

AN OVERVIEW OF PM_{2.5} CHEMICAL SPECIATION NATIONWIDE NETWORK PROGRAM IN THE UNITED STATES

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ABSTRACT

Particulate matter (PM) with particle aerodynamic diameters of 2.5 μm and smaller (PM_{2.5}) in ambient air has been associated with respiratory and other health-related problems. It has also been shown to contribute to atmospheric visibility impairment and regional haze. Negative health effects have been statistically correlated to total mass concentration ($\mu\text{g}/\text{m}^3$) of PM_{2.5} in ambient air, but whether the correlation is actually to total mass concentration or to concentrations of specific chemical species comprising PM_{2.5} has not yet been determined.

The deployment of a new PM_{2.5} monitoring network by the U.S. Environmental Protection Agency (EPA) is a critical component in the national implementation of the PM_{2.5} National Ambient Air Quality Standards (NAAQS). The compliance (mass) monitoring portion of the network was established first. Data from the compliance network are used to determine attainment with the NAAQS. EPA has supplemented the network with a chemical speciation monitoring program to provide complementary data on the chemical composition of PM_{2.5} for the purposes of identifying sources, developing implementation plans, and supporting ongoing health effects research. The program has grown significantly over the last 4 years and currently RTI International is providing chemical speciation support to over 225 PM_{2.5} monitoring sites established throughout the United States and Puerto Rico.

Challenges encountered in the operation of this program include sample handling, sampling and analytical problems, data validation, and reporting. This paper will present an overview of the network, and some results from the first 4 years of speciated measurements, including observation of elevated elements such as potassium as the result of Independence Day fireworks and forest fires.

INTRODUCTION

On July 18, 1997, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The NAAQS applies to the mass concentration of particles with aerodynamic diameters of 2.5 μm or less (PM_{2.5}) and 10 μm or less (PM₁₀). The standards are detailed in 40 CFR, Parts 50, 53, and 58.^[1] Deployment of a PM_{2.5} monitoring network by the EPA is a critical component in the

*RTI International is a trade name of the Research Triangle Institute.

¹ U.S. Environmental Protection Agency. "National Ambient Air Quality Standards for Particulate Matter Final Rule, 40 CFR, Part 50." *Federal Register*, 62(138), 8651-8760, 1997.

national implementation of the new PM_{2.5} NAAQS. Data derived from this PM_{2.5} monitoring network include both aerosol mass measurements and chemically resolved or speciated data.

The initiation of a PM_{2.5} chemical speciation network of approximately 54 core sites within the National Air Monitoring Stations (NAMS) for routine speciation monitoring by EPA is described by the National Academy of Sciences.^[2] Speciation samples are collected over a 24-hour period every third day at NAMS sites. In addition to the 54 required sites, EPA set up another 200 sites specifically for speciated data collection. The sampling frequency at these sites varies, depending on the specific data application requirements developed by the individual states where the sampling is performed.

The PM_{2.5} chemical speciation program involves both sampling and analysis components. Sampling is performed by non-RTI International (non-RTI) personnel. These are typically representatives from state or local government agencies. In July 1999, to obtain consistent data, the monitoring and data validation branch of the EPA Office of Air Quality Planning and Standards located in Research Triangle Park, NC, initially awarded a 4-year, simple laboratory support contract to RTI. They recently renewed the contract with RTI for 5 additional years. The purpose of this contract, titled, "Chemical Speciation of PM_{2.5} Filter Samples," is to assist state and local agencies with the operation of PM_{2.5} chemical speciation monitoring networks by providing filter media and analytical support for the analysis of sampler filters for mass, selected elements (Al through Pb), organic and elemental carbon, anions (sulfate and nitrate), and cations (ammonium, sodium, and potassium), as well as analysis of semivolatile organics and microscopic analysis of selected filters. The program has grown significantly over the last 3 years, and RTI is currently providing chemical speciation support to over 225 PM_{2.5} monitoring sites established throughout the United States and Puerto Rico.

OVERVIEW OF LABORATORY SUPPORT ACTIVITIES

A detailed description of the laboratory support activities for chemical speciation of PM_{2.5} has been presented elsewhere.^[3] SASS samplers (MetOne) are predominantly used (69%) for sample collection in the network. The samplers used at the remaining sites include MASS (URG), RAAS (Anderson), and R&P speciation samples. A modified sequential FRM sampler manufactured by R&P is used at 19 Texas sites.

PM_{2.5} speciation samplers typically have from two to five (or more) flow channels that can be used to collect PM_{2.5} on various types of filters. A Teflon[®] filter is used to collect PM_{2.5} for measurement of total mass by gravimetry, elements by X-ray fluorescence, and in some cases, anions and cations by ion chromatography. A nylon filter is used to collect PM_{2.5} for measurement of anions and cations by ion chromatography, and a quartz filter is used to

² Committee on Research Priorities for Airborne Particulate Matter, National Research Council. "Research Priorities for Airborne Particulate Matter: 1-Immediate Priorities and a Long-Range Research Portfolio." National Academy of Sciences, 1998. (Available at <http://books.nap.edu/books030906094x/html/index.html>.)

³ Peterson, M. R., W. F. Gutknecht, R. L. Perkins, R.K.M. Jayanty, and E. D. Hardison. "Laboratory Support for Chemical Speciation of PM_{2.5}," *Environmental Manager*, pp. 17-22, August 2000.

collect PM_{2.5} for measurement of organic, elemental, carbonate, and total carbon. A nylon filter is typically preceded by a denuder coated with magnesium oxide or sodium carbonate to remove acid gas molecules from the sampled air before they are absorbed by the nylon filter.

Laboratory support for chemical speciation of PM_{2.5} begins with a request for service from the sponsoring agency or client, for example a state. Scheduling includes associating specific speciation samplers at specific locations for sampling on specified days. Sampling schedules implemented in the speciation network include 1 in every 3 days, 1 in every 6 days, EPA alternate 1 in every 3 days, EPA alternate 1 in every 6 days, and a separate schedule for the Texas sampling programs. EPA alternate schedules were implemented for the convenience of some sites, which may not be able to perform weekend sampling or shipping. All parties involved in a monitoring program are given copies of the shipping and receiving schedule and asked to ship only on the specified dates.

The Sample Handling and Archiving Laboratory (SHAL) established at RTI is a critical component of the laboratory operations. SHAL staff prepare a set of sampling modules for each sampler in each sampling event. Clean sampling modules are fitted with clean, acceptance-tested filters and shipped to the field. The laboratory is also responsible for providing denuders coated with magnesium oxide or sodium carbonate as needed. Non-RTI field personnel place the modules, and any required denuder, in the designated sampler before the beginning of the sampling event and retrieve the modules from the sampler after the sampling event. Modules are cooled to 4°C (or below), placed in a bin inside a high-efficiency cooler, and shipped back to the RTI laboratory. Approximately 1800 coolers are shipped back and forth to the laboratory and field sites every month.

SHAL staff measure and record the temperature of the modules in each cooler upon receipt. Filters are distributed to the appropriate speciation laboratories for analysis. The components of the disassembled sampling modules are cleaned by SHAL staff, and the modules are reassembled with clean filters and shipped back to the field sites according to schedule for a subsequent sampling event.

ANALYTICAL METHODS

Determination of Gravimetric Mass

The gravimetric analysis of PM_{2.5} filters is performed according to guidelines specified in 40 CFR, Parts 50, 53, and 58, and the EPA *Quality Assurance Guidance Document 2.12*, "Monitoring PM_{2.5} in Ambient Air Using Designated Reference or Class I Equivalent Methods." New Teflon[®] filters received from the manufacturer are checked for defects and defect-free filters are placed in the walk-in weighing chamber for conditioning and determination of lot stability. The chamber is maintained at a temperature of 20 to 23°C and a relative humidity of 30 to 40%. Weighing is performed with a microbalance having a readability of ≤ 1 µg. Laboratory quality control checks include lot stability blanks, replicate weighing of laboratory blanks and working mass standards, and replicate filter weighing.

Analysis of Elements by Energy Dispersive X-Ray Fluorescence

The method of choice for the determination of trace metals collected on PM_{2.5} filter samples is energy dispersive X-ray fluorescence (ED-XRF). The analysis is typically performed using EPA Method IO-33.^[4] Currently the national EPA PM_{2.5} chemical speciation program requires the analysis of 48 metals and non-metals in a single scan. The detection limit achieved varies with each element (0.04 to 0.40 µg/filter).

Analysis of Ions by Ion Chromatography

Water-extractable ions are measured using ion chromatography, a precise and accurate instrumental method of analysis. The standard operating procedures followed for the EPA PM_{2.5} speciation efforts were developed by RTI over 14 years ago. In the current EPA PM_{2.5} chemical speciation program, the anions sulfate and nitrate and the cations ammonium, sodium, and potassium are being measured. The detection limits are generally low (~0.1 µg/filter).

The samples are collected on Teflon[®] or nylon filters. Teflon[®] filters from commercial sources have been found to have acceptable blank levels (set by EPA at < 1 µg/filter) for each species of interest. Nylon filter blank contamination (sodium and sulfate) is a potential problem. Nylon filters directly from the supplier have been found to be loaded with more than 10 µg sodium per filter; this loading varies with the manufacturer's lot number. The washing procedure has been modified several times in response to increasing levels of contamination. RTI has implemented a thorough filter-washing procedure to combat this problem.

Organic, Elemental, and Total Carbon by Thermal-Optical Analysis

The EPA-approved method for carbon analysis is National Institute of Occupational Safety and Health (NIOSH) Method 5040, *Elemental Carbon (Diesel Particulate)*, with some specific conditions. Organic, elemental, carbonate, and total carbon in PM_{2.5} are determined by thermal-optical analysis of a portion of the sample collected on a quartz-fiber filter.

Several ongoing issues in the organic carbon/elemental carbon analysis include: filter contamination by ambient volatile organic compounds (VOCs) and definition of the split point between organic and elemental carbon. Researchers both at RTI and elsewhere are reporting some of these issues.^[5,6]

⁴ U.S. Environmental Protection Agency, Office of Research and Development. "Method IO-33, Determination of Metals on Ambient Particulate Matter Using X-ray Fluorescence, Compendium Methods for the Determination of Inorganic Compounds in Ambient Air; Atmospheric Acidic Constituents." EPA/625/R-93-010a, Washington, DC, September 1997.

⁵ Flanagan, J.B., M.R. Peterson, R.K.M. Jayanty, and E.E. Rickman. "Analysis of PM_{2.5} Speciation Network Carbon Blank Data." Presentation at the Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, November 2002.

Data Validation and Reporting

A custom database management system (DBMS) has been developed for the PM_{2.5} chemical speciation program. A versatile DBMS is essential for quality control validation checks. Currently more than 100 data items are being reported for each sample. Key validation checks are summarized in Table 1.

Type	Validation Check
Field data checks	Total volume Elapsed time Operator observations and validation flags from sampler
Disassembly checks	Shipper received intact, with all components? Temperature in container < 4°C? All forms received, numbers checked against original? Module end caps in place? Evidence of filter damage (ripped, contaminated, creased, etc.)?
Analysis laboratory checks	Laboratory validation flags are assigned by the analysts based on laboratory quality control results and are entered into the database along with the analytical data (mass per filter). Laboratory validation procedures vary widely and are determined primarily by the respective standard operating procedures.
Data screening and review: Internal consistency checks	Correct number and type of samples by date and site Verification of scheduled vs. actual exposure information
Outlier tests based on prescribed acceptance ranges	Flow rate Elapsed sampling time Holding time(s)
Temperatures	Filter-ambient Shipping
Other within-sample tests	Cation/anion ratios Mass conservation Visual and statistical screening

Table 1. Speciation Trends Network (STN) Validation Checks.

⁶ Peterson, M.R. and M.H. Richards. "Thermal-Optical Transmittance Analysis of Organic, Elemental, Carbonate, Total Carbon, and OCX₂ in PM_{2.5} by the EPA/NIOSH Method." Presentation at the Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, November 2002.

Flags for data uploaded to EPA's Air Quality System (AQS) are assigned based on more detailed flags that have been entered into RTI's database. There are two kinds of validation codes in AQS: (a) *null-value codes*, which overwrite data that are considered completely invalid; and (b) *AQS validation codes*, which indicate when a data item is suspicious, but do not overwrite the data value.

Participants in the program can download any or all of the reports for their sites from a secure Web page. Access to data is restricted by means of an assigned username and password. The fully validated data are loaded into AQS within 60 days of the initial data report to the monitoring agencies.

DATA ANALYSIS OF CERTAIN EPISODES

High Potassium from Fireworks

Independence Day for the United States is July 4. It has been a long tradition that fireworks are displayed on this date throughout the country. Fireworks materials generally consist of potassium compounds such as nitrates or perchlorates. PM_{2.5} data for the past 4 years were analyzed, and it was found that many sites showed elevated levels of potassium in early July. Comparison of potassium data obtained by ion chromatography (IC) and by XRF confirmed that the phenomenon was real. This pattern has been repeated every July between 2000 and 2003. Figure 1 shows the plot of all routine monitoring data for potassium for the past 4 years. The maxima in early July are clearly the result of Independence Day fireworks shows throughout the United States. This finding shows the sensitivity of the method.

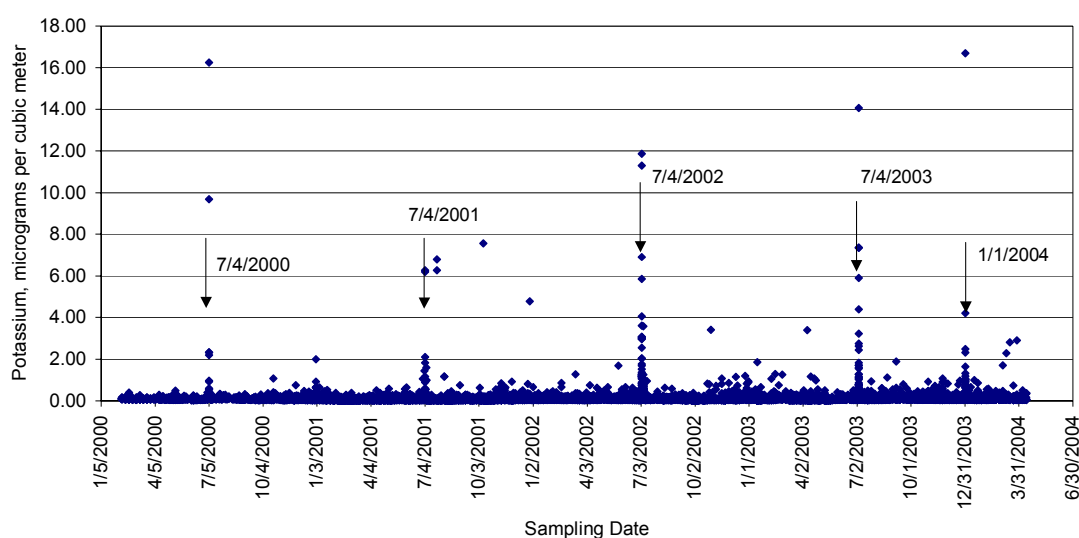


Figure 1. PM_{2.5} Potassium Data for February 2000 through March 2004.

California Forest Fires

In October 2003 wildfires burned over 750,000 acres of land in southern California, which gained national media attention. The locations of some of the largest fires and of several nearby Speciation Trends Network (STN) monitoring sites are shown in Figure 2. Grass and forest fires are known to emit particulate matter containing organic compounds and trace metals, though the composition can vary according to the sources. Air pollutants from fires can travel great distances, potentially affecting the health of people hundreds of miles away.

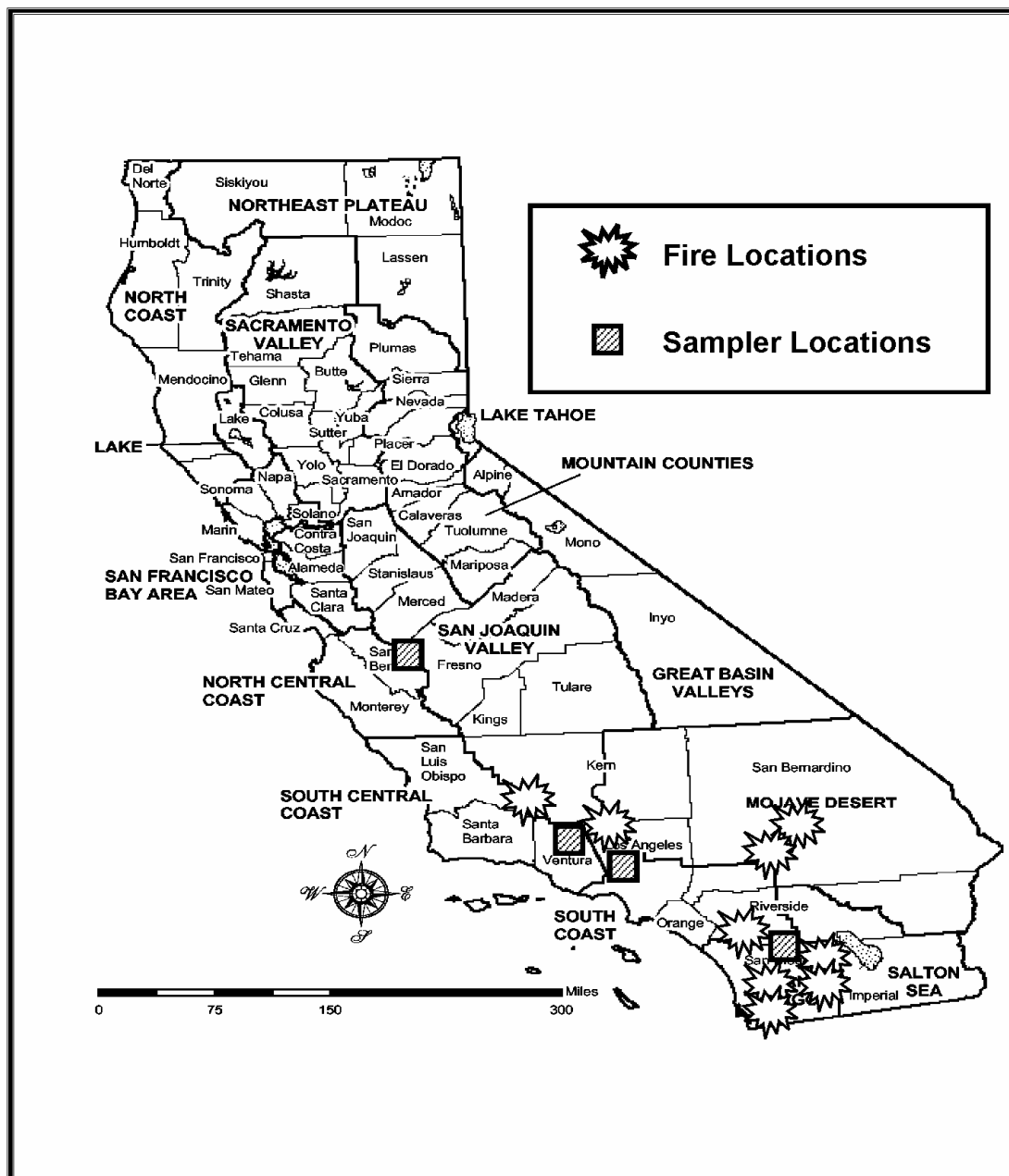


Figure 2. Locations of Fires and Monitoring Sites for 2003 California Fires.

Four STN monitoring locations in southern California were examined for evidence of smoke-related pollutants during this period of time:

- Riverside – This site, to the east of Los Angeles, was the most affected site for the majority of the fire-derived pollutants. This site has two collocated monitors, which agreed well before, during, and after the fire episode.
- Simi Valley – This STN site to the Northwest of Los Angeles was close to a large fire, but prevailing winds minimized the wind-borne pollution during the fire episode.
- North Los Angeles – This site was located farther from the fires than Riverside or Simi Valley, and prevailing winds minimized the impact of smoke-derived pollutants.
- Fresno – Located over 100 miles from the nearest fire, Fresno can be considered to be a background site.

Table 2 shows monitoring results for particulate matter (PM_{2.5}), potassium, organic carbon, and elemental carbon at the four sites (including both Riverside samplers). The table shows little elevation in total particulate matter during or after the fire. For potassium, background levels 1 year and 1 month prior to the fires are uniformly low, but are significantly higher during and 1 month after the fires. Elevated potassium 1 month after the fire at Riverside and Simi Valley may be due to blowing ash, which is rich in potassium.

Other species showing elevations during the fire events included organic carbon and elemental carbon (i.e., soot). Elevations were also found for some trace elements such as iron, but no significant increases were found for ions such as sulfate and ammonium during or after the fires at any of the sites.

Regional Patterns of PM_{2.5} Composition

Because of different particulate production mechanisms and sources in various parts of the United States, the composition of the fine aerosol varies as shown in Figure 3. The pie charts summarize the contributions over a 1-year period (4/1/2003 through 3/31/2004). The United States is divided into four areas: East, South, Central, and West. A similar analysis could be made by date, or by individual site. Data for over 4 years are now available.

Some of the general observations regarding PM_{2.5} species are as follows:

- Sulfate – higher in the eastern United States due to sulfur dioxide (SO₂) emissions from a larger number of power plants located in this region.
- Nitrate – higher in the western United States generally due to wood burning, which is prevalent in this region.

- Organic Carbon – higher in the western United States because several types of semivolatile organics (e.g., polycyclic aromatic hydrocarbons [PAHs] and polychlorinated biphenyls [PCBs]) are emitted and adsorbed into the fine particles from the wood combustion.

	Riverside	Riverside collocated	Simi Valley	North Los Angeles	Fresno
Particulate Matter					
1 year before fire event (average for month of fire)	354.26	325.93	134.74	205.11	342.84
Average for 1 month before the fire	314.57	356.60	164.20	227.82	125.95
Average during the fire	312.00	296.50	103.00	225.71	222.17
Average for 1 month after the fire	207.83	200.29	133.00	205.11	328.09
Potassium					
1 year before fire event (average for month of fire)	0.28	0.29	0.23	0.10	1.01
Average for 1 month before the fire	0.52	0.44	0.27	0.38	0.70
Average during the fire	2.61	2.19	0.52	0.86	1.55
Average for 1 month after the fire	2.34	2.71	1.20	0.10	1.67
Elemental Carbon					
1 year before fire event (average for month of fire)	16.48	16.96	6.24	12.30	13.95
Average for 1 month before the fire	9.11	11.88	9.31	11.87	9.28
Average during the fire	21.86	19.65	4.95	23.22	10.76
Average for 1 month after the fire	11.44	14.99	15.69	22.14	13.27
Organic Carbon					
1 year before fire event (average for month of fire)	75.00	73.05	51.69	66.99	105.87
Average for 1 month before the fire	73.60	69.26	59.28	63.24	60.13
Average during the fire	120.37	124.26	39.95	82.11	92.18
Average for 1 month after the fire	88.70	87.83	72.81	66.99	101.48

Table 2. Results for Four Analytes Before, During, and After 2003 Fires.

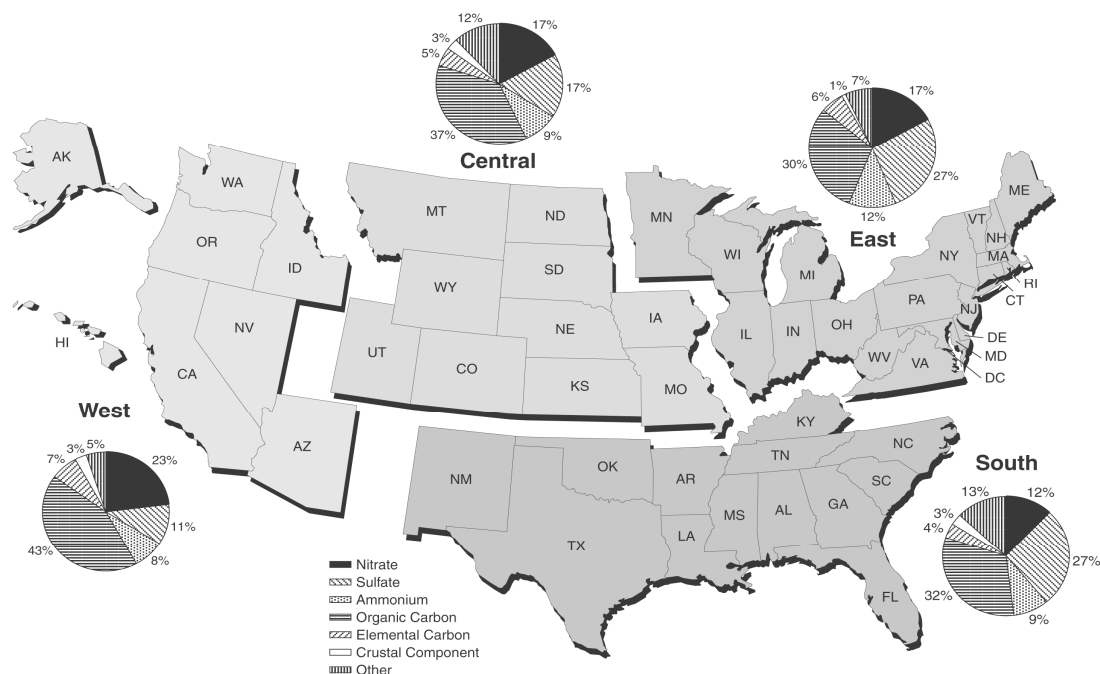


Figure 3. Regional Patterns of PM_{2.5} Composition.

SUMMARY AND CONCLUSIONS

Laboratory support for the PM_{2.5} chemical speciation program requires a complex network of activities that must be performed in a well-choreographed fashion that: keeps sampling modules cycling on a rigid schedule between laboratory and field; keeps filters moving from acceptance testing, to sampling, to analysis, and to archiving; and keeps data flowing from the field and from the chemical speciation analyses through validation and reporting.

RTI has implemented a successful laboratory analysis and sample processing program to support 225 sites in the nationwide network. Several complex challenges involving scheduling, filter blanks, and filter contamination have been identified and addressed to improve data quality.

Speciated particulate data amassed during the past 4 years have been shown to be sensitive to known chemical species such as potassium from fireworks and forest fires. Regional differences in fine particulate composition have also been demonstrated in the data.