. Turner, "Synoptic Scale Weather Patterns Impacting the St. Louis Aerosol", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Hill J.S., B.P. Goodwin and J.R. Turner, "Middle Scale Source Contributions to High Time Resolution Particulate Matter Measurements at the Saint Louis – Midwest Supersite", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Hill J.S. and J.R. Turner, "Exploiting High Time Resolution Measurements for Insights into Aerosol Climatology", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Hill J.S. and J.R. Turner, "Deconvoluting High Time Resolution Data to Obtain Insights into Spatial Scales of Representation", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).

- Hill J.S., E.R. Ryszkiewicz, J.R. Turner and K.J. Goohs, "Fi8eld Performance Evaluation of the Thermo Electron Model 5030 SHARP for Measurement of Ambient PM-2.5 Mass Concentration", 2006 Annual Meeting of the Air & Waste Management Association (June 2006, New Orleans, LA).
- Kim E., P.K. Hopke and J.R. Turner, "Analysis of Ambient Continuous Data Collected at the St. Louis Midwest Supersite", 2006 International Aerosol Conference (Sepember 2006, St. Paul, MN)
- Lee J.H., P.K. Hopke, J.R. Turner and J.J. Schauer, "Identification of Sources to Airborne PM2.5 at the St. Louis Midwest Supersite", 2005 Annual Meeting of the American Association for Aerosol Research (October 2005, Austin, TX).
- Manolopoulos H., J.J. Schauer, M.D. Purcell, T.M. Rudolph, M.L. Olson, B. Rodger, D.P. Krabbenhoft and J.R. Turner, "A Receptor-Based Approach to Understanding Sources of Reactive Mercury in the Atmosphere", 7th International Conference on Mercury as a Global Pollutant (June 2004, Ljubljana, Slovenia).
- McDonald R., P. Biswas, S. Hu, J.R. Turner, D. Martuzecicius, S. Grinshpun and G. Lemasters, "Fractal Dimensions of Ambient and Source Aerosols", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Ondov J.M., J.P. Pancras, S. Gazula, M.N.S.Yu, J.R. Turner, A. Robinson, S. Pandis, N.D. Poor and R.K. Stevens, "Highly Time-Resolved Measurements of Elemental Composition at the Baltimore, St. Louis, Pittsburgh, and Tampa Supersites Using the UM High-Frequency Aerosol Slurry Sampler: Unprecedented Resolution of the Sources of Primary Atmospheric Aerosol", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Ondov J., P. Pancras, N. Poor, J.R. Turner, M.N.S. Yu, E. Lipsky, E. Weitkamp and A. Robinson "PM Emission Rates from Highly Time-Resolved Ambient Concentration Measurements", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA
- Rauer D.G., J.R. Turner and L.T. Angenent, "Ambient Biological Particulate Matter Characterization at the St. Louis Midwest Supersite", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).
- Reid C.S., J.R. Turner and S.V. Hering, "Fine Particulate Matter Nitrate Measurements by Flash Volatilization: Results from the St. Louis Midwest Supersite", A&WMA Symposium on Air Quality Measurement Methods and Technology (April 2005, San Francisco, CA).
- Reid C.S., J.R. Turner and S.V. Hering, "Matrix Effects in the Measurement of Fine Particulate Matter Nitrate by Flash Volatilization", 2005 Annual Meeting of the American Association for Aerosol Research (October 2005, Austin, TX).
- Sakurai H., Q. Shi, X. Wang, K. S. Woo and P. H. McMurry, "Continuous measurement of the atmospheric aerosol particle size distribution at the St. Louis-Midwest Supersite, 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).

- Schauer J.J, M.S. Bae, Y.C. Chang, S. Gazula, P. Koutrakis, J.M. Ondov, J.P. Pancras, J.R. Turner, W.H. White and M.N.S. Yu, "New Insights into the Dynamics of Sources of Fine Particulate Matter Using Semicontinuous Chemical Speciation Samplers", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Schauer J.J., M.S. Bae and J.R. Turner, "Variations in the Average Daily Composition of the Organic Fraction of PM-2.5 in the Urban Atmosphere", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Sheesley R.J., J.J. Schauer, J. DeMinter, M. Mieritz and J.R. Turner, "TD-GCMA Analysis of Daily PM2.5 Samples from the St. Louis Midwest Supersite", 2006 International Aerosol Conference (September 2006, St. Paul, MN)
- Shi Q., H. Sakurai, X. Wang and P. H. McMurry, "Continuous measurement of the atmospheric aerosol size distributions in St. Louis, MO", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Simon E.S., G.A. Allen, S.A. Duthis, P. Koutrakis and J.R. Turner, "Particulate Matter Mass Concentration Measurements at the Saint Louis Midwest Supersite", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Sullivan A., R. Weber, A.L. Clements, J.R. Turner, M.S. Bae and J.J. Schauer "Water-Soluble Organic Carbon and Organic and Elemental Carbon in St. Louis Using Near Real-Time Aerosol Monitors", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Sullivan A., R. Weber, A.L. Clements, J.R. Turner, M.S. Bae, and J.J. Schauer, "On-line Measurement of Ambient Particle Humic-Like Substances (HULIS) Using a Particle-Into-Liquid-Sampler Coupled to a Total Organic Carbon (TOC) Analyzer and XAD-8 Column", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).
- Turner J.R., G.A. Allen, T. Bahadori, J.C. Chow, D.A. Hansen, P. Koutrakis, P.H. McMurry, J.M. Ondov, J.J. Schauer, J.G. Watson, R.J. Weber and W.H. White, "Overview of the Saint Louis Midwest Supersite", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Turner J.R., "Semi-Continuous Measurement of Particulate Matter Sulfate and Nitrate", EMEP Particulate Matter Measurement and Modeling Workshop (April 2004, New Orleans, LA).
- Turner J.R., "Carbonaceous PM-2.5: Lessons [Being] Learned from the Saint Louis Midwest Supersite", EPA Workshop on Carbonaceous Particulate Matter: The State of the Science (CPM-II) (April 2004, Research Triangle Park, NC).
- Turner, J.R., N.D. Deardorff, B.P. Goodwin, J.S. Hill, M.S. Bae and J. J. Schauer, "Aerosol Black Carbon Climatology at the St. Louis Midwest Supersite", 2004 Annual Meeting of the American Association for Aerosol Research (October 2004, Atlanta, GA).

- Turner J.R., "The USEPA Supersites Program: Elucidating Spatial Variability in Particulate Matter Size and Composition, AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA). [plenary]
- Turner J.R., G.A. Allen, T. Bahadori, J.C. Chow, D.A. Hansen, P. Koutrakis, P.H. McMurry, J. Ondov, J.J. Schauer, R.P. Weber and W.H. White, "Aerosol Climatology at the St. Louis Midwest Supersite", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).
- Turner, J.R, E.R. Ryszkiewicz, J.L. Garlock, J.J. Schauer, M.S. Bae and G.A. Allen "Semicontinuous PM Composition Measurements at the St. Louis – Midwest Supersite", EPA – STAPPA/ALAPCO National Air Monitoring Conference (November 2006, Las Vegas, NV).
- Turner, J.R., "Characterizing Ambient Fine Particulate Matter Mass in St. Louis", EPA STAPPA/ALAPCO National Air Monitoring Conference (November 2006, Las Vegas, NV).
- White W., G. Allen, M.S. Bae, P. Koutrakis, P. McMurry, H. Sakuri, J. Schauer, Q. Shi and J.Turner, "Diurnal Cycles and Irregular Peaks in East Saint Louis Aerosol Exposures", 2003 AAAR PM Meeting "Particulate Matter: Atmospheric Sciences, Exposure and the Fourth Colloquium on PM and Human Health" (April 2003, Pittsburgh, PA).
- Wittig A., J.R. Turner and D.T. Allen, "Synthesis of Supersite Program Findings: Regional Transport of Fine PM, 2005 Annual Meeting of the American Association for Aerosol Research (October 2005, Austin, TX).
- Wilson W.E., H.S. Han, J. Stanek, J.R. Turner and D.Y.H. Pui "Deposition of Particle Surface Area in the Human Respiratory Tract: Relation to Particle Concentration (Number, Surface Area and Volume) and to the "Active" Surface Area as Measured by a Diffusion Charger", 2003 Annual Meeting of the American Association for Aerosol Research (October 2003, Anaheim, CA).
- Yu M.N.S., A.C. Clements, J.R. Turner and R.P. Weber, "Fine Particulate Matter Ion Measurements at the St. Louis – Midwest Supersite by the Particle-into-Liquid Sampler (PILS)", AAAR PM Supersites Program & Related Studies Conference (February 2005, Atlanta, GA).