

Final Report

**SPATIAL AND TEMPORAL CHARACTERIZATION OF
PARTICULATE MATTER**

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and the
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SUMMARY

In 1999, the North American Research Strategy for Tropospheric Ozone (NARSTO), commissioned a report summarizing the state of science for suspended particles in the lower atmosphere (troposphere), as it is relevant to managing particulate matter (PM) air quality in North America. The report has been prepared by 39 author-scientists and will be released in March, 2003. It was reviewed by the Committee to Review NARSTO's Assessment of Airborne Particulate Matter, a collaboration of the U.S. National Research Council, the Royal Society of Canada, and the United States-Mexico Foundation for Science.

The California Air Resources Board provided support for preparation of Chapter 6, "Spatial and Temporal Characterization of Particulate Matter." This chapter is provided here as a report to the California Air Resources Board, along with two accompanying appendices.

The principal conclusions of Chapter 6 pertaining to management of PM are:

- (1) Long term measurements (typically 10 years) are required to assess trends.
Commitment should be made to routinely monitor at representative site gases and particulate properties of interest for studies of population exposures, effects, model performance, and efficacy of emissions control measures. These measurements should extend to properties other than mass, including size, composition, etc.
Implication: Comprehensive measurements of the multipollutant mixture over a period of at least 10 years are required to understand relationships between emissions, ambient concentrations and effects.

- (2) There is a relationship between the spatial scale over which particulate pollutants are distributed and the spatial and temporal scales of measurements needed to assess their impacts. Relatively coarse spatial and temporal resolution is typically adequate for regional pollutants. For locally emitted pollutants or pollutants that vary diurnally due to photochemical production or variations in temperature and relative humidity, measurements must be made with much higher spatial and temporal resolution.
Implication: It is essential to carry out measurements with adequate spatial and temporal resolution to document population exposure patterns and to obtain data that can be used to evaluate the performance of chemical transport models.

- (3) $PM_{2.5}$ and PM_{10} exhibit seasonal dependencies that vary with location. For example, $PM_{2.5}$ concentrations in eastern North America tend to reach their highest values during summer, when high relative humidities and solar radiation favor the formation of sulfates from regional sulfur dioxide emissions, while in Mexico PM_{10} concentrations reach their maxima during the dry period from November through May. *Implications:* Control strategies, especially those for short-term standards, need to take account of seasonal patterns and to focus on species and processes that lead to the elevated concentrations.
- (4) The composition of $PM_{2.5}$ varies with region and locale. For example, sulfates and organic carbon are relatively abundant in eastern North America; the contribution of nitrates increases in winter, when low temperatures favor the condensed phase. Organic carbon and nitrates are abundant in much of California. Within a given region, local emissions lead to urban concentrations that are ~25% higher than concentrations at nearby nonurban sites. *Implication:* PM control strategies should take account of local, regional and seasonal differences in concentrations.
- (5) In areas where local emissions are low, PM concentrations are likely to be determined by small contributions from many distant sources. For example, regional haze is affected by emissions that occur in regions that are hundreds or thousands of kilometers in extent. *Implications:* When local concentrations are dominated by long range transport, PM control strategies need to account for the impact of multiple distant sources on PM concentrations.
- (6) Many air pollutants are related either through commonality of emissions sources or atmospheric processes. Considering how the concentrations of different pollutants co-vary helps indicate if changes in the emissions of one pollutant, or its precursors, may lead to changes in the ambient concentrations of another. For example, between 1989 and 1998, sulfate concentrations in the Eastern United States and Canada have declined approximately in proportion to SO_2 emissions, which decreased by about one third, while in Los Angeles a 70% reduction in SO_2 emissions between 1976 and 1996 led to a halving of ambient sulfate concentrations. Such empirical observations, however, need to be examined in light of what is known about the behavior of the multipollutant mixture. Assuming that historical trends will continue in the future can lead to errors. *Implication:* Empirical relationships between emissions and

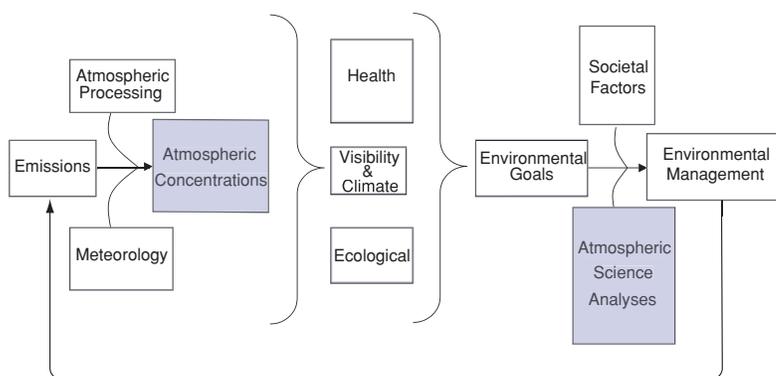
ambient concentrations from historical data can provide valuable insights into changes in ambient concentrations that might be anticipated in the future if emissions change. Confidence in such extrapolations will be improved if the extrapolated trends can be confirmed using available modeling tools.

- (7) Intercontinental transport of dust from Asia or Africa occurs but does not contribute significantly to annual average concentrations of particulate mass concentrations in North America. It is possible, however, that it may occasionally contribute significantly to 24-hour average concentrations. *Implication:* Intercontinental transport of dust typically does not significantly impact on particulate matter mass concentrations in North America. PM management in North America should continue to focus on manageable local and regional PM and precursor emissions. Intercontinental transport of dust should be tracked, allowing for exclusion of rare and unmanageable events from PM management.

- (8) Forest fires or biomass burning can contribute significantly to local particulate mass concentrations. Satellite images and measurements of composition can be used to determine periods when such fires are significantly affecting concentrations. *Implications:* Air quality forecasting can be used to determine periods when the effects of smoke emissions from controlled burns can be minimized. Data that are routinely collected can be used to identify periods when smoke emissions from distant fires are affecting local particulate mass concentrations.

CHAPTER 6

Spatial and Temporal Characterization of Particulate Matter



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6.1 INTRODUCTION

Geographical and temporal variations of the concentration and composition of $PM_{2.5}$ influence PM exposure (Chapter 2) and provide important insights into the processes that influence particle formation and distribution (Chapter 3). Characterizing the temporal, spatial, and chemical variations of particles and their precursor gases, as well as the size properties of particles, enhances understanding of emission sources (Chapters 4 and 7), secondary PM formation, and transport. This information establishes key features of the data that should be reproduced by modeling studies and allows air-quality models to be tested against ambient measurement data (Chapter 8). Measurements thereby support the use of models as an important tool for assessing proposed emission management strategies or evaluating source contributions to existing aerosol concentrations. Where a data record exists that is long enough to support trend assessments (typically decadal), characterization of trends provides an important technique for evaluating the success of ongoing management programs.

In this chapter, the spatial and temporal patterns of PM mass concentration and composition are presented. The topics covered are:

- Section 6.2: spatial variations of PM across North America
- Section 6.3: regional and urban contributions to PM
- Section 6.4: influence of intercontinental aerosol on North America

- Section 6.5: trends, along with their implications for source attribution and management
- Section 6.6: covariation of PM and ozone concentrations
- Section 6.7: summary
- Section 6.8: policy implications.

Two appendices provide further information on data availability and monitoring networks (Appendix C) and the global distribution of aerosols (Appendix D). Chapters 7 (Receptor Modeling) and 10 (Conceptual Models) extend upon the present chapter through discussion of methods for analyzing observations (Chapter 7) and presentation of regional case studies (Chapter 10).

The terminology presented in Chapter 1 is used throughout this chapter: $PM_{2.5}$ is defined as particles of aerodynamic diameter 2.5 micrometer and less, PM_{10} is particulate matter of aerodynamic diameter 10 micrometer and less, and $PM_{10-2.5}$ consists of particles between 2.5 and 10 micrometer aerodynamic diameter. Because PM regulations are expressed in terms of mass, rather than aerosol number or surface area, the data in this chapter are presented in mass units (micrograms per cubic meter, or $\mu g/m^3$).

6.1.1 General Features Affecting Particulate Levels in North America

Regional and local PM concentrations in North America are affected by the location and magnitudes

of anthropogenic and natural emissions, topography, land cover, winds, and a variety of processes affecting the rates of conversion of gases to particles. Human population densities are greatest in central Mexico, the northeastern United States, southeastern Canada, and portions of the Pacific Coast, leading to higher anthropogenic emissions of primary particles and particulate precursors in those areas compared with other parts of North America (Chapter 4, Figures 4.1 and 4.2). However, the relative sparseness of vegetation in parts of the southwestern United States and Mexico favors airborne suspension of dust in those areas during the dry seasons.

Topography, through its influence on circulation, strongly affects daily variations of PM mass concentrations in some locations. Mexico City (Edgerton et al., 1999) and Los Angeles are two notable examples where terrain substantially influences the circulation of air masses, affecting the concentrations of PM mass from day to day.

The general pattern of air movement across North America influences the prevailing transport directions for particles. During summer, a generally south-to-north-or-northeast transport direction is expected for eastern North America, whereas a west-to-east pattern is more typical of western North America (Figure 6.1). Prevailing air-mass patterns make it possible for particle-laden air masses to reach the Gulf Coast states in the United States from northern Africa, or for air pollutants to travel from Asia to western North America (see Appendix D).

The potential transport distances of particles depend strongly upon particle size (see Chapter 3) and wind speed. Typical residence times for particles of 0.1–1.0 μm aerodynamic diameter are on the order of ten days. However, this residence time can vary with altitude. Within the atmospheric boundary layer (the lowest 1 to 2 km), the typical residence time is about 3 to 5 days. If aerosols are lifted to ~1 to 10 km in the troposphere (e.g., by deep convection at fronts or convergence zones), they can be transported for weeks and many thousand kilometers before removal. Particles at higher levels of the atmosphere may or may not affect ground-level concentrations, so information about particle plumes derived from satellite measurements typically needs to be compared with data from surface monitors.

6.1.2 Spatial and Time Scales of Interest

The spatial and temporal distributions of aerosols are determined by the patterns of their causal factors: emissions, transport, deposition, and chemical reactions. Consequently, temporal and spatial pattern analysis of PM data is particularly useful for source identification and characterization.

In the atmosphere, larger spatial scales are associated with longer time scales (Chapter 1, Figure 1.3). However, regulatory approaches for managing PM exposure use both 24-hr and annual-average standards, applicable at all spatial scales. Spatial scales of interest for health impacts include the neighborhood scale (1 to 10 or more km) for characterizing individual and community exposure, the urban scale (10 to 100 or more km) for characterizing population exposure, and regional (100 to 1000 or more km), continental, and intercontinental scales for characterizing large-scale contributions to PM mass upon which urban aerosol concentrations are superimposed. Management of PM mass concentrations focuses on the full range of spatial and temporal scales to address a set of linked problems: sorting out the regional, urban, and neighborhood contributions to measured PM mass concentrations, establishing the spatial representativeness of monitoring locations, apportioning PM observed at a receptor back to its sources, and designing monitoring networks capable of characterizing population exposure.

Full characterization of the spatial variations of PM is exceedingly difficult. Virtually the entire record of PM mass and composition underestimates the true variability occurring in the atmosphere, because monitors operated at fixed locations typically do not capture concentration variations occurring over distances of tens to hundreds of meters. Indeed, monitors are generally located where the measurements may be considered representative of conditions over tens to hundreds of kilometers (urban to regional scales). Yet, health effects may occur on finer spatial scales than typical PM networks can resolve, such as adjacent to roadways (Brunekreef et al., 1997).

Visibility concerns focus primarily on the regional scale, especially in the scenic vistas of western North

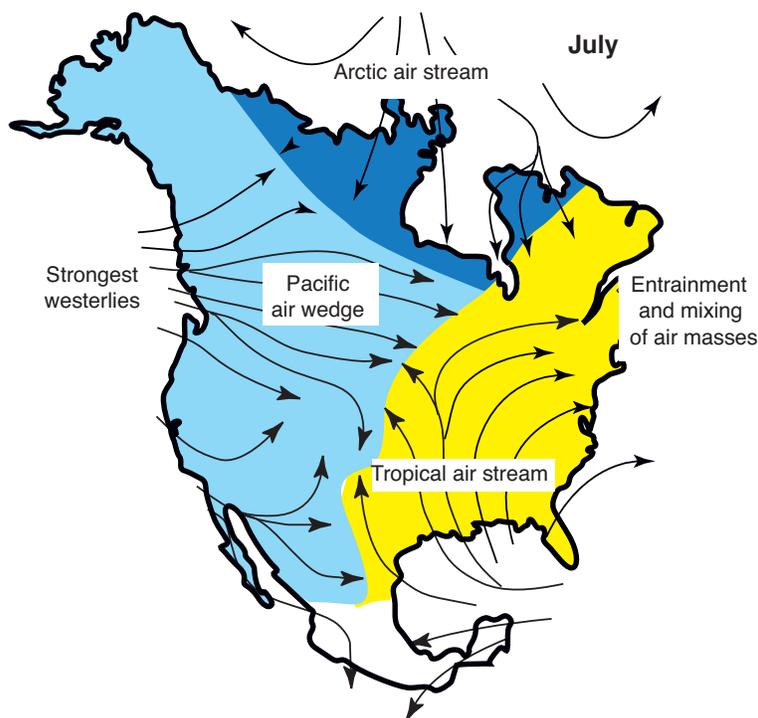


Figure 6.1. Average air mass source regions and transport during July (Source: redrawn from Bryson and Hare, 1974).

America, but also include urban and neighborhood-scale concerns. As noted, time scales of interest expand along with spatial scales, so that multi-day episodes of impaired visibility are typically regional in spatial extent. Visibility impairment is strongly related to $PM_{2.5}$ levels, but linkages to gas-phase pollutant issues exist (Chapters 3 and 9).

6.1.3 Monitoring Capabilities

The data used in this chapter were obtained primarily from multiple surface-based monitoring networks that were originally designed for differing purposes (Appendix C). As discussed in Chapter 5, measurements of PM mass obtained by different methods typically agree within 20 percent. Comparability across techniques for specific PM components can be better or worse than comparability for mass, depending on the difficulty of the measurement: about 10 percent for sulfate, ~35 percent for nitrate, approximately 10 percent to 30 percent for trace elements, 20 percent to 50 percent

for OC and 20 percent to 200 percent for BC (see Chapter 5). Spatial patterns and time trends compiled across monitoring networks may reflect some of the variability among sampling and measurement methods. However, analyses of the spatial and temporal variations using data derived from consistent measurement techniques need not reflect the full range of variability across measurement methods, though the absolute magnitudes of any set of measurements will reflect whatever biases may exist in the techniques.

6.2 CONTINENTAL AND REGIONAL VARIATIONS OF PM CONCENTRATIONS

In this section, the spatial patterns of aerosol concentrations and composition are examined across

North America and by region. Spatial and temporal variations, and their significance, are discussed using comparisons and contrasts of measurements from nine different regions within North America (Figure 6.2):

- Southeastern Canada (Windsor-to-Quebec City corridor)
- Northeastern United States
- Southeastern United States
- Ohio River Valley
- Mexico City
- Southwestern United States
- Los Angeles, California
- San Joaquin Valley, California
- Pacific Northwest (United States and Canada).

The selected regions illustrate specific characteristics of PM for a variety of situations that represent a wide

CHAPTER 6

range of emission sources, terrain, and meteorological characteristics. Both urban and regional measurements are considered, with the aim of showing the relation of urban and regional PM in each area. Much of the material from this chapter will be applied further in Chapter 10, where key information is condensed in terms of region-specific “conceptual models” of PM behavior. It should be noted in this context, however, that the areas designated on Figure 6.2 correspond only loosely to the conceptual model regions in Chapter 10.

The eastern regions illustrate conditions in which sulfate is a major component of $PM_{2.5}$ during much or most of the year. SO_2 emission densities are greater in the Ohio Valley than in any other region, and SO_2 emissions in the other three eastern regions exceed those in western North America (Chapter 4).

Distinguishing features of the southeastern United States include the widespread, persistent haze observed over much of the region, especially in summer, the amount of rural power generation, and rapidly growing urban areas (Chapter 9). Organic carbon and sulfates are usually major constituents of that haze. More needs to be understood about the sources of the carbonaceous component of the particle samples obtained in the southeastern United States, including primary particle emissions and secondary contributions from atmospheric chemical reactions involving volatile organic carbon compounds.

With about 20 million inhabitants, Mexico City is one of the largest urbanized areas in the world. Unlike U.S. and Canadian cities, it is situated in a tropical latitude (19 degrees north). Its elevation of

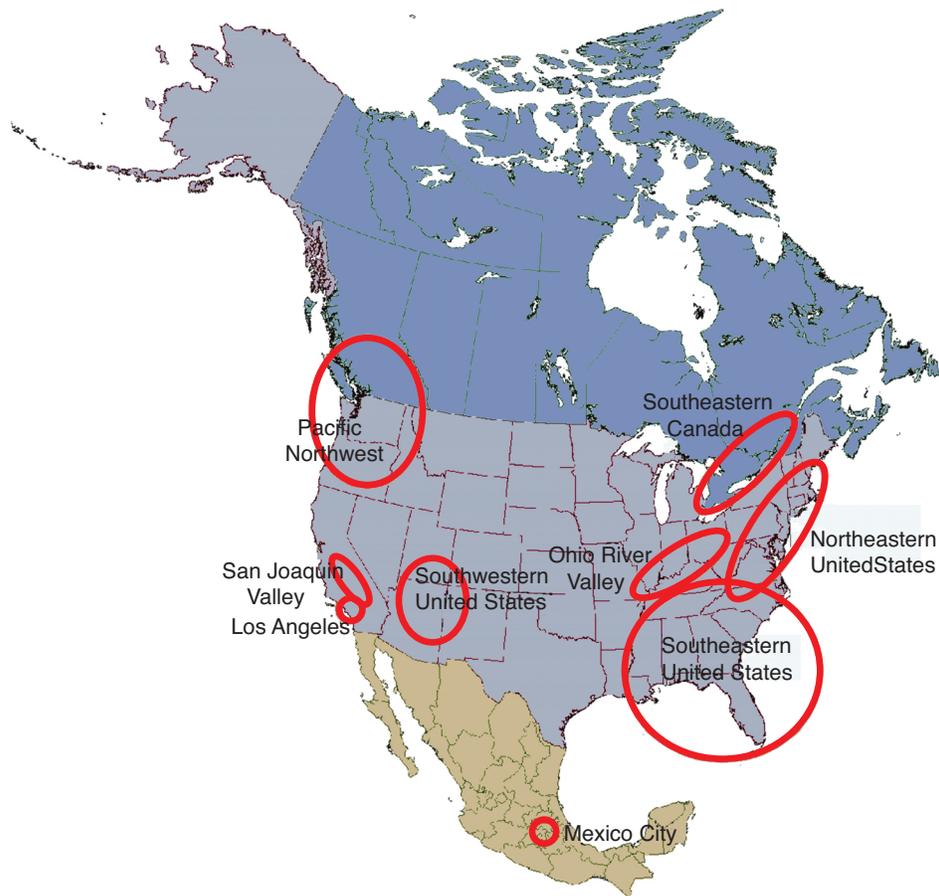


Figure 6.2. Locations of study regions.

approximately 2240 m provides it with a temperate climate. Mexico City occupies an area of about 1300 km² within the Valle de Mexico, a basin with mountain ranges rising about 1000 m above the valley floor to the east and west. The terrain limits ventilation, and pollutant concentrations are affected by thermal and topographic circulation patterns. Of particular significance to PM is the presence of urban-rural transition zones with unpaved areas, agriculture, livestock, and deforested areas.

For many years, the southwestern United States, particularly the Grand Canyon region, has been the focus of research on visibility, as well as regulatory efforts aimed at eliminating regional haze and thereby maintaining the scenic vistas of the southwestern United States. Typically, the best visibility in the conterminous United States occurs in a region including the Grand Canyon and other national parks in northern Arizona, southern Utah, as well as portions of Colorado, Nevada, and Wyoming (Malm, 2000).

The California examples illustrate two different sets of conditions, each of which results in some of the highest PM mass concentrations recorded in North America. Whereas the Los Angeles area is primarily urban, with a population density of about 2100 people per square mile, the San Joaquin Valley is primarily rural with several cities of moderate size (~50,000 to 400,000) and an average population density of about 120 people per square mile. Los Angeles borders the Pacific Ocean and exhibits a marine influence with fog commonly occurring during late spring and summer. The San Joaquin Valley is inland, bordered by the Pacific Coast Range to the west and the Sierra Nevada to the east; winter inversion fog is common. In both cases, the presence of fog plays a key role in the conversion of gas-phase species to particles, the growth of hygroscopic particles, and particle volatility.

Sites in the Pacific Northwest exhibit PM mass concentrations lower than in eastern North America, and PM composition differing from that typical of either other portions of western North America or of eastern North America.

6.2.1 Spatial Variations of PM₁₀ Mass: Where and When are PM₁₀ Concentrations Highest?

Substantial spatial (Figure 6.3) and seasonal (Figure 6.4) variations occur in the concentrations of PM₁₀ mass. Annual PM₁₀ averages in Mexico City, Toluca, Ciudad Juarez, Monterrey, and Guadalajara all exceed 50 mg/m³ (Figure 6.3). High concentrations predominate during the months of December through May (Figure 6.4). This period falls within the dry season – cold and dry from November through February and warm and dry from March through June. In Mexico, PM₁₀ mass concentrations drop substantially during the wet season, from July through October.

In the United States, the highest annual PM₁₀ averages are recorded at sites in California, especially in the San Joaquin Valley and the Imperial Valley. During the period 1995 through 1999, maximum 24-hr PM₁₀ mass concentrations ranged from 153 to 279 µg/m³ in the San Joaquin Valley and from 229 to 1342 µg/m³ in the Imperial Valley, based on sampling once every six days (CARB, 2001). Occasional high daily PM₁₀ concentrations occur at many California sites, especially during autumn (e.g., Figure 6.4).

High PM₁₀ mass concentrations occur along much of the U.S.-Mexico border, and represent a transboundary pollution issue, with transport likely occurring in both directions. Mexicali (Baja California), Calexico (California), El Paso (Texas), and Ciudad Juarez (Chihuahua) exhibit annual PM₁₀ averages in excess of 50 µg/m³. The U.S.-Mexico border extends for 3141 km, with over 10 million people living within 100 km on either side of the border (Mukerjee, 2001). This area, which is subject to the 1983 Agreement for the Protection and Improvement of the Environment in the Border Area (La Paz Agreement), is experiencing rapid growth in population and development, especially since the 1993 North American Free Trade Agreement. Ongoing environmental studies are described in Mukerjee (2001) and companion papers. The 1992-93 Imperial/Mexicali Valley Cross-Border PM₁₀ Transport Study documented significant (factor of two) PM₁₀ mass concentration differences within an 80 km by 20 km study area (Chow and Watson, 2001).

From 1984 to 1993, mean PM_{10} mass concentrations varied from 11 to $44 \mu\text{g}/\text{m}^3$ at the 19 sites of the Canadian National Air Pollution Surveillance (NAPS) Network (Brook and Dann, 1997). Average $PM_{2.5}$ mass was 36 to 68 percent of the PM_{10} mass concentrations, with mean coarse ($PM_{10-2.5}$) mass ranging from 4 to $24 \mu\text{g}/\text{m}^3$. Differences in PM_{10} mass concentrations at paired urban-nonurban sites exceeded the differences between regions (Brook and Dann, 1997).

PM_{10} remains a management issue, as exceedances of the U.S. 24-hr PM_{10} standard of $150 \mu\text{g}/\text{m}^3$ and the U.S. and Mexican annual-average PM_{10} standards of $50 \mu\text{g}/\text{m}^3$ occur in both Mexico and the United States (Canada does not have a standard for PM_{10} but is considering a standard for $PM_{10-2.5}$).

PM_{10} mass concentrations can show substantial variations over urban-scale (10 to 100 km) distances. Five-fold variations of average annual PM_{10} mass concentrations are evident over distances of about 100 km or less (Figure 6.3). In urban areas having multiple monitoring sites, average PM_{10} mass may vary by up to roughly a factor of two over distances as small as approximately 10 to 20 km. For example, recent data from southern California, shown in Figure 6.5, reveal two-fold or greater differences in average PM_{10} mass within the metropolitan area.

Mexico City shows twofold variations of annual average PM_{10} concentrations (Figure 6.6). The northeastern monitoring site (Xalostoc; XAL in Figure 6.6) is located in an industrialized area and has historically shown the highest concentrations of

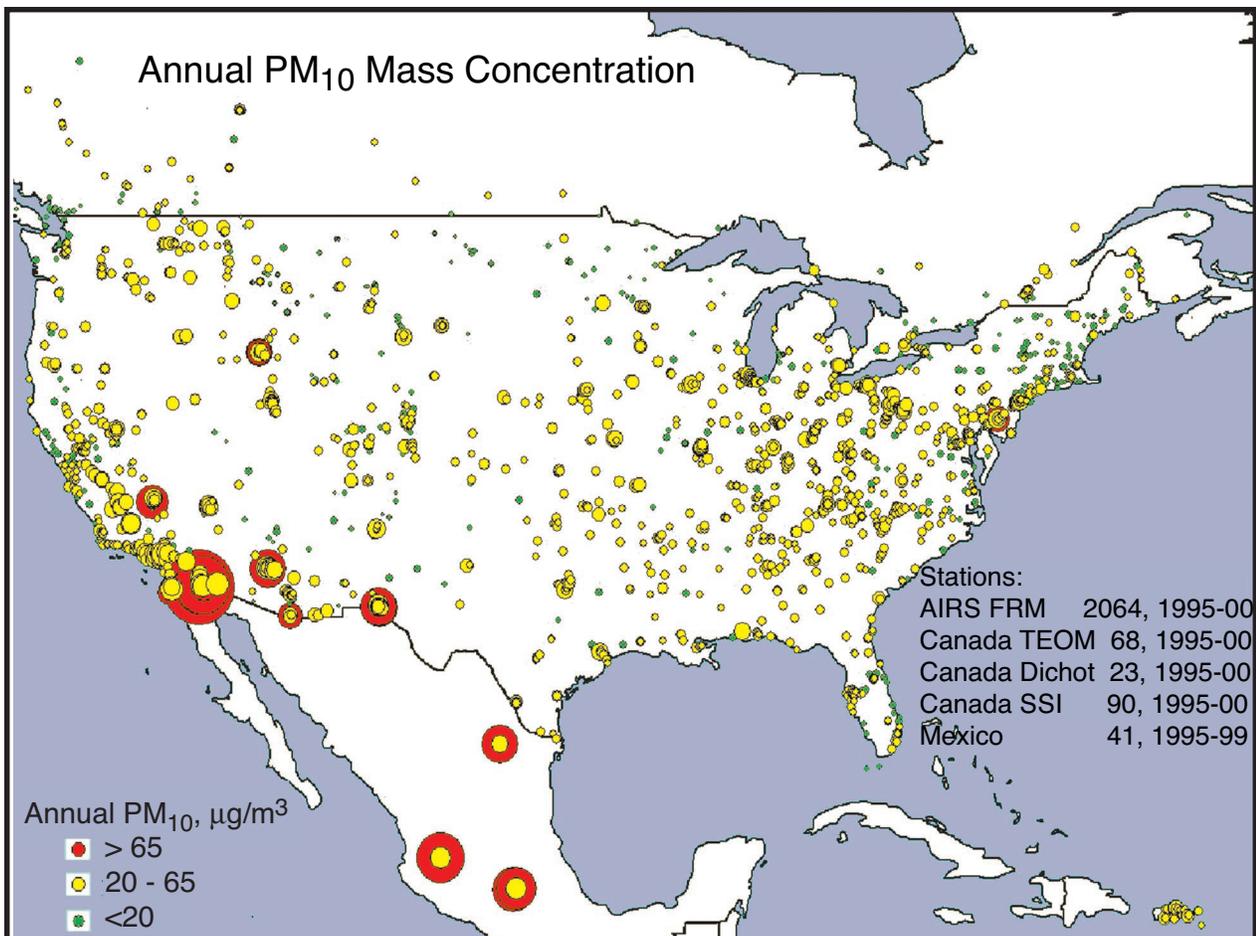


Figure 6.3. Average annual PM_{10} mass concentrations. The U.S. data are from sites in the EPA AIRS database. Canadian data were provided by Environment Canada. PM_{10} data were available for five cities in Mexico. Spot diameter varies in proportion to concentration. (Source: R. Husar, pers. comm.).

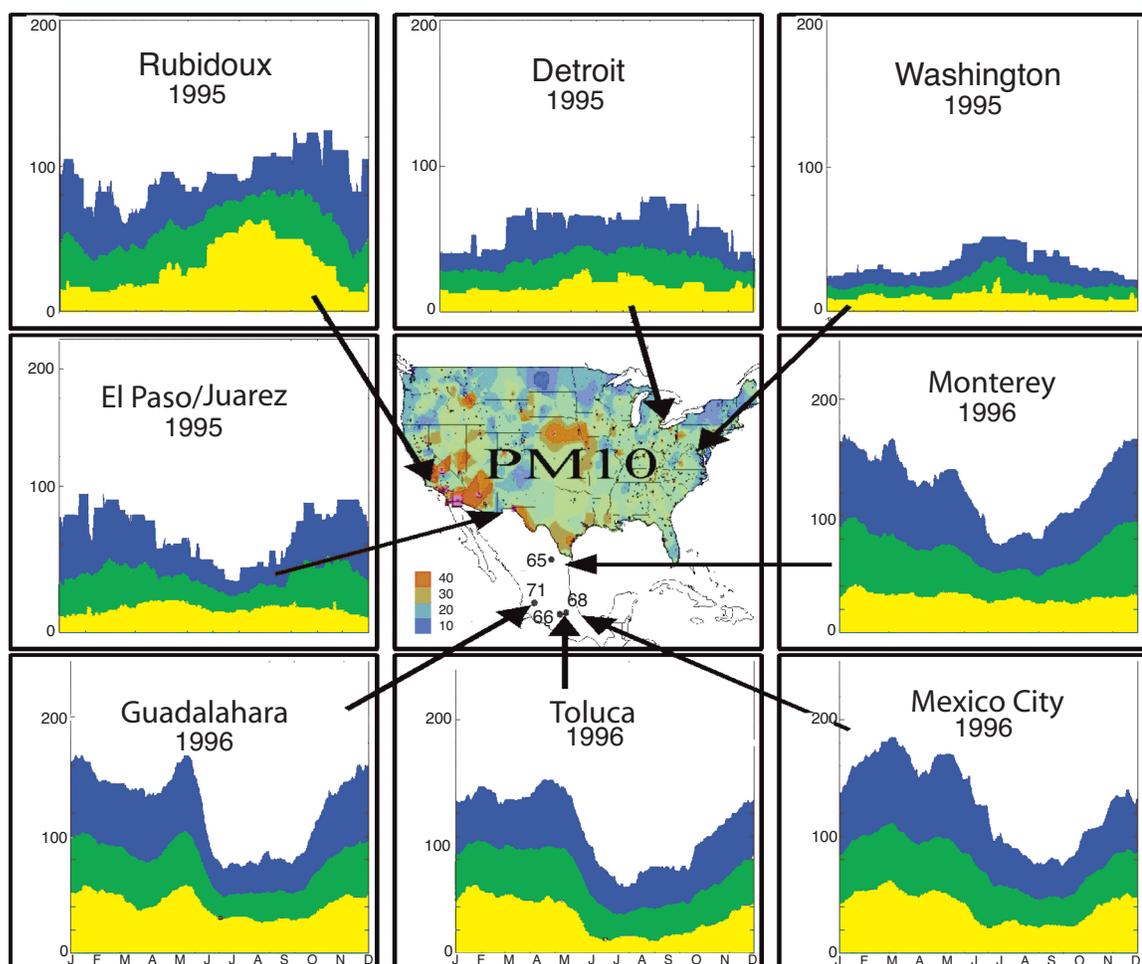


Figure 6.4. Seasonal variation of PM_{10} mass concentrations at selected monitors in the United States and Mexico. The graphs indicate the estimated 20th percentile (yellow), average (green), and 90th percentile (blue) on each date beginning in 1995 or 1996. Data for U.S. locations represent one site; data for Mexican locations include five to eight sites per location. Statistical smoothing procedures were applied to each time series in estimating the percentiles (Source: R. Husar, pers. comm.).

total suspended particulate (Vega et al., 2002). The eastern site (Netzahualcoyotl; NET in Figure 6.6) is surrounded by paved and unpaved roads, loose dirt surfaces, and open landfills (Chow et al., 2002). PM_{10} concentrations in the eastern and northeastern areas may also be influenced by resuspended dust from the bed of dry Lake Texcoco, which is 5 km east and 10 km north, respectively, of the monitors at Xalostoc and Netzahualcoyotl (Vega et al., 2002; Chow et al., 2002). Such variations of ambient outdoor PM mass concentrations suggest that people living in different portions of the Mexico City urban area are experiencing substantially different levels of exposure to PM.

Spatial variations of PM_{10} mass concentrations are also evident in other urban areas. In Montreal, two long-term monitoring locations have shown mean PM_{10} concentrations differing by $14 \mu\text{g}/\text{m}^3$ (28 compared with $42 \mu\text{g}/\text{m}^3$) and a short-term (34 day) study that placed an additional seven monitors at 1 or 3 km distances around the two primary locations revealed daily (24-hr) concentration differences ranging from ~ 5 to a maximum of $20 \mu\text{g}/\text{m}^3$ (Brook et al., 1999). A special study in California's San Joaquin Valley during December 1995 and January 1996, using 25 monitors in Fresno (population $\sim 480,000$) and 12 in Bakersfield (population $\sim 300,000$), showed that mean concentrations of PM_{10}

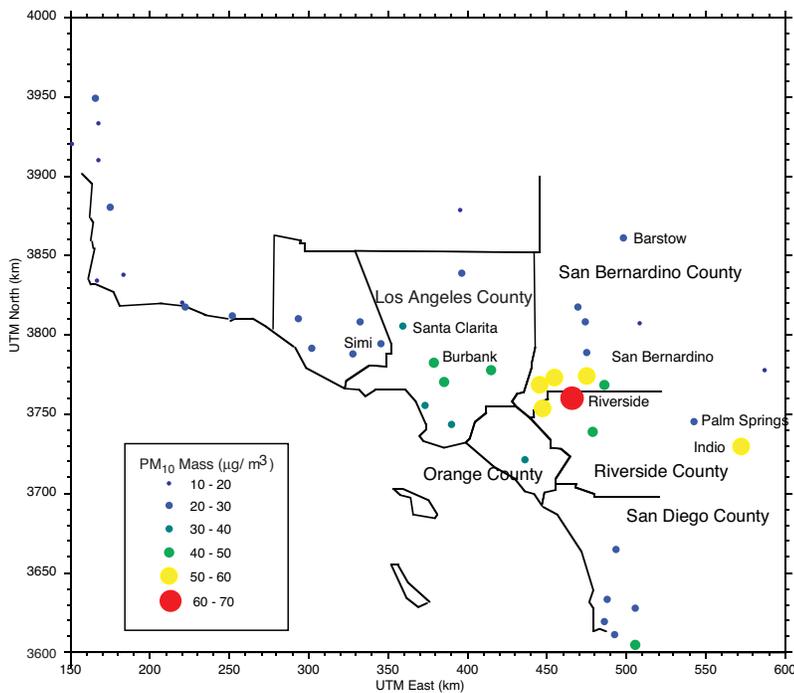


Figure 6.5. Variations of average PM_{10} mass concentrations at monitoring sites in southern California over the years 1997-99. The Los Angeles metropolitan area includes Orange County, the southern portion of Los Angeles County (south of Santa Clarita), and the western portions of Riverside and San Bernardino counties (west of Riverside and San Bernardino).

and its constituents varied by 10 to 15 $\mu\text{g}/\text{m}^3$ (~20 percent of mean values) over distances of 4 to 14 km (Blanchard et al., 1999).

The observed intra-urban variations of PM_{10} and its constituents imply that local (within about 10 km) emission sources often contribute much (i.e., greater than half) of the PM_{10} mass on an annual average basis; it is possible for local contributions to be greater on shorter time scales (daily or hourly). These variations also imply that annual PM_{10} exposure may vary by a factor of two or more across an urban area, with potentially larger variations occurring in daily exposure. As a result, epidemiological studies run the risk of misclassifying PM_{10} exposures if the number of monitors within an urban area is insufficient to represent the spatial variations of outdoor population exposures.

6.2.2 Spatial Patterns of $PM_{2.5}$ Mass

The highest mean annual $PM_{2.5}$ concentrations in North America occur at sites in California and over a broad portion of the eastern, and especially the southeastern, United States (Figure 6.7) (short-term $PM_{2.5}$ data for Mexico City indicate the occurrence of high fine mass concentrations there as well). Throughout North America, both urban and rural monitoring locations may exhibit $PM_{2.5}$ mass concentrations exceeding the national standards of Canada or the United States (Mexico does not currently have a fine particulate standard). Although determination of compliance with PM standards is the responsibility of various regulatory agencies, the ambient air quality standards established by those agencies provide a useful benchmark for delineating the dimensions of the $PM_{2.5}$ management task.

In comparison with PM_{10} concentrations, annual-average $PM_{2.5}$ levels show less regional variation (Figures 6.7 and 6.3). Nonetheless, intra-urban annual-average $PM_{2.5}$ mass concentration can vary up to a factor of two over distances of about 50 to 100 km, as is the case in Los Angeles (Figure 6.8). Factor of two inter-site differences also occur among locations in Mexico City (Edgerton et al., 1999; Chow et al., 2001). Paired monitoring locations within Toronto and Montreal show mean $PM_{2.5}$ concentrations differing by 2.3 and 4.0 mg/m^3 , respectively (for mean values of ~15 to 20 mg/m^3) (Brook et al., 1999).

Daily (24-hr) $PM_{2.5}$ concentrations usually exhibit more spatial variability than do annual averages. U.S. FRM data from 1999 show that daily $PM_{2.5}$ mass concentrations were strongly correlated ($r > 0.9$) at all pairs of multiple monitoring locations within only 5 of 28 metropolitan areas (Lefohn, 2001). Statistically

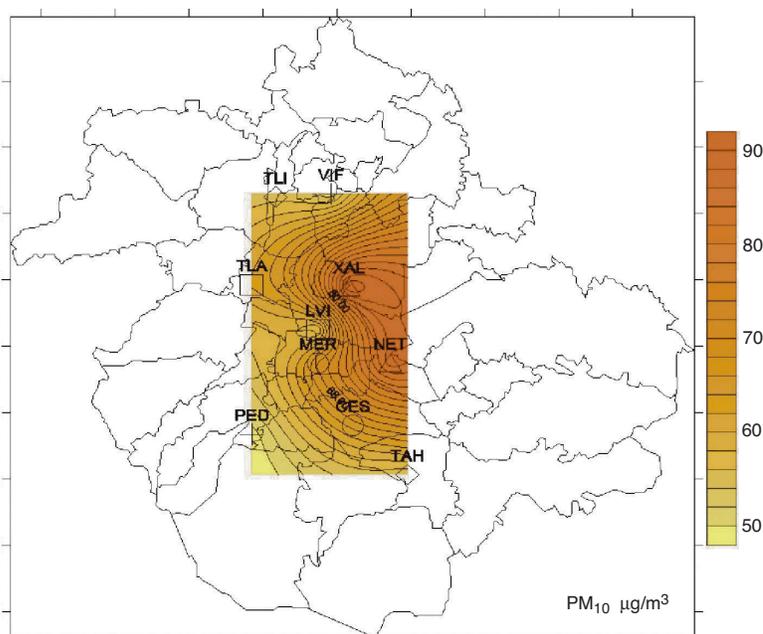


Figure 6.6. Variations of average PM_{10} mass concentrations at monitoring sites in Mexico City over the years 1995 to 2000. The area covered by the monitoring sites is approximately 20 km in the east-west direction by 45 km in the north-south direction. (Source: E. Vega, pers. comm. Summary data are given in Cicero-Fernandez et al., 2001. Spatial distributions of PM_{10} mass in the Mexico City metropolitan area are also presented in Cicero-Fernandez et al., 2001, and Molina and Molina, 2002).

significant differences between daily $PM_{2.5}$ concentrations occurred up to 50 percent of the time; median intra-urban daily differences ranged from zero to 8.4 mg m^{-3} and maximum daily differences exceeding 30 µg/m^3 were frequent.

The typically smaller spatial variations of $PM_{2.5}$ mass than PM_{10} mass are consistent with the well-known long residence time of fine aerosol, which permits transport over distances of 10 to 1000 km and tends to homogenize spatial variations in mass concentrations. As is the case for PM_{10} , epidemiological studies run the risk of misclassifying $PM_{2.5}$ exposures if the number of monitors within an urban area is insufficient to represent the spatial variations of outdoor population exposures. Further attention to network-design requirements is needed to ensure that future monitoring data are adequate to properly characterize exposure.

For 1998 and 1999, urban locations from Chicago to Mississippi and Ohio to Georgia showed annual-average $PM_{2.5}$ mass concentrations exceeding the U.S. federal standard of 15 µg/m^3 , with sites in Tennessee and in northern Alabama, Mississippi, and Georgia exhibiting mean annual $PM_{2.5}$ levels exceeding 18 µg/m^3 (Figure 6.7). A substantial inland-to-coast gradient of mean PM concentrations exists in the southeastern United States and monitoring locations near the Gulf or Atlantic coasts exhibit mean annual $PM_{2.5}$ levels less than the U.S. federal standard of 15 µg/m^3 . The spatial variations indicated for FRM sites in Figure 6.7 are also characteristic of the concentrations reported by the IMPROVE and Clean Air Status and Trends Network (CASTNet) networks, which consist almost exclusively of rural sites.

For the first year of FRM monitoring in 1999, 68 of the 73 FRM samplers in California had data and 33 sites showed annual-average $PM_{2.5}$ mass concentrations exceeding the U.S. federal standard of 15 µg m^{-3} (the exceeding locations recorded annual means ranging from 15.1 to 30.2 µg/m^3). All eight FRM monitors with one year of data in the San Joaquin Valley had annual $PM_{2.5}$ averages over 15 µg/m^3 (range 19.6 to 27.0 µg/m^3), as did 14 of 16 monitors in the Los Angeles metropolitan area (exceeding means ranged from 17.3 to 30.2 µg/m^3). Fine-particulate measurements made since 1987 at 8 IMPROVE (or IMPROVE-protocol) sites and 32 sites in three networks operated by the California Air Resources Board provide a long-term record confirming that mean $PM_{2.5}$ mass concentrations in southern California and the San Joaquin Valley typically exceed the annual-average $PM_{2.5}$ standard (Motallebi et al., 2003a; 2003b).

A longer monitoring record is available for Canada, where 11 of 22 monitoring sites in the NAPS exhibited 98th percentile 24-hr $PM_{2.5}$ mass

concentrations exceeding the Canada Wide Standard (CWS) during the period 1997 through 1999 (the CWS is $30 \mu\text{g}/\text{m}^3$ expressed as a three-year average of the 98th percentile 24-hr values). All eleven were located in the provinces of Ontario and Quebec, and included nine urban and two rural sites. From Windsor, Ontario, eastward, the three-year mean annual $\text{PM}_{2.5}$ concentrations ranged from $4.9 \mu\text{g}/\text{m}^3$ to $13.6 \mu\text{g}/\text{m}^3$ at Toronto-Evans. The four monitoring locations in British Columbia (Vancouver and Victoria) all had three-year mean annual $\text{PM}_{2.5}$ concentrations less than $10 \mu\text{g}/\text{m}^3$, and Victoria recorded the minimum 98th percentile 24-hr value of $16.5 \mu\text{g}/\text{m}^3$.

Long-term monitoring data, from which 98th percentile 24-hr values or mean annual concentrations may be computed, are not available for Mexico City. However, data from many short-term studies do exist and indicate the occurrence of some of the highest $\text{PM}_{2.5}$ and PM_{10} concentrations in North America. Recent measurements from an intensive field study during February and March 1997 yielded monthly average $\text{PM}_{2.5}$ concentrations ranging from 21.6 to $50.0 \mu\text{g}/\text{m}^3$ at six monitoring locations within Mexico City (Edgerton et al., 1999). The maximum 24-hr $\text{PM}_{2.5}$ concentrations ranged from 33.9 to $183.7 \mu\text{g}/\text{m}^3$. While Mexico has no fine PM standard, Mexico's 24-hr PM_{10} standard of $150 \mu\text{g}/\text{m}^3$ was exceeded at one or more sites on 7 of the 28 days sampled. The

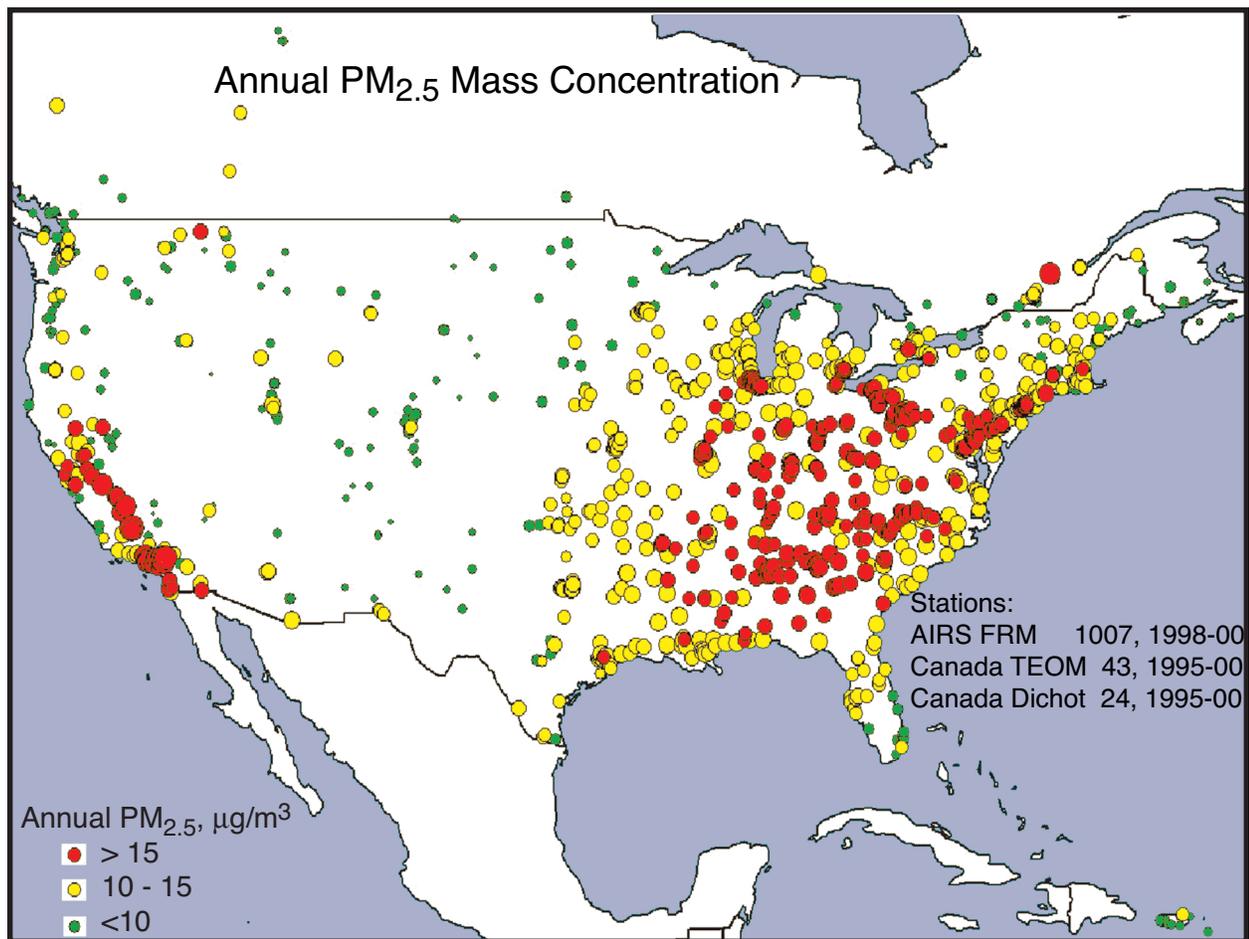


Figure 6.7. Average $\text{PM}_{2.5}$ concentrations. The U.S. data are from FRM monitors at sites in the EPA AIRS database for July 1998 through July 2000. Canadian data are from TEOM and dichotomous samplers operating from 1995 through 2000. The currently available data from sites in Mexico represented less than one year of sampling and were excluded from the computation of annual averages. Spot diameter varies in proportion to concentration. (Source: R. Husar, pers. comm.).

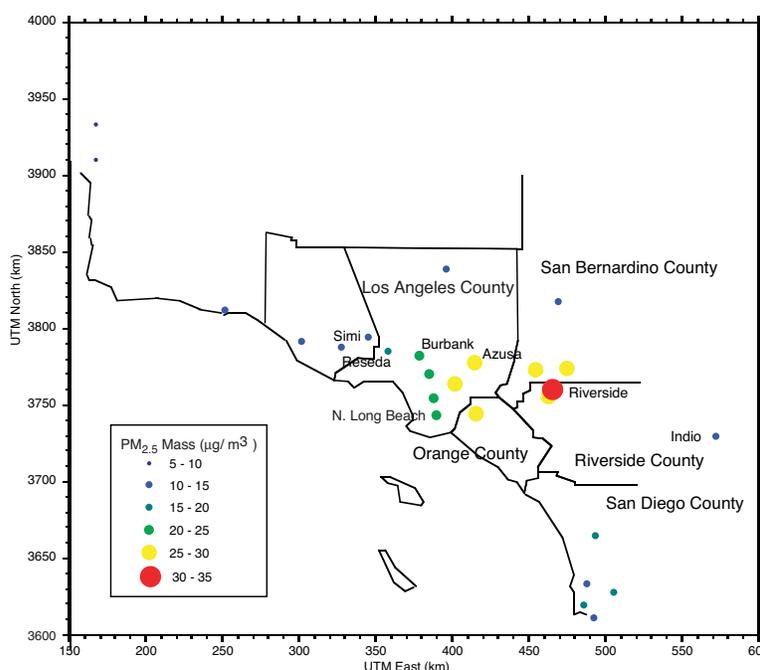


Figure 6.8. Example urban-scale variations of average $PM_{2.5}$ mass concentrations in southern California. The data are the 1999 average concentrations from all monitoring locations having at least 11 months data. (Source: data provided by California Air Resources Board).

$PM_{2.5}$ mass concentration was typically about half the PM_{10} mass concentration.

In five of the seven geographical regions shown in Figure 6.9, the 98th percentile 24-hr $PM_{2.5}$ mass concentrations at the majority of urban U.S. and Canadian monitoring sites exceeded $30 \mu\text{g}/\text{m}^3$ (the level of the Canada Wide Standard). In three regions, California, the southeastern United States, and the Ohio Valley – Great Lakes states, annual-average $PM_{2.5}$ mass concentrations at about half the urban sites exceeded the U.S. three-year average annual mean standard of $15 \mu\text{g}/\text{m}^3$ (Figure 6.9). With the exception of California, few sites had 98th percentile 24-hr $PM_{2.5}$ exceeding the level specified by the U.S. 24-hr standard ($65 \mu\text{g}/\text{m}^3$). Thus, in the United States, achieving the annual $PM_{2.5}$ standard will be the focus of the regulatory effort at most sites, whereas in Canada the regulatory effort will necessarily be oriented to the 24-hr Canada Wide Standard. In California, PM management needs to address both the U.S. annual and 24-hr standards.

$PM_{2.5}$ concentration measurements typically exhibit strongly skewed frequency distributions, dominated by a large number of low values and including a smaller number of high concentrations (Figure 6.10). At locations where exceedances of national 24-hr or annual-average $PM_{2.5}$ standards occur, numerous episodes of elevated PM mass concentrations contribute. High concentrations do not occur on the majority of days, but neither are they rare events: as shown in Figure 6.10, the ten-year record at 15 California sites shows 2.7 percent of the samples exceeding the U.S. 24-hr standard of $65 \mu\text{g}/\text{m}^3$. Similarly, during the months of June through September at NAPS sites in Ontario, approximately 5 to 15 percent of the days exhibit 24-hr $PM_{2.5}$ concentrations exceeding $30 \mu\text{g}/\text{m}^3$. For skewed pollutant distributions, such as shown in Figure 6.10, the arithmetic average and the median are not identical. The

difference between these two measures of the central tendency of the distribution, with the mean being greater than the median, indicates the influence of the relatively fewer high concentration samples on the average. Particle-management strategies that reduce the frequency and magnitude of high PM mass concentrations will help reduce the annual mean, though in many instances (e.g., California sites), elimination of the highest concentrations will not suffice to bring the annual averages below the U.S. annual standard.

6.2.3 Seasonal Variations of $PM_{2.5}$ Mass

Most monitoring locations exhibit seasonal variations of $PM_{2.5}$ mass, as well as some or all of its major constituents. In much of eastern North America, higher $PM_{2.5}$ concentrations tend to occur during the summer (Figure 6.11). Winter stagnation episodes also occur in eastern North America, but less often than during summer. For example, during the period 1994-98, 6 percent of February days and 16 percent

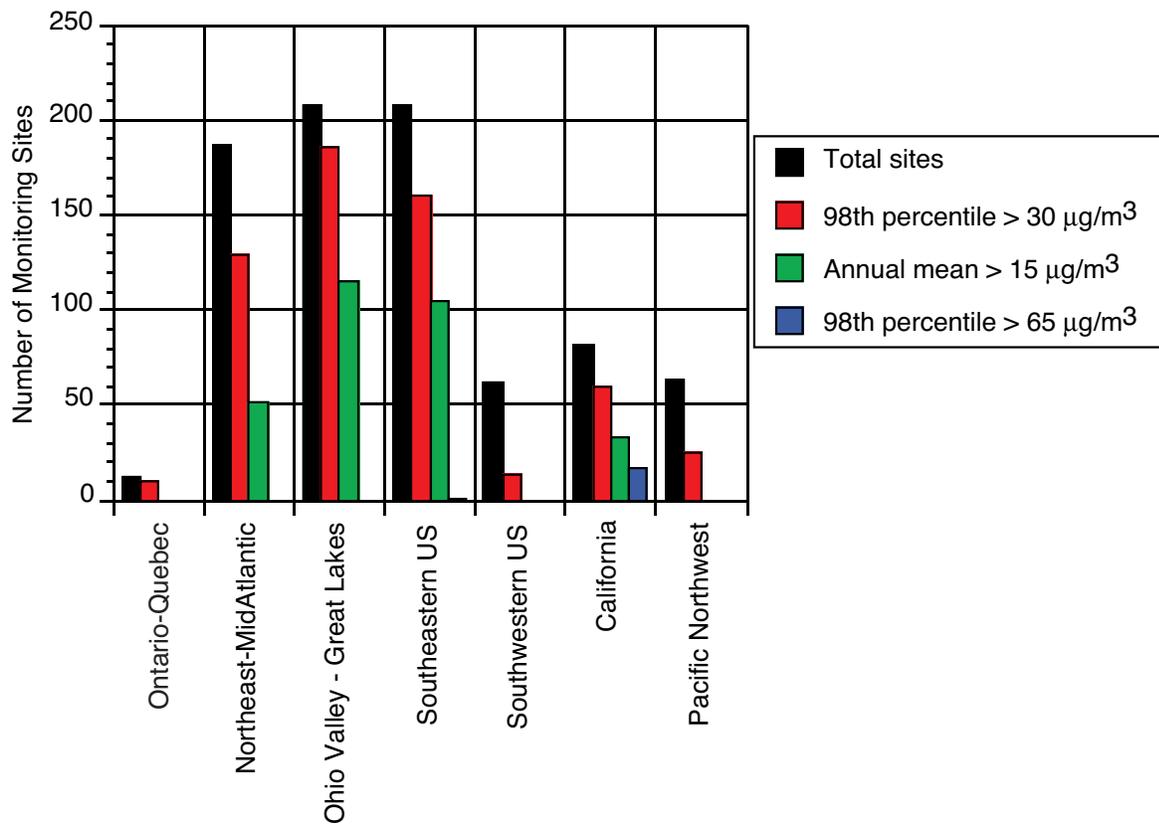


Figure 6.9. Numbers of $PM_{2.5}$ monitoring sites exceeding three benchmark levels. The reference levels are the CWS of $30 \mu\text{g}/\text{m}^3$ expressed as a three-year average of the 98th percentile 24-hr values, the U.S. three-year average annual mean standard of $15 \mu\text{g}/\text{m}^3$, and the U.S. 24-hr standard of $65 \mu\text{g}/\text{m}^3$ expressed as a three-year average of the 98th percentile 24-hr values. Data from Canada are for the period 1997 through 1999 (1995 through 1997 at two sites) and are measurements made using dichotomous samplers operated for 24 hours once every six days. Data from the United States are for 1999 and 2000 and are measurements from FRM samplers operated for 24 hours once every one, three, or six days. Site averages and completeness levels were compiled by the U.S. EPA. Sites were included if completeness levels indicated at least 30 days per year (50 percent sampling completeness for sampling schedules of once every six days). The standard U.S. EPA reporting protocol of 75 percent completeness eliminates many of the sites. The Northeast-MidAtlantic region includes all monitors in the states from Maine through Maryland and the District of Columbia. The Ohio Valley - Great Lakes region includes all monitors in West Virginia, Kentucky, Ohio, Michigan, Indiana, Illinois, and Wisconsin. The Southeastern U.S. includes monitors located in Virginia, North Carolina, South Carolina, Tennessee, Georgia, Florida, Alabama, Mississippi, and Louisiana. The Southwestern U.S. includes monitors in New Mexico, Arizona, Colorado, Utah, and Nevada. The Pacific Northwest includes monitors in British Columbia, Washington, and Oregon.

of August days exceeded the Canada Wide Standard at sites in Ontario (Vet et al., 2001). The seasonal variation of the average PM values may differ from the seasonal variations of the highest concentrations (Figure 6.11).

In eastern North America, SO_2 emissions are greater than elsewhere (Chapter 4), and sulfate is a substantial component of $PM_{2.5}$, especially during summer. Higher insolation and humidity during summer months enhance both homogeneous and

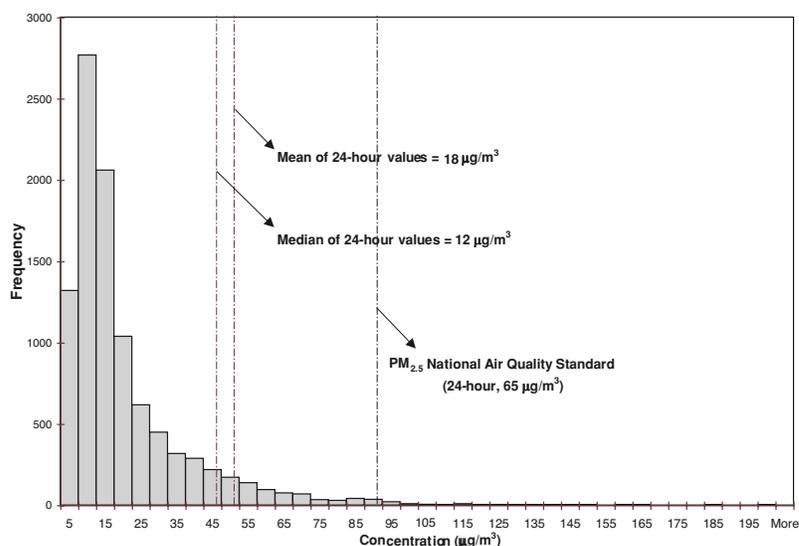


Figure 6.10. Statistical distribution of 24-hr $PM_{2.5}$ concentrations at 20 sites in California over the period 1988 through 1998. The measurements were made using dichotomous samplers. The mean and median of the data are shown. The maximum value was $195 \mu\text{g}/\text{m}^3$ and 25 measurements exceeded $100 \mu\text{g}/\text{m}^3$. (Source: California Air Resources Board; Motallebi et al., 2003a; 2003b).

heterogeneous reactions that produce secondary sulfate particles. Photochemical reactions that produce particulate organic carbon from gas-phase precursors also proceed at faster rates during summer months, though evidence for significant secondary organic aerosol formation is inconclusive at present.

Historical analyses of visual range indicate that haze levels in the eastern United States changed from seasonal maxima in winter during the period 1948 through 1954 to seasonal maxima in summer during 1975 through 1983 (Husar and Wilson, 1989). These patterns, with different rates of change occurring in the northeastern and southeastern states, corresponded to a historical shift from higher emissions of SO_2 during winter to roughly comparable emission levels during winter and summer (Husar and Wilson, 1989).

PM mass concentrations tend to be higher during winter in many parts of California (basins with poor ventilation), though this seasonal pattern may not occur in areas removed from population centers (Figure 6.11). In Los Angeles and the San Joaquin Valley, $PM_{2.5}$ concentrations are highest during the

autumn or winter months of October through February, with 50 to 100 percent of the highest PM mass concentrations occurring during those months. Throughout California, sulfate is a lesser fraction of total PM and nitrate is greater than at eastern locations. Particulate nitrate exists in equilibrium with its gas-phase precursors, and the equilibrium favors the particulate species under cool, moist conditions, such as prevail during winter in California. Meteorological factors also play a role in favoring winter PM maxima. Winter is the rainy season in California, but between frontal passages, dispersion is weaker during winter than summer. Cooler temperatures, lower wind speeds, and lower inversion heights result in weaker mixing, and pollutants tend to remain within the confines

of enclosed air basins such as the Los Angeles area and the San Joaquin Valley. In the San Joaquin Valley, winter PM mass concentrations typically build up over several days and valley-wide episodes occur. Such episodes are associated with high pressure over the southwestern United States, restricted vertical mixing, weak or offshore pressure gradients, flow reversals, and net transport speeds of about 1 m/s. Fog also plays a role in PM accumulation in the San Joaquin Valley.

Measurements of $PM_{2.5}$ made by the California Air Resources Board from 1988 through 1994 at Yosemite and Sequoia National Parks in the Sierra Nevada, east of the San Joaquin Valley, show that the park locations experienced higher summer levels of $PM_{2.5}$ and lower winter concentrations, a pattern opposite to that of all the valley sites. Since the summer $PM_{2.5}$ mass concentrations at the two parks were of comparable magnitude to summer concentrations at urban locations such as Sacramento and Bakersfield, the data indicate different degrees of coupling of the San Joaquin Valley and the western slope of the Sierra Nevada during summer and winter. The lower winter inversion height inhibits dispersion

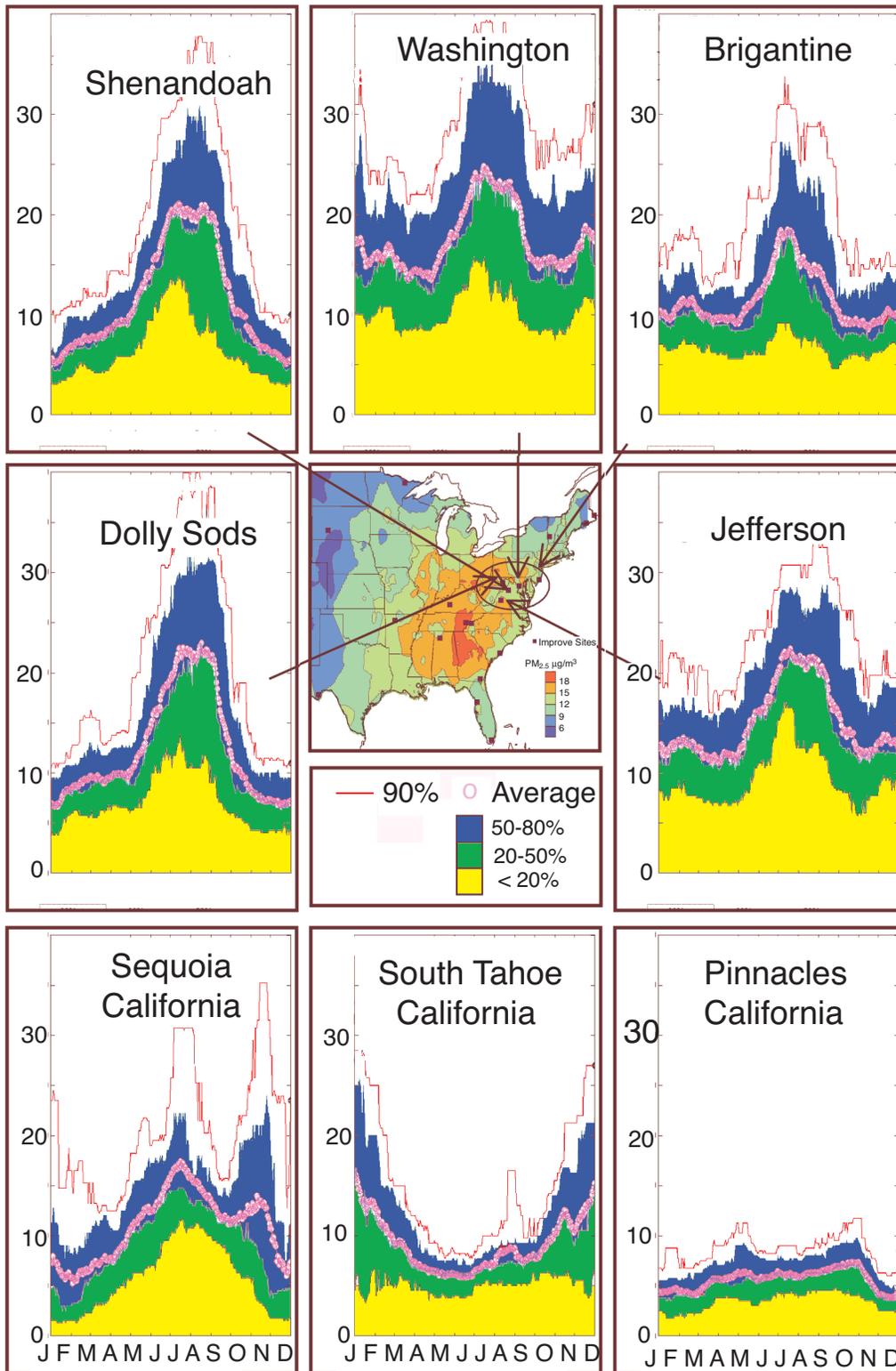


Figure 6.11. Seasonal variations of $PM_{2.5}$ mass concentrations at selected IMPROVE monitoring locations (1992-1999) for the cleanest (20 percent), moderate (20-50 percent), and highest PM (50-80 percent and 90 percent) days. The units of measurement are $\mu g/m^3$. (R. Husar, pers. comm.).

within the valley, resulting in higher PM mass concentrations there. Similarly, the IMPROVE monitoring site at San Geronio National Monument, east of Los Angeles, also exhibits summer PM maxima, when dispersion within and from the Los Angeles basin is more limited than during summer. In addition, ammonia concentrations at mountain sites may be lower than in the San Joaquin Valley or the Los Angeles area, affecting aerosol nitrate concentrations.

Many other urban locations (e.g., Phoenix, Tucson, Salt Lake City, Denver) in the western United States exhibit seasonal patterns with higher winter PM concentrations. As for urban California sites, limited dispersion during winter months is a contributing factor. In some locations residential wood combustion may also play a role.

Mexico lacks a long-term record of fine mass, but as previously noted PM₁₀ mass concentrations are lowest during summer, the rainy season (Figure 6.4). The seasonal variations of PM₁₀ mass are related to rainfall.

6.2.4 The Composition of PM_{2.5} and Its Geographical Variation

The average composition of PM_{2.5} varies considerably among geographical regions. In eastern North America, sulfate aerosol typically constitutes about one-fifth to one-half the average annual PM_{2.5} mass concentration (Figure 6.12). Along with the associated ammonium, roughly one-quarter to over one-half the average fine mass is ammonium sulfate in eastern North America. Maximum North-American sulfate levels occur in the Ohio River Valley, mid-Atlantic states, and the southeastern United States (Figure 6.13). This area is largely coincident with the area of maximum anthropogenic SO₂ emissions (Chapter 4, Figure 4.3).

Besides sulfate, the components most affecting geographical variations in PM_{2.5} mass concentration are carbon and nitrate. Carbon and nitrate concentrations are, in turn, affected by geographical variations in emissions and in the influences of atmospheric processes on secondary particle formation. Organic carbon mass, which includes

carbon and associated elements such as oxygen and hydrogen, constitutes roughly one-fifth to one-half the average annual PM_{2.5} mass at monitoring locations throughout North America (Figure 6.12). Mexico City shows higher carbon concentrations than do other North American cities, with nearly a factor of two difference in PM_{2.5} mass concentration among different locations within the city (Figure 6.12). Although the data shown are from a single month, other short-term studies confirm the importance of organic species as contributors to total PM_{2.5} in Mexico City. For example, organics were 22 ± 2 percent of the mean PM_{2.5} mass concentration of 42 ± 4 µg/m³ during September 1990 and 47 ± 2 percent of the mean PM_{2.5} mass concentration of 39 ± 6 µg/m³ during February 1991 (Miranda et al., 1994).

Fires, both as wildfires and controlled biomass combustion, are an important and geographically dispersed source of organic carbon during summer, especially in Mexico, the western United States, and western Canada. Fireplace burning contributes significantly to PM in the winter in western North America. The relative importance of secondary organic particle formation from gas-phase VOC precursors is not well understood and may be more significant in the southeastern United States than in other areas.

Particulate nitrate concentrations are greatest at California sites, representing over one-quarter of the average annual PM_{2.5} mass there (Figure 6.12). At sites in California's San Joaquin Valley, nitrate accounts for ~30 percent of the annual-average PM_{2.5} particle mass (Figure 6.12). In Los Angeles, nitrate also accounts for ~30 percent of the annual-average PM_{2.5} particle mass at sites in the western and central portions of the basin (Figure 6.12), but this fraction increases to ~40 percent in the eastern basin. Annual-average nitrate concentrations in the two areas range from about 6 to 16 µg/m³, with daily-average nitrate levels reaching as high as 100 µg/m³ on some days in the eastern Los Angeles basin. The ammonium associated with nitrate typically accounts for ~10 to 20 percent of the annual-average PM_{2.5} particle mass in the San Joaquin Valley and southern California.

Nitrate is also a significant component of the annual-average PM_{2.5} mass concentration at some locations in southeastern Canada and the northeastern United

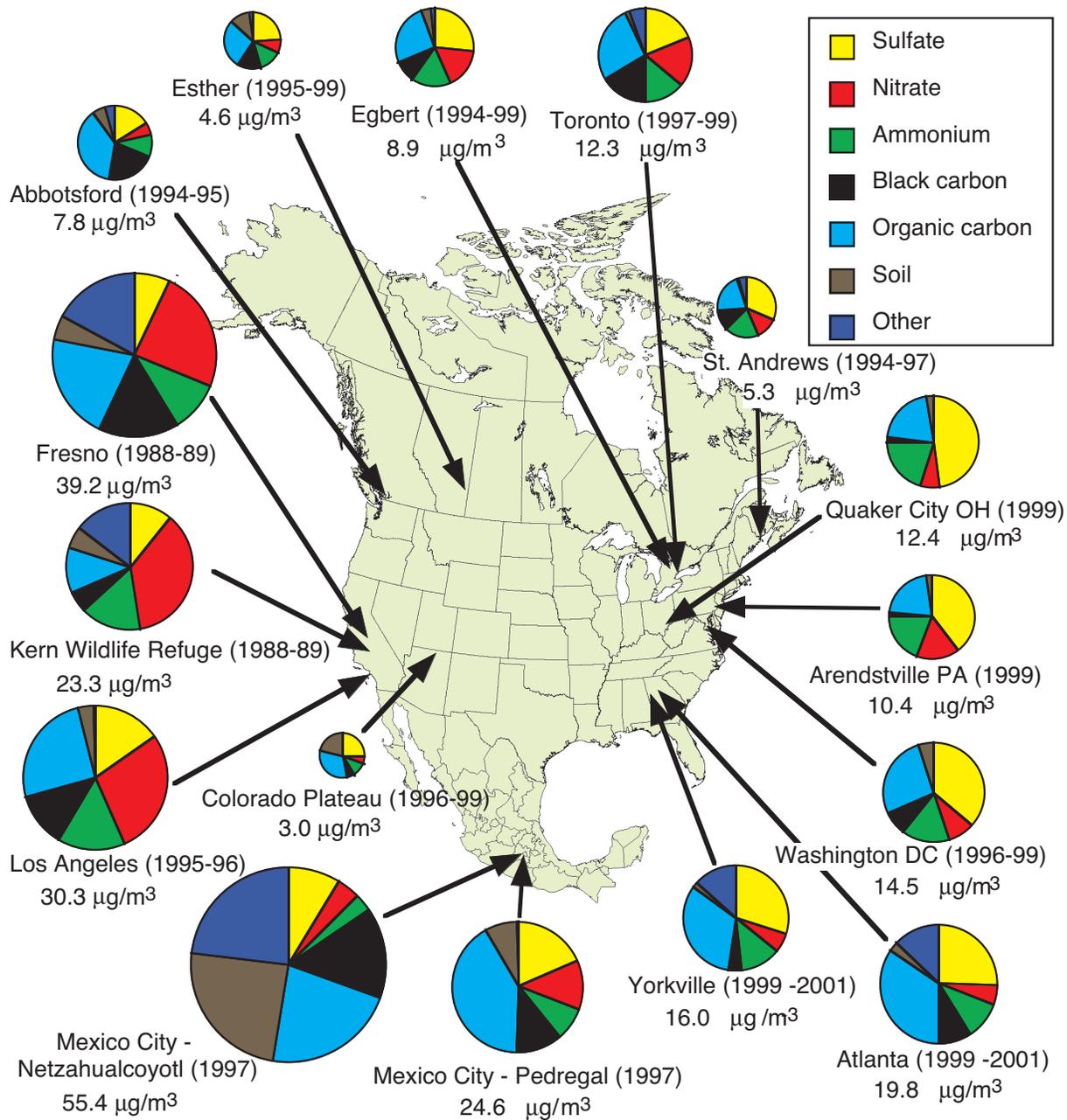


Figure 6.12. Composition of $PM_{2.5}$ at representative urban and rural locations. The urban sites are Toronto, Washington DC, Atlanta, Mexico City, Los Angeles, and Fresno. Averaging periods and average $PM_{2.5}$ mass are indicated. All sites have at least one year of sampling except Mexico City, for which the average was determined from one month (14 days). More recent short-term measurements from December 1995 and January 1996 at Fresno and Kern Wildlife refuge show lower $PM_{2.5}$ mass concentrations but similar composition to the data displayed here. The Colorado Plateau data are the averages of the IMPROVE sites located at Bryce Canyon, Canyonlands, Grand Canyon, Petrified Forest, Mesa Verde, and Zion National Parks. (Source: Vet et al., 2001; Malm, 2000; Hansen et al., 2003; Chow et al., 1993; U.S. EPA, 2000; Kim et al., 2000).

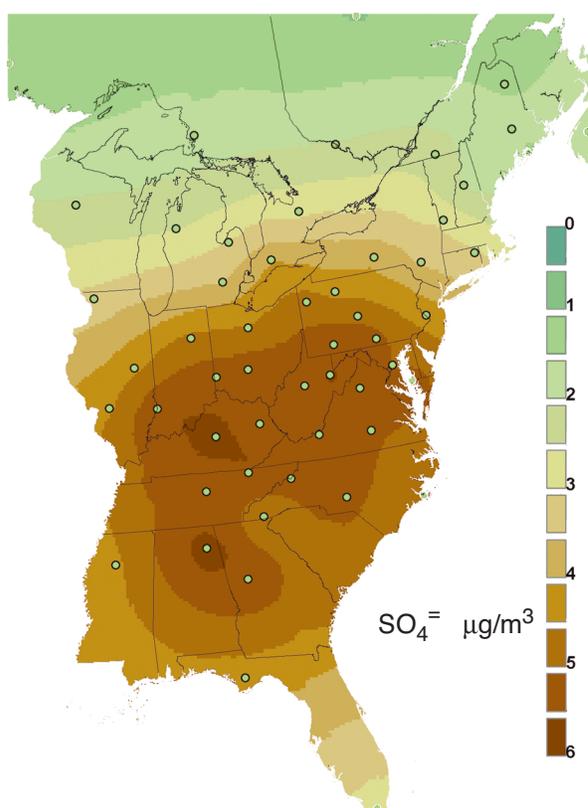


Figure 6.13. Mean annual sulfate concentration in eastern North America during 1997-98. Measurements are from CASTNet and CAPMoN sites. (Source: J. Narayan, Environment Canada).

States (Figure 6.12). Nitrate levels in eastern North America tend to be higher in urban than in rural locations (section 6.3).

Particulate nitrate derives partially or predominantly from the equilibrium reaction between two gas-phase species, nitric acid and ammonia (Chapter 3). The equilibrium favors the condensed phase at lower temperatures and higher humidities, so particulate nitrate concentrations are generally higher during winter months.

Ammonia reacts preferentially with sulfuric acid, and, if sufficient ammonia is available, it then combines with nitric acid to form particulate nitrate. In California, particulate sulfate concentrations are typically lower than in many other parts of the country (Figure 6.12), and sufficient ammonia is available at most times and locations to allow the formation of particulate ammonium nitrate (Blanchard et al., 2000). In contrast, the availability of ammonia limits

particulate nitrate formation during most times at sites in the southeastern United States (Blanchard and Hidy, 2003).

Since the availability of ammonia typically does not limit the amount of particulate nitrate occurring at most California locations, the amount of particulate nitrate that forms depends upon the amount of nitric acid. This amount in turn depends upon the rate of conversion of NO_2 to nitric acid. During winter in the San Joaquin Valley, NO_2 concentrations typically exceed concentrations of nitric acid (Kumar et al., 1998), implying that the rate of conversion of NO_2 to nitric acid is a key determinant of ambient concentrations of nitric acid, and, hence, of particulate nitrate levels. Initial modeling efforts suggest that in one of the urban areas of the San Joaquin Valley, nitric acid formation is limited by the availability of radical species, and particulate nitrate formation may be more effectively reduced through reductions of VOC than NO_x emissions (Pun and Seigneur, 2001). Outside the urban areas, however, nitric acid formation in the San Joaquin Valley may be responsive to NO_x emissions (Stockwell et al., 2000), especially over multiday stagnation episodes. *These findings have significant implications for the management of PM, and additional research efforts are needed for fully understanding the implications.*

While summer nitrate concentrations in eastern North America are low in comparison with sulfate levels, higher winter nitrate concentrations occur in some areas. On an annual basis, particulate nitrate levels in eastern North America show a geographical pattern that closely parallels the particulate ammonium pattern (Figure 6.14), except that nitrate levels are lower where sulfate concentrations are highest (Figure 6.13). Some analyses suggest that the availability of ammonia may limit particulate nitrate levels in much of eastern North America during summer months, with more ammonia available during winter months when sulfate levels are lower (Vet et al., 2001). The response of particulate nitrate concentrations to reduced SO_2 emissions and lower sulfate concentrations is of importance for the management of PM concentrations in eastern North America. *Further research efforts are needed for fully characterizing the relations between particulate sulfate and nitrate concentrations in eastern North America.*

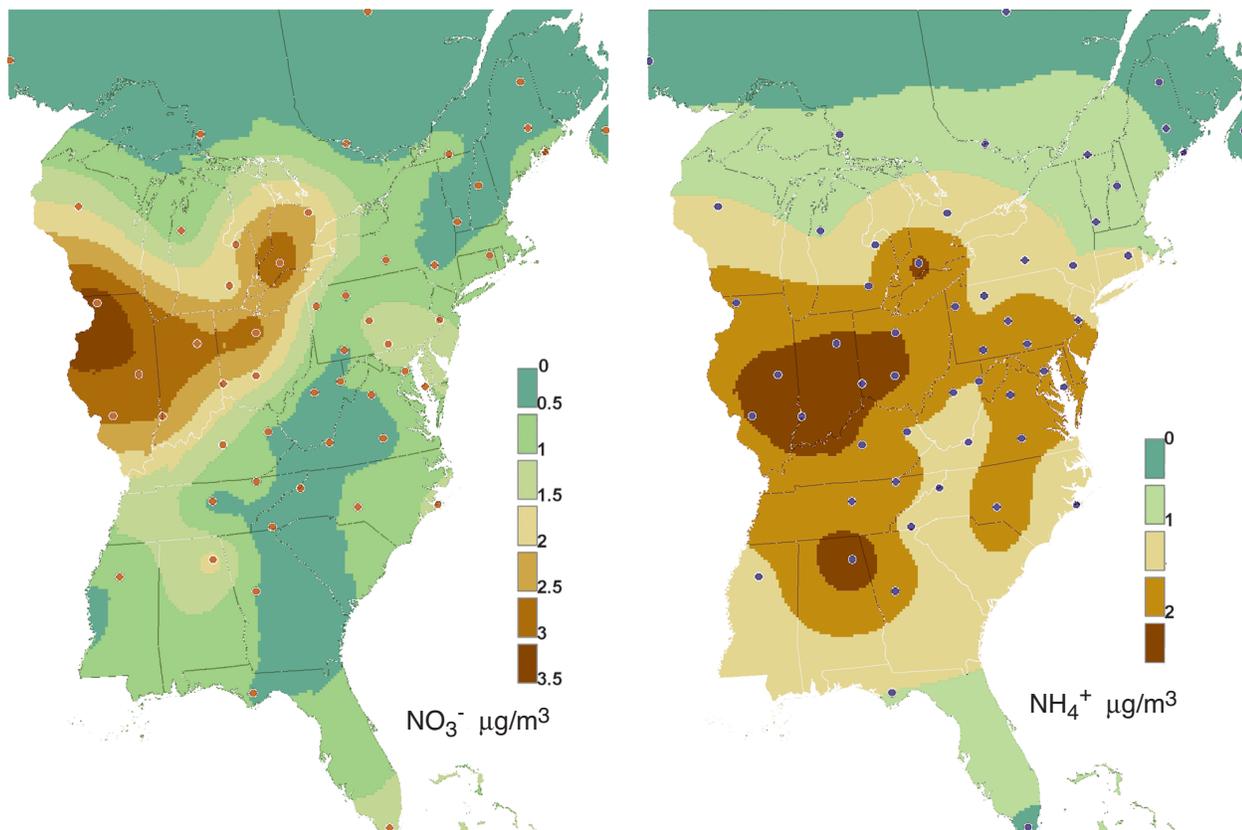


Figure 6.14. Mean ammonium and nitrate concentrations during 1997-98. Measurements are from the CASTNet and CAPMoN networks. (Source: J. Narayan, Environment Canada).

Trace elements, such as antimony, arsenic, beryllium, cadmium, cobalt, chromium, iron, lead, manganese, mercury, nickel, selenium, and zinc, typically represent a portion of the $PM_{2.5}$ mass that is too small to be apparent in illustrations such as Figure 6.12. While they do not contribute much to mass, such species are of special interest because current research has not yet determined which, if any, PM components are related to health effects, and because such trace elements are designated as hazardous pollutants by one or more North American governments and are useful in PM studies for apportionment.

The principal anthropogenic sources of most of the trace elements are industrial operations. Antimony, arsenic, cadmium, chromium, lead, nickel, and zinc may be present in the plumes of smelters. Zinc is also present in emissions from waste combustion. Iron is typically associated with foundry emissions. Manganese, mercury, and selenium are found in emissions from coal-fired power plants; manganese and selenium are also crustal elements. Mercury is

emitted as a vapor (elemental mercury) or as particles (mercury compounds). Selenium tends to follow transport paths similar to sulfur, being emitted as gas-phase SeO_2 in hot stack gases; SeO_2 is condensable at ambient temperatures.

Monitoring data typically show larger intersite differences in trace-element concentrations than in $PM_{2.5}$ mass concentrations. Median concentrations of the most abundant trace elements vary by factors of two to four among Canada's NAPS sites, reflecting differing source influences (Brook et al., 1997). Within Montreal, median iron, lead, and zinc concentrations show twofold differences. Proximity to oil-combustion sources affects vanadium and nickel concentrations at the Halifax site, and the higher concentrations of selenium in Toronto and Montreal than at other NAPS sites appear linked to coal-combustion sources (Brook et al., 1997).

In California, factor-of-two or greater variations occur among air-toxic monitoring locations within

single metropolitan areas. The five sites located in the San Francisco Bay area show mean multi-year (1990-99) averages of 0.5 to 0.9 ng/m³ for arsenic, 10.5 to 18.8 ng/m³ for lead, and 10.1 to 19.1 ng/m³ for manganese. The six sites located in Los Angeles area show mean multi-year averages of 0.8 to 5.3 ng/m³ for arsenic, 20.9 to 47.0 ng/m³ for lead, and 26.1 to 60.5 ng/m³ for manganese. The two monitoring sites in Fresno (San Joaquin Valley) recorded 1.4 to 7.2 ng/m³ for arsenic, 14.0 to 106 ng/m³ for lead, and 28.2 to 54.0 ng/m³ for manganese. These geographical variations within and between urban areas have not been thoroughly examined, particularly with respect to their implications for spatial variations of personal exposure to hazardous air pollutants.

Two other networks presently supplying trace-element monitoring data from locations in the United States and Canada are the Integrated Atmospheric Deposition Network (IADN) and the Mercury Deposition Network (MDN), which is a component of the National Atmospheric Deposition Program (NADP). These networks provide estimates of wet and dry deposition of lead, cadmium, and mercury, as well as organic compounds. The average wet deposition of mercury reported by the MDN is about 10 µg/(m²y) with higher precipitation concentrations and deposition amounts during summer than winter, and a low-to-high deposition gradient from New England and eastern Canada (lowest) to southern Florida (highest) (Sweet et al., 1999).

With the exception of lead, virtually no long-term monitoring measurements exist with sampling frequencies sufficient for providing good comparisons over time. The reduction of ambient lead levels between 1970 and the present, in large part due to removing lead from gasoline, has been one of the principal successes of North American air pollution management programs. Since about 1990, for example, virtually all U.S. monitoring locations have reported ambient lead levels below the EPA ambient air quality standard for lead (U.S. EPA, 2000b).

6.3 REGIONAL AND URBAN CONTRIBUTIONS TO PM

6.3.1 Comparisons Between Rural and Urban Sites

Differences between PM mass concentrations at urban and rural monitoring sites help indicate the relative magnitudes of local and regional contributions. In general, the regional contribution includes PM transported from various urban areas or generated in nonurban settings, as well as nonanthropogenic background. Quantitative comparisons usually require pairing of an urban and a nearby rural monitor operating with the same sampling schedule over the same time period; the nonurban monitor should be upwind of the urban area for the most commonly occurring wind directions. In eastern North America, urban-rural differences imply that typical average local urban contributions are roughly 25 percent of the mean urban PM_{2.5} mass concentrations, with regional aerosol contributing the remaining, and larger, portion (Figure 6.15). On average, sulfate and organic carbon are strongly regional in eastern North America, with ~75 to 95 percent of the urban sulfate concentrations and ~60 to 75 percent of the urban organic carbon concentrations occurring at the nonurban sites (Figure 6.15). In Los Angeles, PM mass, sulfate, nitrate, and black carbon contributions are strongly local; the mean sulfate concentrations at the upwind (offshore) site were about one-third of the urban concentrations (a recirculation pattern that moves air from the mainland offshore and back onshore at a later time is known to transport sulfate from the city to the upwind location at times).

The magnitude of the regional component of PM varies among regions. Data from the IMPROVE network indicate that mean annual PM_{2.5} levels exceed 10 µg/m³ at rural locations in much of the southeastern United States. Rural locations in other portions of the eastern United States, California, Ontario, and Quebec exhibit mean annual PM_{2.5} levels of 5 to 10 µg/m³. It will be difficult to meet PM standards in urban areas where the regional

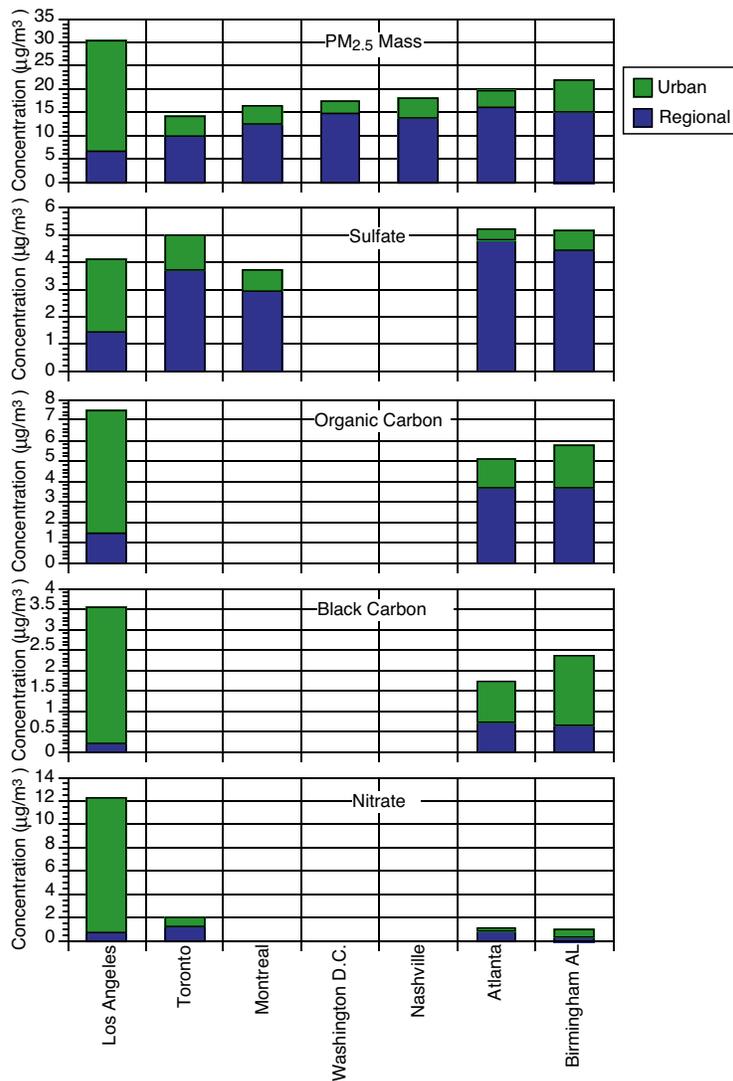


Figure 6.15. Comparisons of average PM_{2.5} mass and species concentrations at paired urban and rural locations. The mean urban concentration is given by the sum of the estimated urban and rural contributions. Not all species were measured at all sites. (Source: Brook et al., 1999; Kim et al., 2000; Hansen et al., 2003).

concentration is at present close to the standards, and regional PM management programs may be required.

Nitrate concentrations in eastern North America are higher at urban than at rural locations (Figure 6.16). This comparison indicates the potential importance of nitrate within urban areas, and implies that one or both of the gas-phase precursors of particulate nitrate (ammonia and nitric acid) are present at higher concentrations in urban areas (Chapter 3 and section 6.2.3). Since the sampling devices used for collecting the urban samples are known to underestimate nitrate

concentrations, due to losses caused by volatilization, the actual ambient nitrate levels at the urban locations are even greater than those shown in Figure 6.16. PM management strategies in eastern North America may therefore need to address urban-scale nitrate formation.

6.3.2 Evidence for Local PM Sources: Temporal Variations

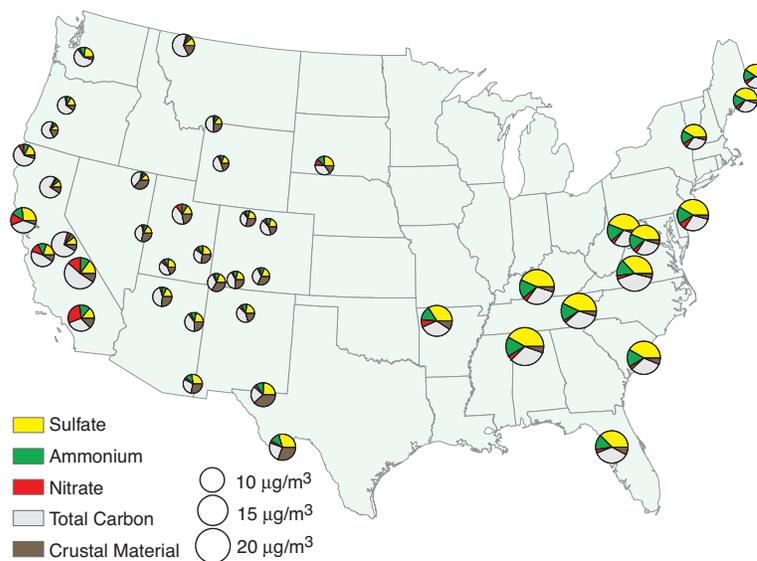
Significant variations in PM mass concentrations can occur on time scales of a few days, a few hours, or even a few minutes. Such short time-scale variations result from meteorological or emission changes occurring over relatively short periods or distances, and provide additional insights into the relative magnitudes of local and regional PM contributions.

At most urban monitoring locations, a weekly cycle is apparent in either PM₁₀

or PM_{10-2.5} mass concentrations (Figure 6.17). The weekly periodicity is attributable to weekly variations of anthropogenic emissions, and provides one indication of the magnitudes of PM₁₀ or PM_{10-2.5} mass contributions from relatively local emission sources. Nonurban monitoring sites generally do not show prominent weekly PM₁₀ or PM_{10-2.5} mass cycles (Figure 6.17). Weekly cycles of PM_{2.5} concentrations tend to be less evident than weekly cycles of PM₁₀ concentrations, reflecting the larger fractions of secondary species and regional contributions to the PM_{2.5} mass.

SPATIAL AND TEMPORAL CHARACTERIZATION OF PARTICULATE MATTER

Annual Average PM_{2.5} Concentrations (µg/m³)
and Particle Type in Rural Areas, 1999



Annual Average PM_{2.5} Concentrations (µg/m³)
and Particle Type in Urban Areas, 2001

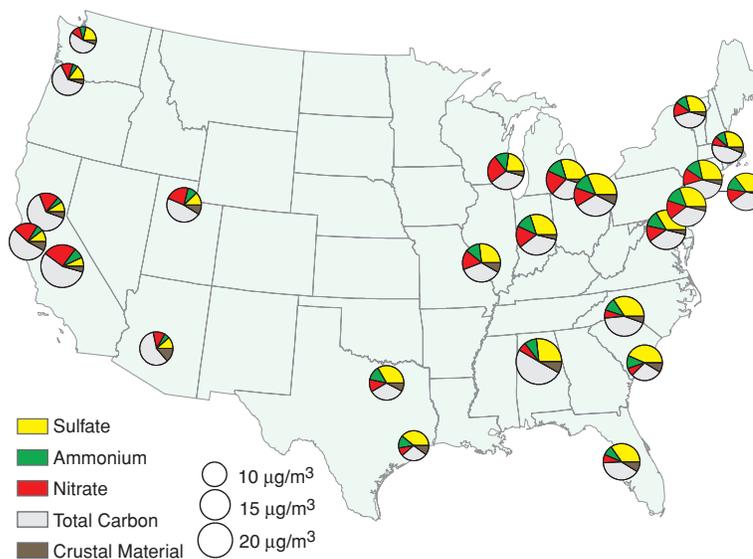


Figure 6.16. Comparisons of average PM_{2.5} mass and species concentrations at urban and rural locations. The rural data are from the IMPROVE network, while the urban data are from the EPA Speciation Trends Network. Note that urban nitrate concentrations are distinctly higher than rural levels. Direct comparison of the information in these two maps should take into consideration: the fact that they represent different years; that one is an urban network and the other is a rural network; and that there are also differences in instruments and measurement methods (Source: U.S. EPA, 2002).

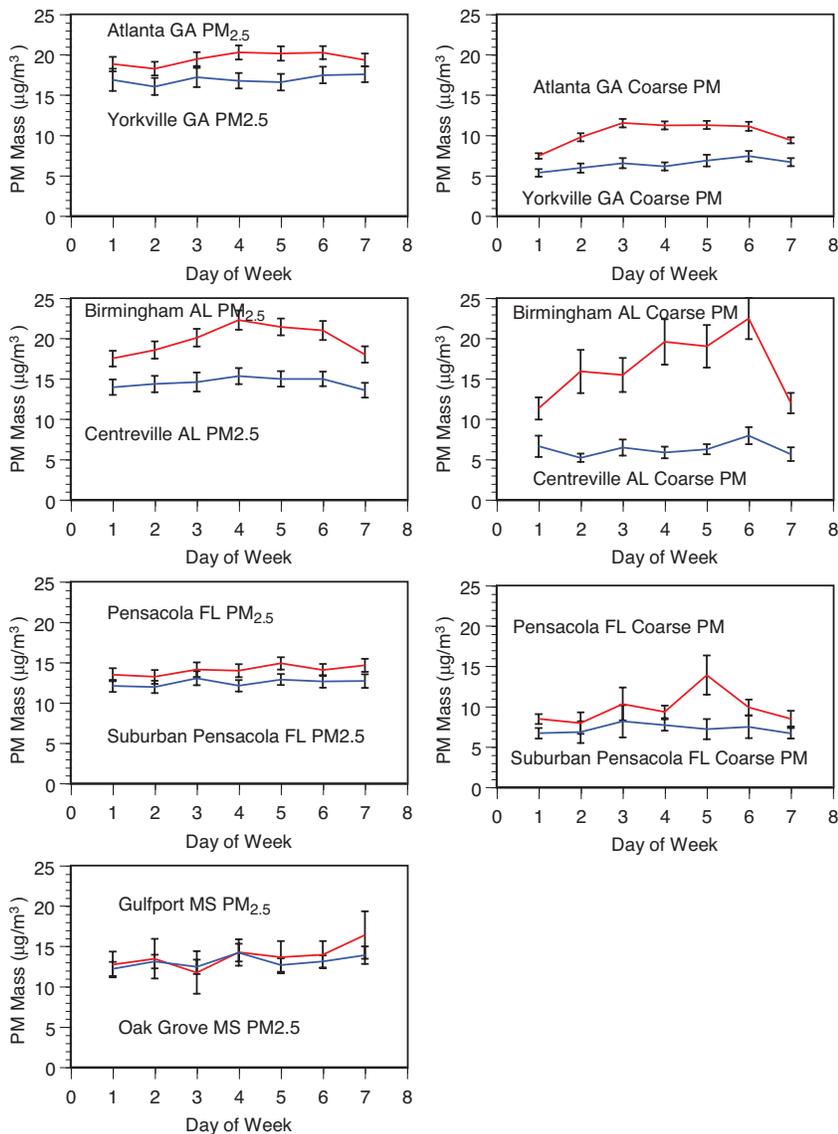


Figure 6.17. Example day-of-week variations of PM_{2.5} mass (left side) and coarse mass (PM_{10-2.5}, right side) concentrations at paired urban and nonurban sites in the southeastern United States (showing standard errors of the means). (Source: Edgerton et al., 2003, and 1998-2000 data from SEARCH network, from SEARCH public archive www.atmospheric-research.co/searchhome.htm).

Diurnal patterns of PM mass concentrations provide even stronger evidence of the influence of local PM sources on PM₁₀ concentrations in some areas. For example, sites in Mexico City show diurnal concentration changes consistent with the patterns of human activities (Figure 6.18). In contrast, diurnal PM_{2.5} variations do not always provide evidence for local source contributions. However, local source

influences on PM_{2.5} mass concentrations were evident during a special study from December 1995 through January 1996 in California's San Joaquin Valley. PM_{2.5} concentrations were lowest from about 3:00 a.m. to 3:00 p.m. at two urban sites, increased during late afternoon, and persisted at their highest levels through midnight, whereas two rural sites showed the reverse pattern (Chow et al., 1999). The diurnal profiles of sulfate, nitrate, and organic and elemental carbon showed that the variation of the PM mass at the urban sites was driven by the variation of organic and elemental carbon, which appeared to be strongly influenced by local (~20 km scale) residential wood combustion.

6.3.3 PM Mass Concentrations at Remote Locations

The magnitude of nonanthropogenic background PM mass concentrations is difficult to quantify because anthropogenic influences extend even to remote monitoring sites. Moreover, background levels vary among locations and seasons. Surface monitoring at global background locations provides a long-term record of surface-level PM concentrations. Data are available from several monitoring locations within the Global Atmosphere Watch (GAW) network (<http://www.wmo.ch> with links to GAW). These locations may show elevated PM_{2.5} mass concentrations at times, influenced by anthropogenic emissions (e.g., at Arctic sites) or strong natural sources (e.g., Sahara

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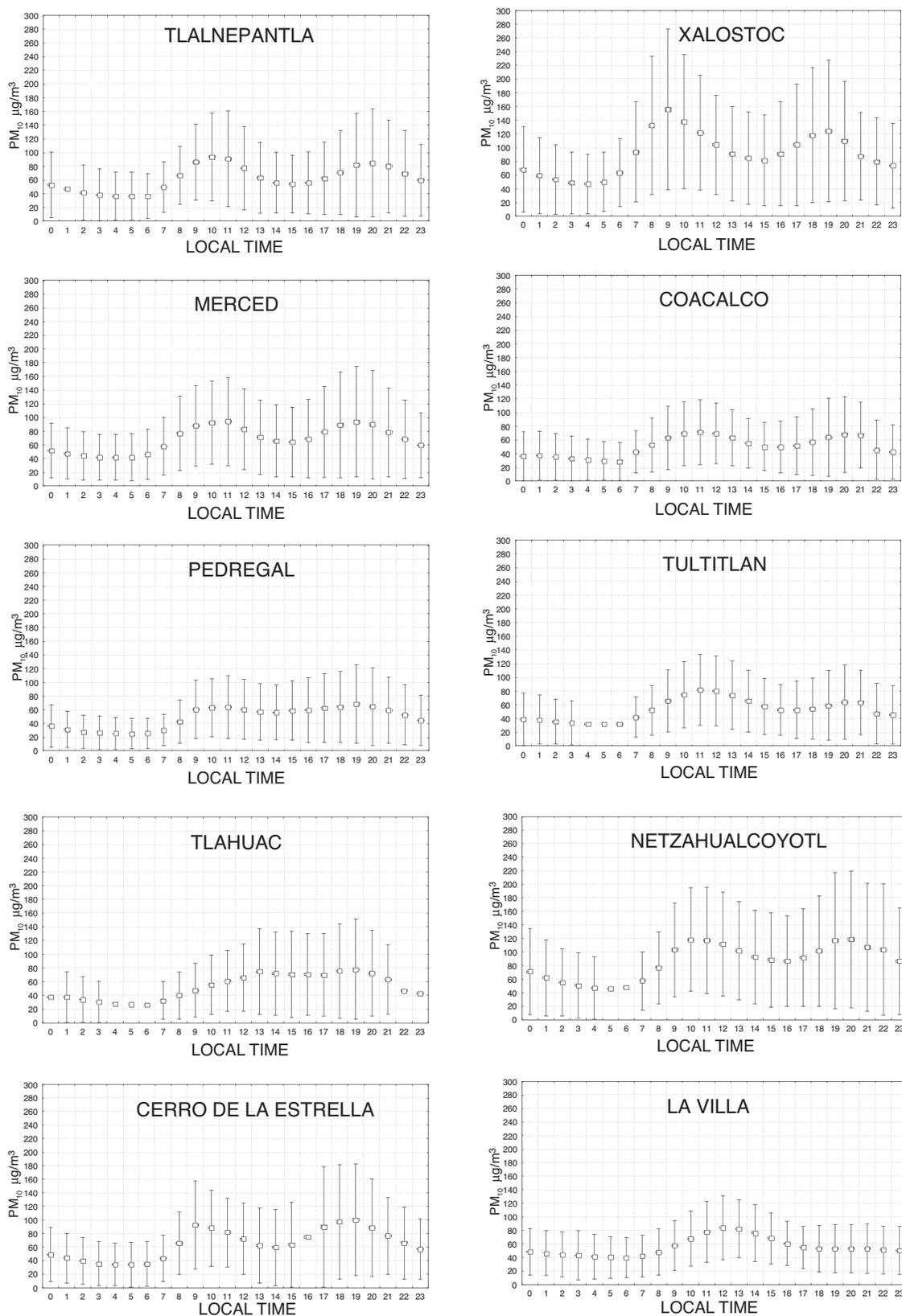


Figure 6.18. Example diurnal variations of PM_{10} mass concentration at ten sites in Mexico City. (Source: E. Vega, data from Manual Atmospheric Monitoring Network, 1995-99).

desert dust at Canary Islands and Bermuda). Crustal material is the largest component at many such sites, such as Izana in the Canary Islands (e.g., Maring et al., 2000). The mean annual sulfate concentrations at GAW sites are a few tenths up to less than $1 \mu\text{g}/\text{m}^3$. Carbon concentrations exceed sulfate concentrations at some sites.

Data from two monitoring locations, Point Reyes National Seashore in northern California and San Nicolas Island in southern California, have been used by the California Air Resources Board (CARB) to characterize coastal California background $\text{PM}_{2.5}$ mass levels. During 1995, the annual-average $\text{PM}_{2.5}$ mass concentrations were $6.5 \mu\text{g}/\text{m}^3$ at Point Reyes and $5.6 \mu\text{g}/\text{m}^3$ at San Nicolas Island (Motallebi et al., 2003a; 2003b). Sea salt, as sodium chloride, was 27 percent of the average mass at Point Reyes and 22 percent at San Nicolas Island. The average sulfate concentrations were 1.2 and $1.4 \mu\text{g}/\text{m}^3$, while the average organic carbon concentrations were 1.0 and $1.2 \mu\text{g}/\text{m}^3$. However, wind recirculation patterns are known to transport anthropogenic pollutants from coastal, urban locations to these monitoring sites at times.

6.3.4 Regional Transport

The Sulfate Regional Experiment (SURE), a pioneering field study conducted during 1977 and 1978, provided observational evidence for regional transport of sulfate aerosol in eastern North America and linked transport distances to specific weather patterns (for information on SURE, see Hidy, 1984 and references therein). Regionally elevated sulfate concentrations occurred during summer most often under two types of meteorological conditions. When a high-pressure system dominated the area along the Atlantic coast, the resulting stagnation on the lee (western) side of the system caused sulfate concentrations to increase at monitoring locations across eastern North America. Transport distances under such stagnation conditions were usually within roughly 100 km, not exceeding over about 300 km. However, in a typical summer pattern, a frontal system would then advance slowly south and east from Canada into the United States across the Great Lakes, channeling windflow between the advancing front and the Atlantic high-pressure system along the

line of the Appalachians. More rapid transport then developed from south to northeast, along the western side of the Atlantic high-pressure system, leading to observable transport distances of about 500 to 700 km. Higher concentrations of sulfate at locations in southern Ontario were linked to transport from the midwestern and southern United States.

During October of the SURE study, the stagnation conditions became more important than transport (Hidy, 1984). By January, high sulfate concentrations were associated almost entirely with regional stagnation or with nonregional events. Winter stagnation events indicated that maximum sulfate concentrations were centered within about 100 km of areas of highest SO_2 emissions.

In contrast with the evidence for sulfate transport developed by the SURE study, PM mass (TSP) showed only local (less than approximately 100 km) areas of source influence (Hidy, 1984). The spatial patterns of TSP were identifiable with a west-east industrialized region south of Lake Erie and with specific areas of higher particulate and SO_2 emissions densities. At that time, 24-hr sulfate concentrations during summer events were generally in the range of 10 to $40 \mu\text{g}/\text{m}^3$, whereas TSP concentrations often exceeded $100 \mu\text{g}/\text{m}^3$.

Continuing study of meteorological influences on PM mass concentrations has led to several methods for classifying meteorological conditions and characterizing their association with high PM mass concentrations in eastern North America. In eastern Canada, PM mass concentrations have been shown to vary among as many as nineteen types of meteorological conditions (Vet et al., 2001). As for the SURE study, regional PM episodes were characterized by the presence of a quasi-stationary high pressure system sitting over eastern North America, with a high pressure ridge oriented in an east-west direction across Virginia and North Carolina. (Regional episodes were defined as periods when mass concentrations exceeded $30 \mu\text{g}/\text{m}^3$ as a 24-hr average for two or more consecutive days at sites in two of the three regions of eastern Canada, i.e., Ontario, Quebec and Atlantic Canada, and, on one of those days, exceeded $30 \mu\text{g}/\text{m}^3$ at sites in all three regions). The episodes typically lasted five to six days and ended when a trough of low pressure

moved rapidly (typically in one day) from the Great Lakes to the eastern seaboard, displacing the high-pressure ridge.

Back trajectories (e.g., Chapter 7, Figure 7.4) calculated from Canadian cities during regional episodes indicate the potential for transport from the United States. Trajectories do not in themselves establish the actual occurrence of transport, since they do not indicate mass removal nor do they explicitly treat the relative contributions of local and distant emission sources. However, in combination with the SURE study findings and other analyses, the trajectory analysis indicates that emission sources in the midwestern United States and southwestern Ontario sometimes play a role in the formation of large-scale PM_{2.5} episodes in Ontario, Quebec, and the Atlantic provinces. In other cases, locally generated emissions or a combination of local and distant sources may be equally important.

As discussed in Chapter 9, visibility impairment in national parks, particularly those of the southwestern United States whose scenic vistas are highly prized, has been a subject of concern for over twenty years. In its final report to the U.S. EPA in 1996, the Grand Canyon Visibility Transport Commission (GCVTC) recommended a variety of PM management measures for maintaining and improving visibility in the Grand Canyon and other national parks in the southwestern United States (Grand Canyon Visibility Transport Commission, 1996). The recommendations of the GCVTC were based upon many years of scientific studies that indicated the importance of contributions of PM from near (< 100 km) and distant (> 500 km) emission sources or source areas. No single source or group of sources was the dominant contributor.

In an area such as the Grand Canyon National Park, where local emission levels are low, the relative amount of transported PM as a fraction of the total measured ambient PM mass concentrations is typically greater than would be the case in areas where local emissions densities are greater. Thus, while transport distances may not be greater than in eastern North America, the proportions of transported PM may be greater, and PM management needs to focus comprehensively on regional and long-distance (> 500 km) management options, though not to the exclusion of local management measures.

Key contributors to visibility impairment in the southwestern United States include sulfate, derived from SO₂ emissions, fine crustal material, and smoke (carbon from fires, including controlled burns and wildfires). Sulfate plays a particularly important role (Chapter 9), and has therefore been the focus of much study. Inert tracers have been used to investigate sulfate transport (Pitchford et al., 2000). CMB analyses apportioned sulfate concentrations at two locations within the Grand Canyon among four coal-fired power plants and eight regional sources (Eatough et al., 2000). The results of the CMB source apportionment showed that the relative contributions to sulfate were different at the two locations within Grand Canyon National Park, so source proximity was a factor. Sources as far as Los Angeles and Baja California (about 600 km) contributed to sulfate concentrations. The contributions of power generating facilities to SO₂ were greater than to sulfate concentrations, thus indicating that full conversion of primary emissions to particulate sulfate required more time than elapsed during transport.

According to the report of the GCVTC, clean air conditions were related to good ventilation and the occurrence of precipitation along the paths followed by air masses before they arrived at the Grand Canyon. Such conditions occurred more often for air masses arriving from the northwest than from other directions, and these differences, rather than the presence or absence of specific emission sources, accounted for differences in air quality on different days.

6.4 THE INFLUENCE OF INTERCONTINENTAL AEROSOL TRANSPORT ON PM MASS CONCENTRATIONS IN NORTH AMERICA

From the point of view of air-quality management in North America, the transport of aerosols around the world represents a largely uncontrollable contribution to North American particle levels, and is of uncertain magnitude. Appendix D provides an overview of global aerosol patterns, and that information is used here to estimate preliminary

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bounds for the potential contributions of intercontinental transport to North American $PM_{2.5}$ mass concentrations.

Evidence to date suggests that intercontinental aerosol transport typically does not in itself produce surface-level concentrations that violate North American PM standards, but has the potential to contribute to exceedances at some locations when high concentrations from local PM emissions are superimposed upon this long-range background contribution. To date, no systematic quantification of the frequency of occurrence of such transport events, or their average contributions to 24-hr or annual average concentrations, has been completed. However, a number of individual episodes have been studied.

Satellite imagery shows a PM plume from North Africa reaching Central America, Mexico, and the U.S. Gulf Coast states, with the time of maximum impact occurring in July (Appendix D). Measurements at surface sites along the transport path (e.g., Canary Islands, Bermuda) reveal that the dominant component of the North African PM plume is crustal material, also known as soil or dust. In the southeastern United States, sites in the Interagency Monitoring of Protected Visual Environments (IMPROVE) network show seasonal maximum dust concentrations in July. However, on an annual basis, soil, or dust, constitutes only about 5 to 10 percent of the average fine-particle concentrations at IMPROVE (rural) monitoring locations in the southern United States, representing about 0.4 to 1.1 $\mu\text{g}/\text{m}^3$ (annual average). The transported dust therefore is a minor (probably less than 5 percent) contribution to the annual average concentrations.

Analyses by the Texas Natural Resource Conservation Commission indicate that the North African plume contributed as much as 15 to 20 $\mu\text{g}/\text{m}^3$ at sites in the Houston area on two days in June and August, 1997 (Price et al., 1998). On those days, the maximum 24-hr $PM_{2.5}$ concentrations were in the range of 24 to 33 $\mu\text{g}/\text{m}^3$ and no sites exceeded the U.S. 24-hr $PM_{2.5}$ standard. For further comparison, during 1999 only one FRM monitor in the southeastern United States showed a

value exceeding the U.S. 24-hr 98th percentile standard of 65 $\mu\text{g}/\text{m}^3$ and 74 of the 91 sites showed 98th percentile 24-hr $PM_{2.5}$ concentrations between 25 and 45 $\mu\text{g}/\text{m}^3$. These simple comparisons suggest that the North African plume does not contribute enough $PM_{2.5}$ mass to affect the regulatory status of any monitoring locations; however, more precise estimates of the impact of the dust plume on 24-hr and annual-average $PM_{2.5}$ particle concentrations are needed.

Satellite data provide evidence of an aerosol plume reaching into North America from Asia during April 1998 (Appendix D). Elevated surface-level $PM_{2.5}$ mass concentrations were also observed at IMPROVE sites in the Pacific Northwest then, with the most prominent effect being a simultaneous sharp rise of $PM_{2.5}$ mass to 3 to 11 $\mu\text{g}/\text{m}^3$ on April 29, 1998 from more typical peak values of 1 to 3 $\mu\text{g}/\text{m}^3$. Transport episodes of the magnitude of the April 1998 event appear to occur less frequently than once per year and perhaps no more often than the order of once per ten years (Appendix D), so their potential regulatory consequences are likely limited to their effects on 24-hr concentrations. During 1999, no FRM monitors in the Pacific Northwest (Oregon, Washington, and Idaho) showed a 98th percentile value exceeding the U.S. 24-hr 98th percentile standard of 65 $\mu\text{g}/\text{m}^3$ and 28 of the 30 sites showed 98th percentile 24-hr $PM_{2.5}$ concentrations between 25 and 45 $\mu\text{g}/\text{m}^3$. During 1997-99, most sites in British Columbia showed a 98th percentile value less than 20 $\mu\text{g}/\text{m}^3$, well below the level specified by the Canada Wide Standard (30 $\mu\text{g}/\text{m}^3$). These statistical summaries suggest that the Asian plume would rarely, if ever, contribute enough $PM_{2.5}$ mass to affect the regulatory status of any monitoring locations. However, more precise estimates of the impact of the dust plume on 24-hr and annual-average $PM_{2.5}$ concentrations are needed to support this preliminary conclusion.

Fires generate fine particles, consisting especially of organic carbon, which are then lifted by the heat of the fire. PM from fires may affect large areas of North America on a seasonal basis, from northwestern or northeastern Canada and the Pacific Northwest to Central America, Mexico, and the southeastern United States. Satellite data show the

presence of large numbers of fires in Central America and prominent aerosol clouds at times (Appendix D). Such fires represent a significant source of internationally transported $PM_{2.5}$ affecting considerable portions of North America. Analyses of satellite and surface data by the Texas Natural Resource Conservation Commission, for example, indicate that smoke from agricultural burning in the Yucatan Peninsula likely contributed about 2 to 5 $\mu\text{g}/\text{m}^3$ to the daily-average $PM_{2.5}$ mass concentration at Corpus Christi during an episode in May, 1997 (Price et al., 1998) (the 24-hr $PM_{2.5}$ concentration was 21.4 $\mu\text{g}/\text{m}^3$ and no sites exceeded the U.S. 24-hr $PM_{2.5}$ standard). Similarly, fires in Northern Quebec during July 2002 caused extensive haze in regions of Canada and the United States to the south.

As each of these examples of long-range transport indicates, the combined use of satellite and surface measurements provides evidence linking changes in surface PM mass concentrations to visible, transported aerosol plumes. The satellite data provide the means for identifying when long-range plumes are impacting an area, while the surface measurements provide the data needed for quantifying the excess PM levels occurring during those impact periods. While a number of analyses of transport episodes have been documented in the literature, what is now needed is a more systematic and precise quantification of the plume impacts in terms of their potential contributions to 24-hr and annual-average PM mass concentrations, including assessment of their potential for leading to violations of standards when local emissions are superimposed upon the transport component. Since transport episodes occur at irregular intervals, full characterization of the frequency and magnitude of transport requires daily sampling at a number of regionally-representative surface sites; however, the larger number of compliance sites can operate on a more practical schedule of one sampling day every six days. Currently, global plumes may be tracked with satellite data so transport days can be identified and removed from statistics as rare events.

6.5 TRENDS AND THEIR IMPLICATIONS

Comparing emission changes with changes in ambient particle concentrations potentially provides information on the effectiveness of emission management programs. However, emission-related trends (the signal of interest) in ambient concentrations are difficult to quantify because the majority of the day-to-day, and even year-to-year, variation in concentrations is attributable to variations in weather (noise). This variation cannot be removed by simply adding more monitoring locations, because all locations within a particular area tend to experience the same weather patterns and to therefore show highly correlated variations in concentrations.

The detectability and quantifiability of trends in ambient pollutant concentrations depends upon the magnitudes of emission reductions or increases, the quality and length of record of the monitoring data, and the relative magnitudes of the emission-related (signal) and weather-driven (noise) variations in ambient pollutant concentrations. For a signal-to-noise ratio of 1:1, about two to four years of monthly data are typically needed to detect a linear trend with high probability (90 percent) at a 95 percent confidence level, whereas 10 to 20 years of data are generally needed when the signal-to-noise ratio falls to 0.1:1 (Weatherhead et al., 1998). The latter, low signal-to-noise ratio, is usually characteristic of ambient pollutant measurements. No single method for detecting trends in precipitation chemistry and deposition is considered optimal, or even appropriate, for all purposes (Holland and Sirois, 2001), and a similar conclusion likely applies to aerosol concentrations and composition.

Many sites in the IMPROVE network have shown declining $PM_{2.5}$ concentrations over the 11-year period from 1988 through 1998 (Figure 6.19). Statistical significance ($p < 0.05$) of the $PM_{2.5}$ fine mass trends was associated with changes of about 0.05 $\mu\text{g}/\text{m}^3$ per year or greater, or roughly 0.5 $\mu\text{g}/\text{m}^3$ or greater over 10 years (Malm, 2000). For many of the IMPROVE sites, that level of change corresponded to about ten percent of the median $PM_{2.5}$ concentrations, or roughly five percent of the mean

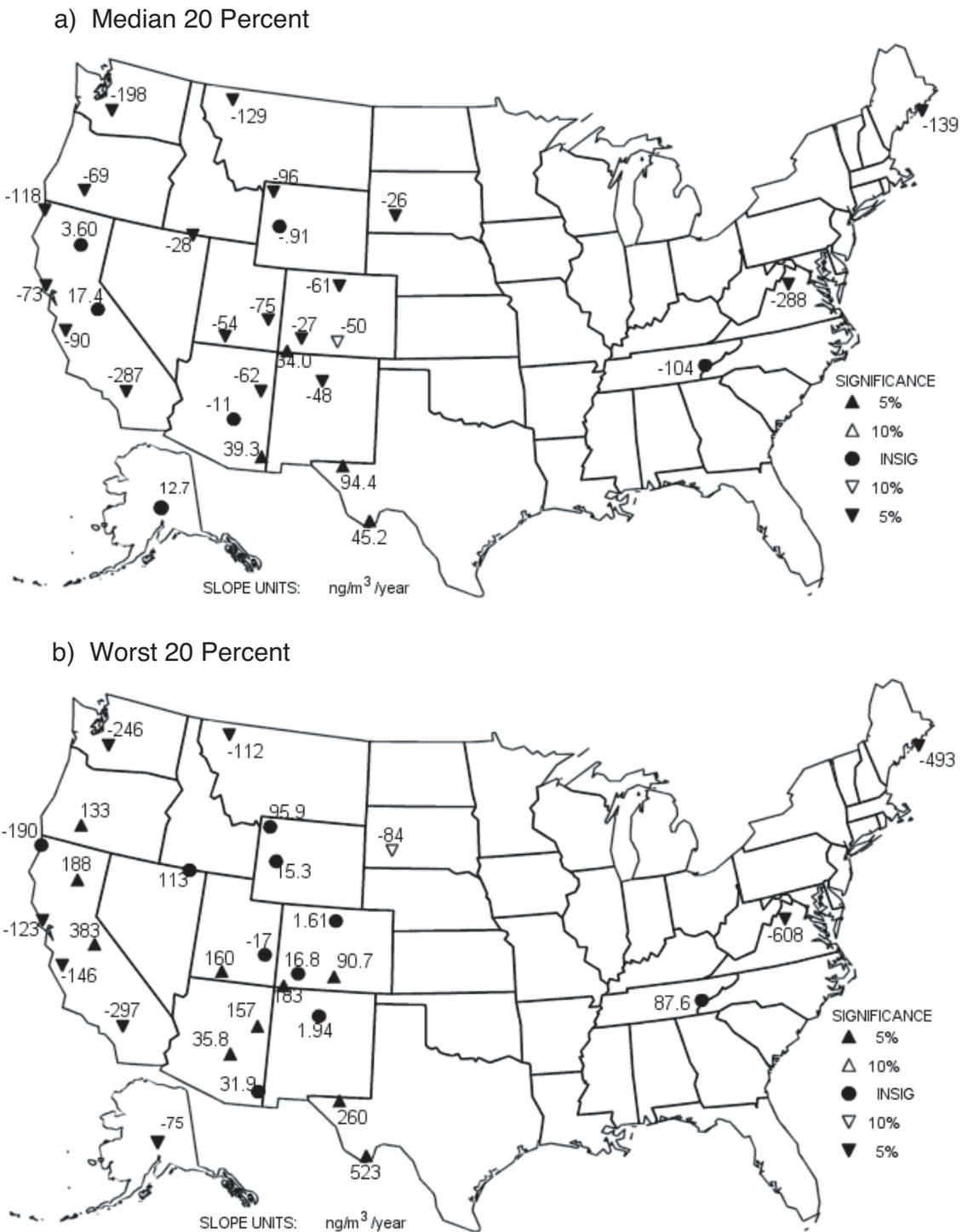


Figure 6.19. Trends in $\text{PM}_{2.5}$ mass at IMPROVE sites, 1988-98. The top panel shows trends in the median reconstructed $\text{PM}_{2.5}$ mass concentrations, while the bottom panel shows trends for the worst 20 percent of the days (highest daily fine mass concentrations). Arrows denote upward or downward trends. Solid arrows indicate significance at $p < 0.05$ while open arrows indicate significance in the range of $0.05 < p < 0.10$. (Source: Malm, 2000).

concentration of the upper 20 percent of the measurements.

Related work on the detection of trends in precipitation sulfate is relevant, as such trends also involve low signal-to-noise ratios. The minimum emission decrease detectable as a trend in precipitation sulfate over 11 years has been estimated as a 10 percent reduction occurring across eastern North America (Schreffler and Barnes, 1996). Reliable detection of changes in precipitation sulfate concentrations resulting from SO₂ emission reductions of ~20 percent occurring over 3 years (1994-96) was predicted to require ~10 years of monitoring before the reduction and 2 to 3 years after (Blanchard, 1999). When emission changes of that magnitude occurred in much of the eastern United States within a single year, with new controls in place by the end of 1994, statistically significant changes in precipitation sulfate were reported 1 to 2 years later (Lynch et al., 1996; Shannon, 1999). The error limits of the regression equations implied uncertainties of about 20 to 40 percent in the estimated magnitudes of the changes in sulfate concentrations, and 10 or more years post-reduction measurements may be required to reduce the uncertainties to less than 20 percent (Blanchard, 1999).

Assessing the effects of emission control strategies on ambient concentrations of pollutants typically requires about a decade. Measurements across North American networks should be designed to enable the determination of spatial and temporal trends of a multipollutant mixture. Issues including reference standards, measurement methodologies and sampling strategies need to be considered in assessing the compatibility of sampling networks. Measurement uncertainties should be as small as possible and should be reported routinely.

Since, as noted, the length of monitoring required for detecting trends depends upon the magnitude and shape (e.g., step change versus gradual change) of the trend, as well as the quality of the monitoring data and the type of statistical procedure used, no simple statement can accurately characterize all situations. As described above, many of the existing trend analyses suggest that a 10-year record is typically necessary for detecting changes on the order

of 10 to 20 percent of the measured concentrations. Indeed, many of the more sophisticated trend techniques have shown the existence of 3-to-5 year cycles in precipitation sulfate concentrations (Sirois, 1993) and in particulate sulfate, nitrate, and ammonium concentrations (Vet et al., 2001). The presence of such multi-year cycles implies that a record of 10 years or more is necessary for establishing the existence and significance of long-term trends.

From a regulatory perspective, it is significant that a pronounced decrease of particulate sulfate concentrations occurred in the eastern United States and Canada during the 1990s, related in part to the U.S. Phase I SO₂ emission controls that were implemented as of the end of 1994 (Figure 6.20). From 1989 to 1998, SO₂ emissions in the states east of and including Minnesota to Louisiana declined by about 25 percent. Average SO₂ and sulfate concentrations at CASTNet monitoring sites in the same region declined by about 40 percent. This decline was not statistically different from the 25 percent reduction in emissions. Furthermore, ambient concentrations of SO₂ and sulfates exhibited a statistically significant correlation with the SO₂ emissions trend (U.S. EPA, 2000b). These associations support the utility of regional reductions of SO₂ emissions for effecting near-proportional reductions of particulate sulfate.

In Canada, PM_{2.5} concentrations from the NAPS network (11 cities nationwide or 6 eastern cities) showed interannual variability from 1986 through 1992, a 40 percent decline in median and 90th percentile values from 1992 through 1996, and a 14 percent increase from 1996 through 1998 (Vet et al., 2001). Although the temporal pattern (a decline from 1992 through 1996) was consistent with the timing of the U.S. Phase I SO₂ emission reductions, the particulate sulfate concentrations did not exhibit a corresponding decline during the 1992-96 time period. However, the rural Canadian Aerosol and Precipitation Monitoring Network (CAPMoN) sites did exhibit declining concentrations of SO₂ and particulate sulfate between 1990 and 1999 (Figures 6.20 and 6.21). At both the CAPMoN (Canada) and CASTNet (U.S.) sites, the ambient SO₂ declines generally exceeded the decreases in sulfate concentrations.

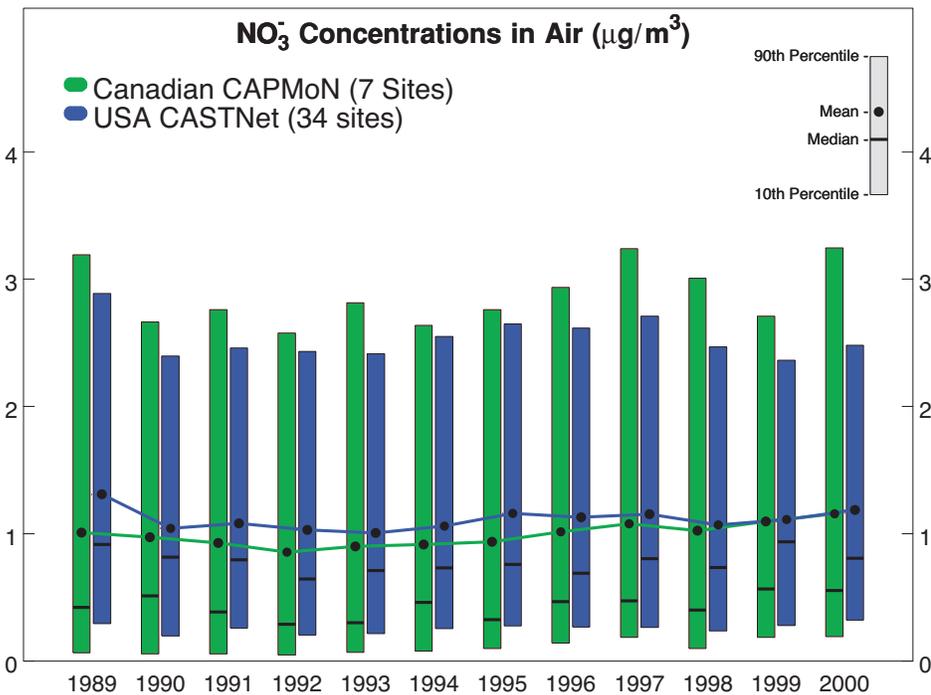
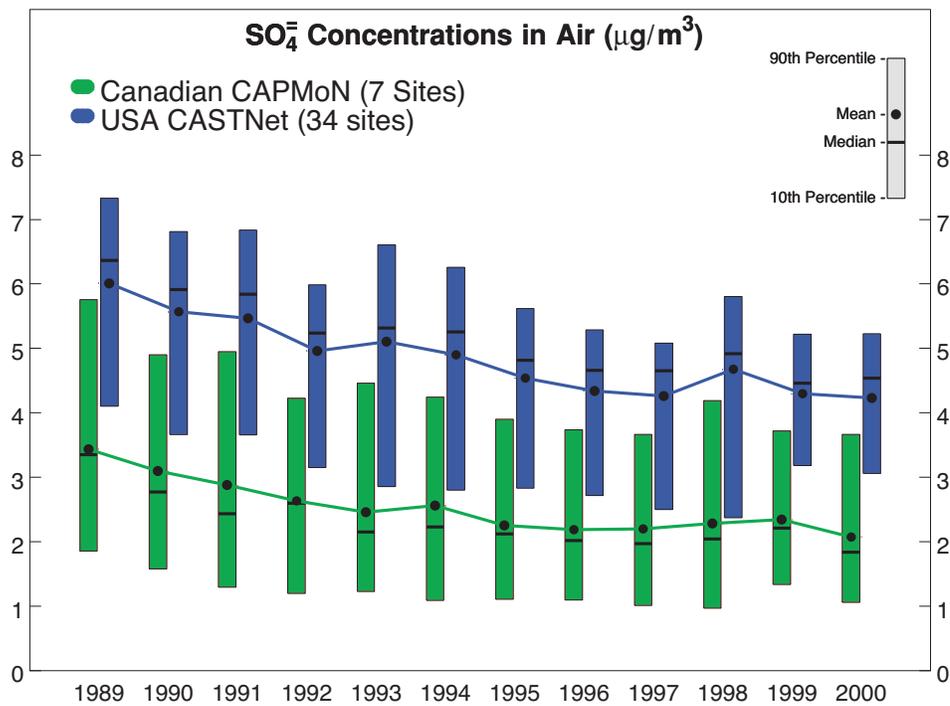


Figure 6.20. Trends in annual particulate sulfate (top) and nitrate (bottom) concentrations based on 34 U.S. CASTNet and 7 Canadian CAPMoN sites. Shown are boxplots of annual mean, median and 10th and 90th percentile concentrations for the combined sites. The calculation of annual means at the sites is as described in US EPA (1999). All concentrations are expressed in μg/m³ at 25 degrees C and 1 atmosphere. CAPMoN data were converted from daily to weekly values to match CASTNet sampling periods before producing the mean, median and percentile values. (Source: M. Shaw, Environment Canada).

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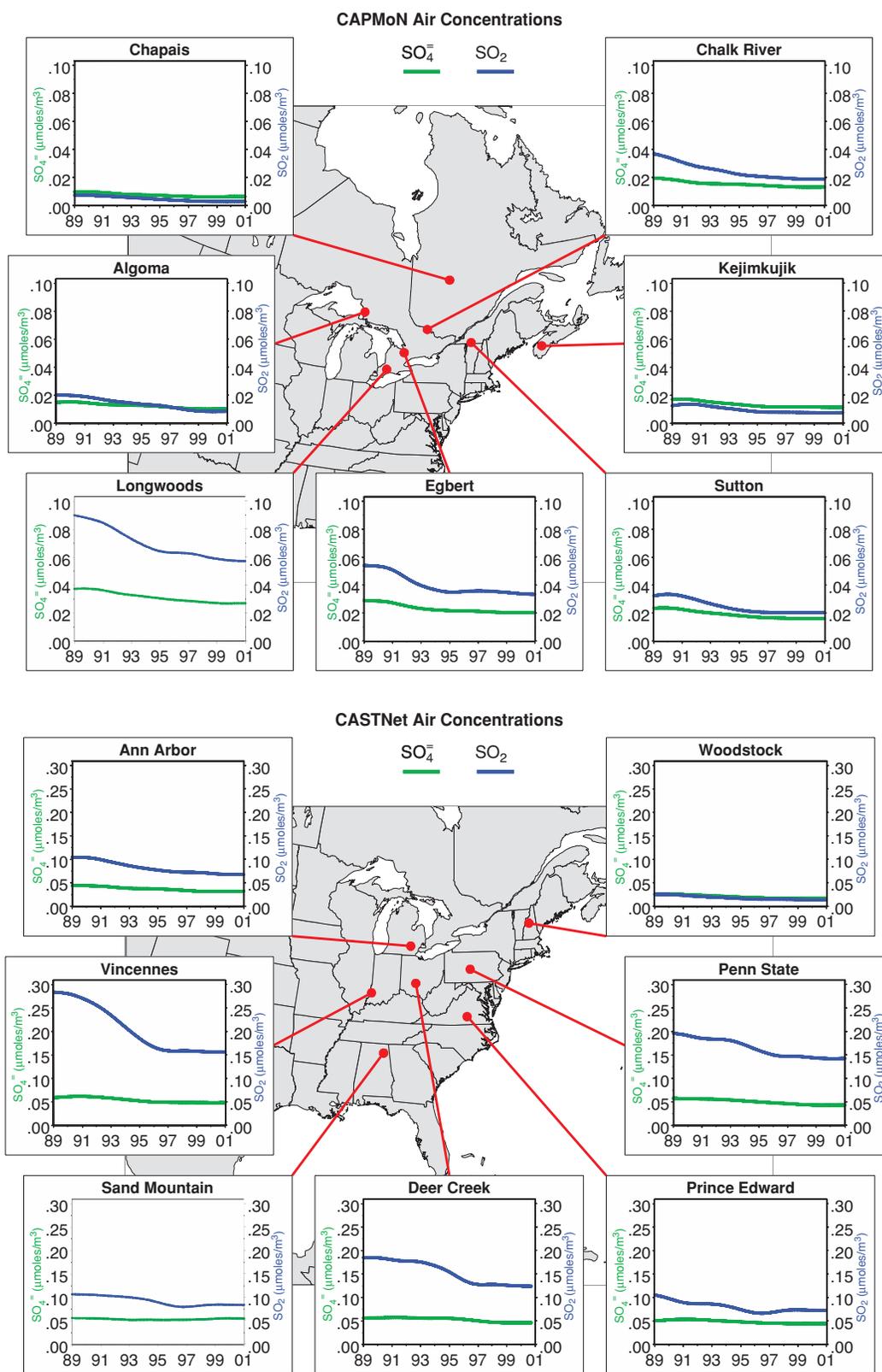


Figure 6.21. Trends in concentrations of SO_2 and sulfate at CAPMoN and CASTNet sites, 1980 - 2000. (Source: Vet et al., 2001; M. Shaw, Environment Canada).

In Los Angeles, SO₂ emissions varied from about 250 to 350 tons per day during the years from 1970 to 1977, and decreased to about 265 tons per day in 1979 and 150 tons per day by 1983 as power plants switched from oil to natural gas beginning in 1978 (Hidy, 1994; Alexis et al., 2001). SO₂ emissions further declined to about 120 tons per day in 1987, following the introduction of low-sulfur gasoline in 1983, and to about 77 tons per day by 1996 with continuing adoption of other control measures. During the period from 1976 to 1996, annual-average SO₂ concentrations in the Los Angeles area declined by over 70 percent, which corresponds closely with the 71 percent decrease in SO₂ emissions from 1979 to 1996. In contrast, annual-average sulfate concentrations declined by about 50 percent from 1976 to 1996 (Hidy, 1994; Christoforou et al., 2000). The decline in sulfate concentrations lagged the SO₂ concentration decline by about five years, and did not become apparent until the ambient SO₂ concentrations had been reduced by over 40 percent. Current scientific understanding indicates that the time lag and nonproportional decline of sulfate concentrations occurred because the conversion of SO₂ to sulfate was oxidant-limited; no other explanations are known. This historical example illustrates the nonproportional response between SO₂ emission changes and ambient SO₂ or sulfate concentrations that may occur in some situations (see also Chapter 3), and the need to maintain a long-term monitoring program over many years to detect and quantify the effects of emission changes.

IMPROVE monitoring sites in the Four Corners states (Arizona, Utah, Colorado, and New Mexico) showed mixed trends in PM_{2.5} concentrations over the period 1988 through 1998 (Figure 6.19). Sulfate trends tended to parallel those shown for PM_{2.5}, and trends in the median concentrations did not always track trends in the upper 20 percent of the measurements (Malm, 2000). At these and other IMPROVE sites, PM_{2.5}, sulfate, and carbon concentrations trended downward from 1988 until approximately early 1996, then leveled off or increased (White, 2001). The linkages to either meteorological variations or emission changes remain to be established.

California monitoring data show downward trends in annual-average PM_{2.5} mass as well as in the

concentrations of some components over the period 1988 through 1998 (Figure 6.19 and Motallebi et al., 2003b). Annual-average PM_{2.5} mass levels declined from a range of ~25 to 30 µg/m³ to ~10 to 25 µg/m³ at sites in southern California and the San Joaquin Valley. Considerable year-to-year variability exists, and these trends are not statistically significant at all locations. However, all California IMPROVE sites showed statistically significant trends in PM_{2.5}, sulfate, nitrate, and organic carbon concentrations. Meteorological differences may be a contributing factor, as the average precipitation during the latter half of the period covered by the trend analyses was up to twice the average during the earlier years. The influence of meteorological cycles is also suggested by the presence of statistically significant trends at Point Reyes National Seashore and Redwood National Park, two locations on the Pacific Coast that are minimally influenced by emissions from sources within California.

Ambient concentrations of sulfate, nitrate, and ammonium are linked through equilibrium reactions. Declining sulfate levels have the potential to exert an increasing influence on particulate nitrate concentrations where ammonia concentrations currently limit the formation of nitrate. Existing measurements are not definitive. In the eastern United States, particulate nitrate levels generally did not decline at CASTNet sites during the 1990s (U.S. EPA, 2000) (Figure 6.20). Of the three eastern IMPROVE sites, nitrate concentrations showed statistically significant declines from 1988 through 1998 at Acadia and Great Smoky Mountains National Parks, but not at Shenandoah National Park (Malm, 2000). Thus, pronounced nitrate trends are not evident in the way that aerosol sulfate shows substantial declines during the 1990s.

As previously noted, at rural CAPMoN monitoring locations in Canada, particulate sulfate and ammonium concentrations decreased from the early to late 1990s (Vet et al., 2001). During this same time period, particulate nitrate concentrations increased. Either, or both, increasing NO_x emissions or increasing rates of particulate nitrate formation (caused by increasing availability of ammonia as sulfate levels declined) may have contributed; both causes are considered probable (Vet et al., 2001). Seasonal data from the CAPMoN sites shows that

particulate nitrate concentrations were highest when particulate sulfate concentrations were lowest and more free ammonia (Chapter 4) was available.

Longer-term records of PM mass concentrations show that PM levels have declined in many or most U.S. cities over the past 40 to 50 years (Lipfert, 1998). Primary PM emissions decreased by 50 to 60 percent from 1940 to 1990. Trends reconstructed from available TSP or PM₁₀ measurements indicate that average TSP concentrations declined by two- to three-fold in urban areas between 1950 and 1980, while PM_{2.5} concentrations (estimated from proxy information on emissions) likely declined by about a factor of two between 1960 and 1990 (Lipfert, 1998). Despite the uncertainties in analyses that of necessity relied on differing types of measurements from different years, the available data indicate that average PM levels in U.S. cities are roughly half those occurring in the 1950s. Thus, present-day exposures of individuals to PM are substantially lower in U.S. cities than those of 50 years ago. These changes are of significance for the characterization of lifetime PM exposures in epidemiological analyses. The compositional changes in PM over this time are unknown, however.

Fifty-year trends in ambient concentrations of PM in Mexico City are unavailable. Population increased six-fold from 1950 to 2000 and monitoring data indicate that PM levels have declined since 1988 (Molina and Molina, 2002).

6.6 COVARIATION OF PM WITH OZONE

Many air pollutants are related either through commonality of emissions sources or atmospheric processes. Considering how the concentrations of different pollutants covary helps indicate if changes in the emissions of one pollutant, or its precursors, may lead to changes in the ambient concentrations of another.

PM is a complex mixture of chemical compounds, varying with particle size, location (source influence), and time of the year or even the day (meteorological factors). Primary PM emissions related to soil derived species (wind blown dust, construction dust,

road dust, sea salt, and other mechanically derived materials, perhaps associated with industrial processes) typically have aerodynamic diameters greater than 2.5 μm , and PM₁₀ concentrations can be dominated by such primary emissions. Seasonal variations of PM₁₀ generally are not strongly related to ozone concentrations (Figure 6.22), and usually have little relation with regional haze and acid deposition. Ozone formation is most rapid during summer when radiation levels are greatest; summer ozone concentrations tend to be highest during conditions of stagnation, when windblown dust would typically be at a minimum.

Secondary particles are formed through photochemical processes, nighttime radical chemistry (such as nitrate via the nitrate radical), and aqueous mechanisms (for example, during foggy conditions where SO₂ can be absorbed into water droplets and oxidized efficiently by H₂O₂ or metal catalysts). Ozone has precursor species (NO_x and VOC) in common with secondary PM. In eastern North America, secondary particles and PM_{2.5} in general tend to accumulate in air during stagnant conditions in the summer, often when ozone forms (Figure 6.22).

At most urban and many rural sites in California, the autumn or winter fine aerosol is often dominated by ammonium nitrate and carbon compounds. During summer, equilibrium favors the precursors of particulate ammonium and nitrate (gas-phase nitric acid and ammonia); as well, semi-volatile organic compounds are also found preferentially in the gas phase in the summer. In the fall and winter, with cooler temperatures, the nitrate equilibrium is shifted to the particle phase. Thus, the winter PM_{2.5} maxima observed in California are associated with low ozone concentrations (Figure 6.22). Changes in NO_x or VOC emissions may have various effects on PM mass concentrations (Chapter 3), depending on whether the nitrate is limited by the amount of nitric acid or ammonia present in air, and on whether the conversion of NO₂ to nitric acid is radical- or NO_x-limited. It is possible that winter PM nitrate concentrations in some locations may not respond to NO_x reductions even though summer ozone concentrations do.

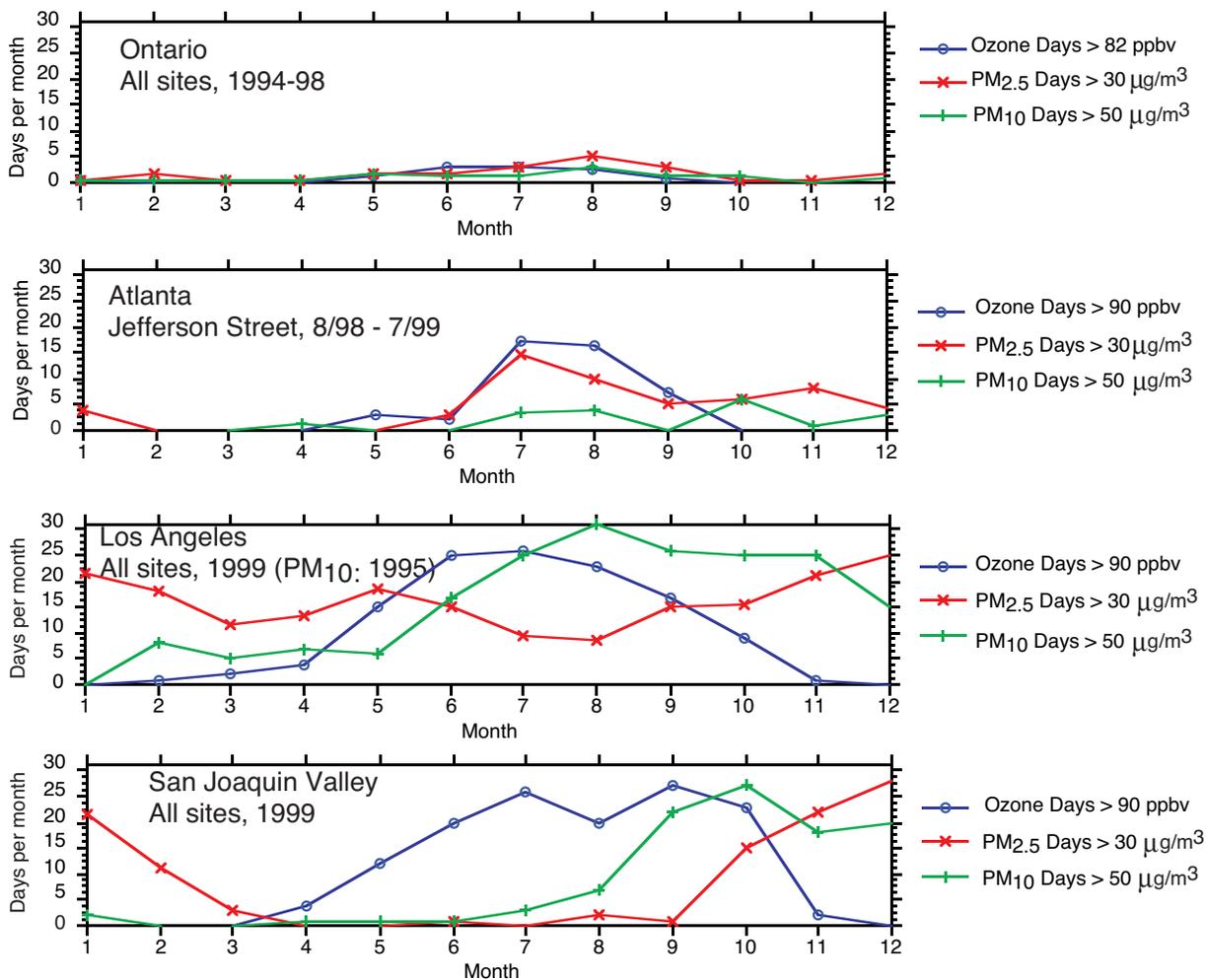


Figure 6.22. Seasonal variation of ozone, PM_{2.5} mass, and PM₁₀ mass at four locations, showing the number of days per month exceeding specified threshold levels. For ozone, the thresholds refer to the peak hourly value. For PM_{2.5} and PM₁₀, the thresholds refer to 24-hr concentrations. PM_{2.5} and PM₁₀ frequencies were scaled according to the number of days with missing data each month. (Source: data provided by Environment Canada; Vet et al., 2001; Hansen et al., 2003; Alexis et al., 2001).

At many locations, seasonally higher concentrations of PM persist throughout the autumn, when ozone levels are declining toward their winter minima (Figure 6.22). Higher PM mass concentrations may occur during periods of stagnation, whereas ozone levels decline with declining seasonal radiation.

In the eastern half of the United States, ammonium sulfate and carbonaceous material dominate during summer. Like ozone, sulfate and some fraction of the carbon are derived from photochemical processes, and higher concentrations of both ozone and PM_{2.5} occur during periods of stagnation. Thus, PM_{2.5} mass tends to correlate with ozone concentrations on a

daily time scale (Figure 6.23), although high PM and ozone concentrations do not necessarily occur on the same day at the same location.

In California, summer ozone and PM mass concentrations typically show statistically significant (but not strong) correlations on a daily time scale in the San Joaquin Valley, but not necessarily in Los Angeles (Figure 6.23). The PM_{2.5} and ozone peaks occasionally coincide, but often do not (Figure 6.23). These summer PM_{2.5} mass concentrations are much lower than those occurring during winter (Figure 6.22). PM₁₀ concentrations are often highest during windy conditions, with wind blown dust being a

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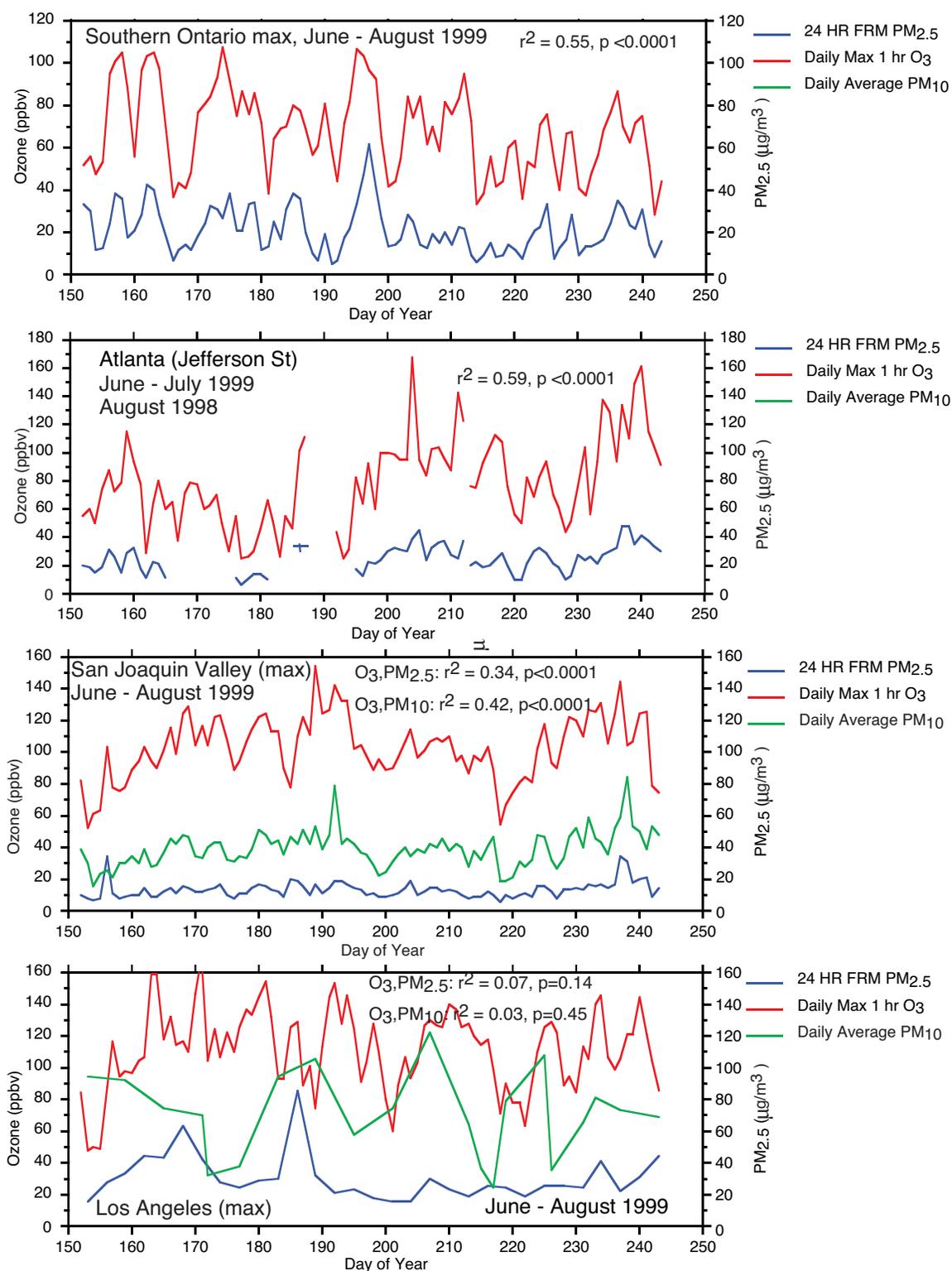


Figure 6.23. Daily variations of ozone, PM_{2.5} mass, and PM₁₀ mass during June through August 1999. In Los Angeles, the sampling frequency for PM_{2.5} was once each three days and for PM₁₀ was once each six days. (Source: data provided by Environment Canada; Vet et al., 2001; Hansen et al., 2003; Alexis et al., 2001).

major contributor, and under conditions when ozone does not accumulate, so peak ozone and peak PM_{10} days do not usually coincide.

On an hourly time scale, summer PM and ozone concentrations at sites in eastern North America do not necessarily track each other, indicative of variations in the relative importance of the different chemical and physical processes that drive ozone and PM formation and accumulation (Figure 6.24). For example, summer data from Atlanta and Ontario show that the typical diurnal profile observed in ozone levels is not seen in $PM_{2.5}$ mass concentrations (Figure 6.24). In the summer Atlanta data, periods of both correlation and anticorrelation occur; these periods also appear as time lags between hourly ozone and $PM_{2.5}$ maxima. The Ontario data clearly reveal the dependence of both ozone and PM mass concentrations on multi-day meteorological

variations. During winter, ozone continues to show daytime maxima, whereas $PM_{2.5}$ mass concentrations are typically greatest at night and appear to respond more to the presence or absence of the nocturnal inversion or to emissions such as woodsmoke (Figure 6.24).

6.7 SUMMARY

The highest mean annual $PM_{2.5}$ concentrations in North America occur at sites in California and over a broad portion of the eastern, and especially the southeastern, United States. Shorter-term monitoring data from Mexico City suggest that mean annual $PM_{2.5}$ concentrations there could be among the highest recorded in North America.

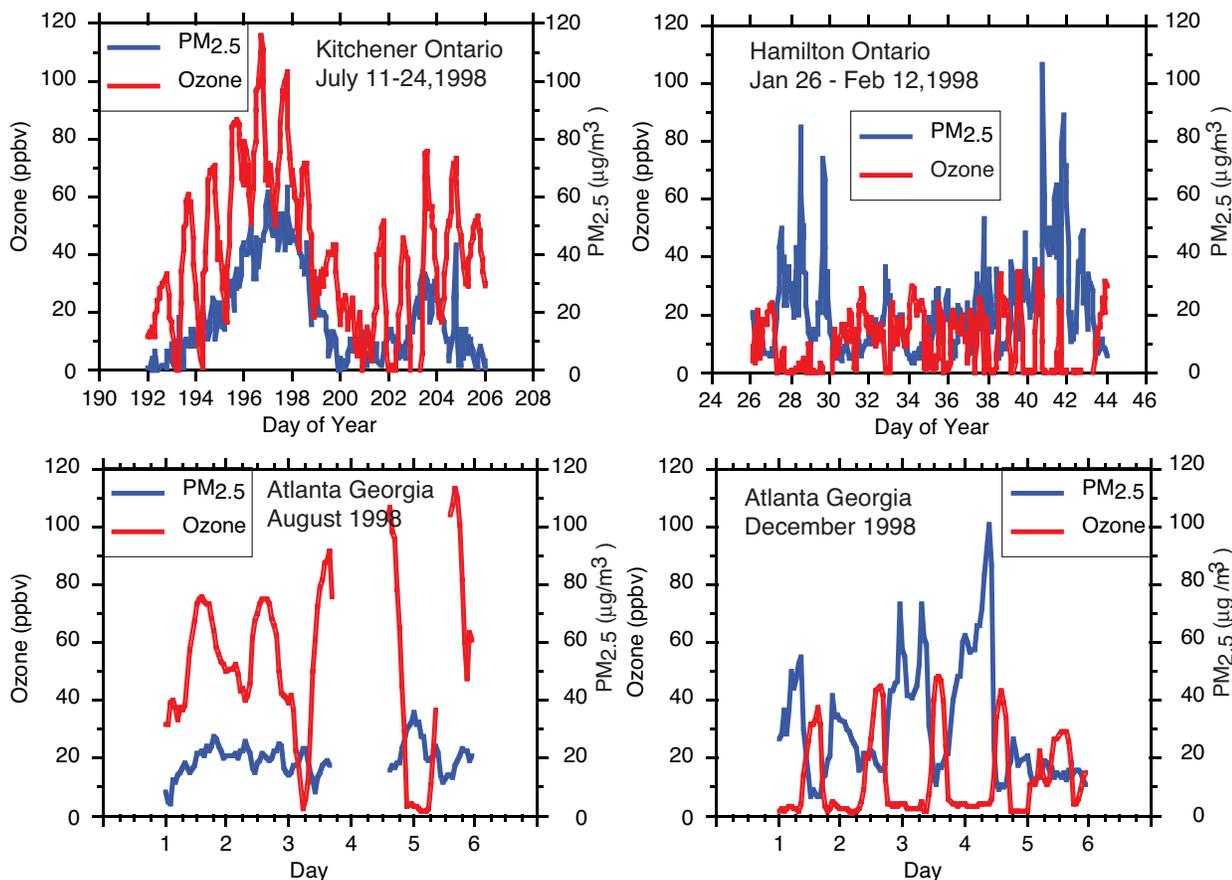


Figure 6.24. Hourly variations of ozone and $PM_{2.5}$ mass during two time periods at two monitoring sites in Ontario (top) and one site (Jefferson Street) in Atlanta. (Source: data provided by Environment Canada; Vet et al., 2001; Hansen et al., 2003; Alexis et al., 2001).

Although determination of compliance with PM standards is the responsibility of various regulatory agencies, the ambient air-quality standards established by those agencies provide a useful benchmark for delineating the dimensions of the PM management task. Throughout North America, both urban and rural monitoring locations may exhibit $PM_{2.5}$ concentrations exceeding the levels specified by the national standards of Canada, the United States, or Mexico. The 98th percentile 24-hr $PM_{2.5}$ mass concentrations at the majority of urban U.S. and Canadian monitoring sites exceeded $30 \mu\text{g}/\text{m}^3$ (the level of the Canada Wide Standard; U.S. FRM data are presently limited to two years of measurements). With the exception of California, few sites had 98th percentile 24-hr $PM_{2.5}$ mass concentrations exceeding the level specified by the U.S. 24-hr standard ($65 \mu\text{g}/\text{m}^3$). In California, the southeastern United States, and the Ohio Valley – Great Lakes states, annual average $PM_{2.5}$ mass concentrations at about half the urban sites exceeded the U.S. three-year average annual mean $PM_{2.5}$ mass standard of $15 \mu\text{g}/\text{m}^3$ in 1999 and 2000. Thus, in the United States, achieving the annual $PM_{2.5}$ standard will be the focus of the regulatory effort at most sites, whereas in Canada the regulatory effort will necessarily be oriented to the 24-hr Canada Wide Standard. In California, PM management needs to address both the U.S. annual and 24-hr standards.

$PM_{2.5}$ concentration measurements typically exhibit strongly skewed frequency distributions, dominated by a large number of low values and including a smaller number of high concentrations. At locations where exceedances of national 24-hr or annual-average $PM_{2.5}$ standards occur, numerous episodes of elevated PM mass concentrations contribute. High concentrations do not occur on the majority of days, but neither are they rare events.

Fine particles are produced from primary emissions, including windblown dust, fires and other combustion sources of carbon compounds, and as secondary particles from precursor emissions of sulfur, nitrogen oxides, ammonia, and VOC. Thus, in virtually all locations the major chemical components of PM are sulfate, nitrate, ammonium, organic carbon, elemental carbon, and crustal-related compounds (e.g., oxides of silicon, iron, calcium, and magnesium, collectively known as soil or dust). Trace elements,

such as antimony, arsenic, beryllium, cadmium, cobalt, chromium, iron, lead, manganese, mercury, nickel, selenium, and zinc, do not contribute much to $PM_{2.5}$, but are of interest because of their possible adverse effects on health and their usefulness as tracers of the sources of fine particulate emissions. Some trace elements are identified as hazardous air pollutants by one or more North American governments.

Of the major components of fine particles, organic carbon is found at all urban and rural monitoring locations, composing typically 25 to 70 percent of the mass in urban locations. Sulfate is a significant component of PM at rural and urban sites in eastern North America during the summer, but in winter sulfate concentrations are lower and nitrate concentrations are greater than in summer. Nitrate is a major constituent at rural and urban sites in California and dust is a contributor at some locations in western North America.

Differences between PM mass concentrations at urban and rural monitoring sites provide indications of the relative magnitudes of local and regional contributions. Regional aerosol includes inter-urban or longer-range transport as well as nonanthropogenic background particulate mass. Urban areas show mean $PM_{2.5}$ levels exceeding those at paired rural sites. In eastern North America, the differences imply that local urban contributions are roughly 25 to 50 percent of the mean urban concentrations, with regional aerosol contributing the remaining, and larger, portion. Sulfate and organic carbon appear to be strongly regional (~50 to 90 percent of the urban values may be due to the regional component). The regional component is large enough that both regional and local PM and PM-precursor emission reductions will be required to meet the U.S. and Canadian $PM_{2.5}$ standards in many urban areas.

The regional contribution to PM varies among regions. Data from the IMPROVE network indicate that mean annual $PM_{2.5}$ levels exceed $10 \mu\text{g}/\text{m}^3$ at rural locations in much of the southeastern United States. Rural locations in other portions of the eastern United States, California, Ontario, and Quebec exhibit mean annual $PM_{2.5}$ levels of 5 to $10 \mu\text{g}/\text{m}^3$. It will be difficult to meet the U.S. annual PM standard in urban areas where the regional component is at

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present close to the level of the standard, and regional PM management strategies may be required.

Specific studies, such as the Sulfate Regional Experiment, the Grand Canyon visibility studies, and the San Joaquin Valley Air Quality Study have examined the long-range transport of pollutants (PM and PM precursors) within North America. These studies have shown that transport of anthropogenic PM_{2.5} can occur over distances of 500 to 1000 km or more. For example, pollutants from Los Angeles have been shown to impact visibility in Class 1 areas in and around the Grand Canyon. While this transport may not cause an exceedance of the U.S. PM_{2.5} standard, it is sufficient to affect visibility in Class 1 areas in the southwestern United States.

Global-scale long-range transport can also affect PM mass concentrations. Both satellite and surface monitoring show that long-range transport to or within North America occurs, from east Asia across the North Pacific, from North Africa to the Caribbean and Gulf Coast states, and from Central America northward into the United States. Evidence to date suggests that such transport typically does not in itself produce surface-level concentrations that violate PM standards, but has the potential to contribute to exceedances when high concentrations from local PM emissions are superimposed upon this long-range background. To date, no systematic quantification of the frequency of occurrence of such transport events, or their average contributions to 24-hr or annual average concentrations, has been completed. However, a number of individual episodes have been studied. Since transport episodes occur at irregular intervals, full characterization of the frequency and magnitude of transport requires daily sampling at designated monitoring sites; however, the larger number of compliance sites can operate on a more practical schedule of one sampling day every six days. Currently, global plumes may be tracked with satellite data so transport days can be identified.

A pronounced decrease of particulate sulfate concentrations occurred in the eastern United States during the 1990s, and its timing indicates that it is a reflection of the U.S. Phase I SO₂ emission controls that were implemented as of the end of 1994. From 1989 to 1998, SO₂ emissions in the states east of and including Minnesota to Louisiana declined by about

25 percent. Average SO₂ and sulfate concentrations at CASTNet monitoring sites in the same region declined by about 40 percent and exhibited a statistically significant correlation with the SO₂ emissions trend. The magnitudes of the emissions and concentrations changes were not statistically different, supporting the utility of regional reductions of SO₂ emissions for effecting near-proportional reductions of particulate sulfate.

In Canada, PM_{2.5} concentrations in six eastern cities showed about a 40 percent decline from 1992 through 1996, and a 14 percent increase from 1996 through 1999. Although the temporal pattern was consistent with the timing of the U.S. Phase I SO₂ emission reductions, the aerosol sulfate concentrations did not exhibit a corresponding decline during the 1992-96 time period. However, the rural CAPMoN sites did exhibit declining concentrations of SO₂ and particulate sulfate between 1990 and 1999, suggesting that the effects of the U.S. management program may have been masked in the urban data by more local influences.

In Los Angeles, a 70 percent reduction of SO₂ emissions between 1977 and 1995 led to a halving of ambient sulfate concentrations, and a time-lag of about 5 years occurred between the onset of emission reductions in 1978 and the first observable declines in ambient sulfate concentrations. This historical example illustrates the potentially nonproportional response between ambient sulfate concentrations and SO₂ emissions, as well as the need to maintain a long-term monitoring program to characterize the effects of the emission reductions.

Ammonia reacts preferentially with sulfuric acid aerosol, and, if sufficient ammonia is available, it also combines with nitric acid to form particulate nitrate. Declining sulfate levels therefore have the potential to cause increasing nitrate concentrations where particulate nitrate formation is limited by the availability of ammonia. Existing measurements are not definitive. At rural (CAPMoN) monitoring locations in Canada, particulate sulfate and ammonium concentrations decreased from the early to late 1990s. During this same time period, particulate nitrate concentrations increased. Either, or both, increasing NO_x emissions or increasing rates of particulate nitrate formation (caused by increasing

availability of ammonia as sulfate levels declined) may have contributed; both causes are considered probable. Seasonal data from the CAPMoN sites shows that particulate nitrate concentrations were highest when particulate sulfate concentrations were lowest and the levels of free ammonium were highest.

Data from California locations indicate the importance of particulate nitrate as a component of $PM_{2.5}$ concentrations there, accounting for ~30 to 40 percent of the annual-average $PM_{2.5}$ mass; annual-average nitrate concentrations ranged from about 6 to 16 $\mu\text{g}/\text{m}^3$. Nitrate is a prominent component of $PM_{2.5}$ at other urban locations in the western United States as well. In California, particulate sulfate concentrations are typically lower than in eastern North America, and sufficient ammonia is available at most times and locations to allow the formation of particulate ammonium nitrate. The amount of particulate nitrate that forms depends upon the amount of nitric acid. This amount in turn depends upon the rate of conversion of NO_2 to nitric acid. Initial modeling efforts suggest that nitric acid formation may be limited by the availability of radical species in one urban location of the San Joaquin Valley, and particulate nitrate formation may be more effectively reduced through reductions of VOC than NO_x . However, nitrate concentrations in nearby rural areas may respond to reductions in NO_x emissions. These findings have significant implications for the management of both PM and ozone, and additional research efforts are needed for fully understanding these implications.

Long-term records of PM show that PM emissions and ambient levels have declined in many or most U.S. cities over the past 40 to 50 years. Primary PM emissions decreased by 50 to 60 percent from 1940 to 1990. Trends reconstructed from available TSP or PM_{10} measurements indicate that average TSP concentrations declined by two- to three-fold in urban areas between 1950 and 1980, while $PM_{2.5}$ concentrations (estimated from proxy information on emissions) likely declined by about a factor of two between 1960 and 1990. Despite the uncertainties in analyses that of necessity relied on differing types of measurements from different years, the available data therefore indicate that average PM levels in U.S. cities are roughly half those occurring in the 1950s. Thus, present-day PM exposures are substantially

lower than those of 50 years ago. The compositional changes in PM are unknown.

In urban areas having multiple monitoring sites, average PM_{10} mass may vary by up to roughly a factor of two over distances as small as approximately 10 to 20 km. In some cities, average $PM_{2.5}$ mass may also show factor-of-two variations, though usually over distances of 50 to 100 km or more. The typically smaller spatial variations of $PM_{2.5}$ mass than PM_{10} mass are consistent with the well-known long residence time of fine aerosol, which permits transport over distances of 10 to 1000 km and tends to homogenize spatial variations in mass concentrations. Monitoring data also indicate that significant short-term (24-hr) variations of $PM_{2.5}$ mass may occur within urban areas. Monitoring data show typically larger intersite differences in trace-element concentrations than in $PM_{2.5}$ mass concentrations. Epidemiological studies run the risk of misclassifying PM exposures if the number of monitors within an urban area is insufficient to represent the spatial variations of outdoor population exposures. Further attention to network-design requirements is needed to ensure that future monitoring data are adequate to properly characterize exposure.

PM management requires strong ambient monitoring programs. Many key dimensions of PM monitoring programs must be specified, including size fractions, chemical species, sampling duration, sampling frequency, number and location of monitors, length of monitoring program, and instrumentation required to accomplish each of the preceding accurately and affordably. Specification of these choices requires clear identification of program objectives. In practice, monitoring networks are resource limited and cost considerations typically limit their ability to address more than a limited number of objectives. Variables are typically optimized for the purpose of each network, and these differences add to uncertainty in the use of the data when applied for different purposes. Therefore, an ongoing need is to provide complete documentation on network methods and comparability of data across networks.

While recognizing that the data required typically vary according to the objectives of each network, an effort should be made to ensure that existing

monitoring networks meet diverse needs with maximum efficiency. Some useful monitoring activities are not now well supported. Apart from limited special studies, virtually no speciated carbon measurements exist. Measurement of a variety of PM carbon compounds at emission sources and receptor locations holds the potential for substantially improving current knowledge of source contributions to ambient organic and black carbon concentrations. Similarly, gas-phase measurements of semivolatile compounds are usually not included within most PM networks, yet they are necessary for fully understanding the behavior of such compounds (e.g., ammonium nitrate and semi-volatile organics). Conversely, with many networks making the same types of measurements, it is likely that duplication of effort exists in some specific locales. With appropriate harmonization of operating schedules and methods, more data could be shared across networks, freeing resources for measurements that are not now made by any network.

6.8 POLICY IMPLICATIONS

Long-term measurements (typically 10 years) are required to assess trends. Commitment should be made to routinely monitor at representative sites gases and particulate properties of interest for studies of population exposures, effects, model performance, and efficacy of emissions control measures. These measurements should extend to properties other than mass, e.g., size, composition. *Implication:* Comprehensive measurements of the multipollutant mixture over a period of at least 10 years are required to understand relationships between emissions, ambient concentrations and effects.

There is a relationship between the spatial scale over which particulate pollutants are distributed and the spatial and temporal scales of measurements needed to assess their impacts. Relatively coarse spatial and temporal resolution is typically adequate for regional pollutants. For locally emitted pollutants or pollutants that vary diurnally due to photochemical production or variations in temperature and relative humidity, measurements must be made with much higher spatial and temporal resolution. *Implication:* It is essential to carry out measurements with

adequate spatial and temporal resolution to document population exposure patterns and to obtain data that can be used to evaluate the performance of chemical transport models.

PM_{2.5} and PM₁₀ exhibit seasonal dependencies that vary with location. For example, PM_{2.5} concentrations in eastern North America tend to reach their highest values during summer, when high relative humidities and solar radiation favor the formation of sulfates from regional sulfur dioxide emissions, while in Mexico PM₁₀ concentrations reach their maxima during the dry period from November through May. *Implications:* Management strategies, especially those for short-term standards, need to take account of seasonal patterns and to focus on species and processes that lead to the elevated concentrations.

The composition of PM_{2.5} varies with region and locale. For example, sulfates and organic carbon are relatively abundant in eastern North America; the contribution of nitrates increases in winter, when low temperatures favor the condensed phase. Organic carbon and nitrates are abundant in much of California. Within a given region, local emissions lead to urban concentrations that are ~25 percent higher than concentrations at nearby nonurban sites. *Implication:* PM management strategies should take account of local, regional and seasonal differences in composition.

In areas where local emissions are low, PM concentrations are likely to be determined by small contributions from many distant sources. For example, regional haze is affected by emissions that occur in regions that are hundreds or thousands of kilometers in extent. *Implications:* When local concentrations are dominated by long range transport, PM management strategies need to account for the impact of multiple distant sources on PM concentrations.

Many air pollutants are related either through commonality of emissions sources or atmospheric processes. Considering how the concentrations of different pollutants co-vary helps indicate if changes in the emissions of one pollutant, or its precursors, may lead to changes in the ambient concentrations of another. For example, between 1989 and 1998, sulfate concentrations in the eastern United States

and Canada have declined approximately in proportion to SO₂ emissions, which decreased by about one third, while in Los Angeles a 70 percent reduction in SO₂ emissions between 1976 and 1996 led to a halving of ambient sulfate concentrations. Such empirical observations, however, need to be examined in light of what is known about the behavior of the multipollutant mixture. Assuming that historical trends will continue in the future can lead to errors. *Implication:* Empirical relationships between emissions and ambient concentrations from historical data can provide valuable insights into changes in ambient concentrations that might be anticipated in the future if emissions change. Confidence in such extrapolations will be improved if the extrapolated trends can be confirmed using available modeling tools.

Intercontinental transport of dust from Asia or Africa occurs but does not contribute significantly to annual average concentrations of PM concentrations in North America. It is possible, however, that it may occasionally contribute significantly to 24-hr average concentrations. *Implication:* Intercontinental transport of dust typically does not significantly impact on PM concentrations in North America. PM management in North America should continue to focus on manageable local and regional PM and precursor emissions. Intercontinental transport of dust should be tracked, allowing for exclusion of rare and unmanageable events from PM management.

Forest fires or biomass burning can contribute significantly to local PM concentrations. Satellite images and measurements of composition can be used to determine periods when such fires are significantly affecting concentrations. *Implications:* Air quality forecasting can be used to determine periods when the effects of smoke emissions from controlled burns can be minimized. Data that are routinely collected (including satellite data) can be used to identify periods when smoke emissions from distant fires are affecting local PM concentrations.

6.9 REFERENCES

- Alexis, A., Delao, A., Garcia, C., Nystrom, M., Rosenkranz, K., 2001. The 2001 California Almanac of Emissions and Air Quality. California Air Resources Board, Sacramento, California.
- Blanchard, C.L., 1999. Methods for attributing ambient air pollutants to emission sources. *Annual Review of Energy and the Environment* 24, 329-365.
- Blanchard, C.L., Carr, E.L., Collins, J.F., Smith, T.B., Lehrman, D.E., Michaels, H.M., 1999. Spatial representativeness and scales of transport during the 1995 integrated monitoring study in California's San Joaquin Valley. *Atmospheric Environment* 33, 4775-4786.
- Blanchard, C.L., Roth, P.M., Tanenbaum, S.J., Ziman, S.D., Seinfeld, J.H., 2000. The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. *Journal of the Air and Waste Management Association* 50, 2073-2084.
- Blanchard, C.L., Hidy, G.M., 2003. Effects of changes in sulfate, ammonia, and nitric acid on particulate nitrate concentrations in the southeastern United States. *Journal of the Air and Waste Management Association*. In press.
- Brunekreef, B., Janssen, N.A., de Hartog, J., Harssema, H., Knape, M., van Vliet, P., 1997. Air pollution from truck traffic and lung function in children living near motorways. *Epidemiology* 8, 298-303.
- Brook, J.R., Dann, T.F., Bonvalot, Y., 1999. Observations and interpretations from the Canadian fine particle monitoring program. *Journal of the Air and Waste Management Association* 49, PM35 – PM44.
- Bryson, R., Hare, F.K., 1974. Climate of North America, Vol 11. Bryson, R., Hare, F.K., eds. *World Survey of Climatology*. Elsevier, New York.

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- California Air Resources Board (CARB), 2001. The 2001 California Almanac of Emissions and Air Quality. California Air Resources Board, Sacramento CA.
- Christoforou, C.S., Salmon, L.G., Hannigan, M.P., Solomon, P.A., Cass, G.R., 2000. Trends in fine particle concentration and chemical composition in southern California. *Journal of the Air and Waste Management Association* 50, 43-53.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., 1993. PM₁₀ and PM_{2.5} compositions in California's San Joaquin Valley. *Aerosol Science and Technology* 18, 105-128.
- Chow J.C., Watson, J.G., Lowenthal, D.H., Hackney, R., Magliano, K., Lehrman, D., Smith, T., 1999. Temporal variations of PM_{2.5}, PM₁₀, and gaseous precursors during the 1995 Integrated Monitoring Study in central California. *Journal of the Air and Waste Management Association* 49, PM16 – PM24.
- Chow, J.C., Watson, J.G., 2001. Zones of representation for PM₁₀ measurements along the US/Mexico border. *The Science of the Total Environment* 276, 33-47.
- Chow, J.C., Watson, J.G., Edgerton, S.A., Vega, E., 2002. Chemical composition of PM_{2.5} and PM₁₀ in Mexico City during winter 1997. *The Science of the Total Environment* 287: 177-201.
- Cicero-Fernandez, P., Torres, V., Rosales, A., Cesar, H., Dorland, K., Munoz, R., Uribe, R., Martinez, A.P., 2001. Evaluation of human exposure to ambient PM₁₀ in the metropolitan area of Mexico City using a GIS-based methodology. *Journal of the Air and Waste Management Association* 51, 1586-1593.
- Dolislager, L.J., Motallebi, N., 1999. Characterization of particulate matter in California. *Journal of the Air and Waste Management Association* 49, PM45 – PM56.
- Eatough, D.J., Farber, R.J., Watson, J.G., 2000. Second generation chemical mass balance source apportionment of sulfur oxides and sulfate at the Grand Canyon during the Project MOHAVE summer intensive. *Journal of the Air and Waste Management Association* 50, 759-774.
- Edgerton, S.A., Bian, X., Doran, J.C., Fast, J.D., Hubbe, J.M., Malone, E.L., Shaw, W.J., Whiteman, C.D., Zhong, S., Arriaga, J.L., Ortiz, E., Ruiz, M., Sosa, G., Vega, E., Limon, T., Guzman, F., Archuleta, J., Bossert, J.E., Elliot, S.M., Lee, J.T., McNair, L.A., Chow, J.C., Watson, J.G., Coulter, R.L., Doskey, P.V., Gaffney, J.S., Marley, N.A., Neff, W., Petty, E., 1999. Particulate air pollution in Mexico City: a collaborative research project. *Journal of the Air and Waste Management Association* 49, 1221-1229.
- Edgerton, E.S., Hartsell, B.E., Jansen, J.J., Hansen D.A., 2003. The Southeastern Aerosol Research and Characterization Study (SEARCH): 2. Filter-based measurements of PM_{2.5} mass concentration and composition. *Journal of the Air and Waste Management Association*. In press. <http://www.atmospheric-research.com/searchhome.htm>
- Grand Canyon Visibility Transport Commission, 1996. Recommendations for Improving Western Vista: Report of the Grand Canyon Visibility Transport Commission to the U.S. Environmental Protection Agency.
- Hansen, D.A., Edgerton, E.S., Hartsell, B.E., Jansen, J.J., Hidy, G.M., Kandasamy, K., 2003. The Southeastern Aerosol Research and Characterization Study (SEARCH): 1. Overview. *Journal of the Air and Waste Management Association*. In press. <http://www.atmospheric-research.com/searchhome.htm>
- Hidy, G.M., 1994. Atmospheric Sulfur and Nitrogen Oxides: Eastern North America Source-Receptor Relationships. Academic Press, San Diego.
- Hidy, G.M., 1984. Aerosols: An Industrial and Environmental Science. Academic Press, San Diego.
- Holland D., Sirois A., 2001. Acid rain modeling. In: *Encyclopedia of Environmetrics*. J. Wiley & Sons.

SPATIAL AND TEMPORAL CHARACTERIZATION OF PARTICULATE MATTER

- Husar, R.B., Wilson, W.E., 1989. Trends of seasonal haziness and sulfur emissions over the eastern United States. In: Mathai, C.V., ed. Transactions: Visibility and Fine Particles, An AWMA/EPA Specialty Conference. Pittsburgh PA: Air & Waste Management Association. pp. 318-327.
- Kim B.M., Teffera, S., Zeldin, M.D., 2000. Characterization of PM_{2.5} and PM₁₀ in the South Coast air basin of southern California: Part I— spatial variations. *Journal of the Air and Waste Management Association* 50, 2034-2044.
- Kumar, N., Lurmann, F.W., Pandis, S., 1998. Analysis of Atmospheric Chemistry During 1995 Integrated Monitoring Study. Sacramento CA: California Air Resources Board.
- Lefohn, A.S., 2001. Assessing the existence of gradients for PM_{2.5} Ambient Concentrations Within MSAs and CMSAs Across the United States. In: American Petroleum Institute Comments on the March 2001 Draft Particulate Matter Criteria Document.
- Lynch, J.A., Bowersox, V.C., Grimm, J.W., 1996. Trends in Precipitation Chemistry in the United States, 1983-1994: An Analysis of the Effects in 1995 of Phase I of the Clean Air Act Amendments of 1990, Title IV. USGS 96-0346. United States Geological Survey, Washington DC. <http://water.usgs.gov/public/pubs/acidrain>
- Malm, W.C., 2000. Spatial and seasonal patterns and temporal variability of haze and its constituents in the United States. National Park Service.
- Maring, H., Savoie, D.L., Izaguirre, M.A., McCormick, C., Arimoto, R., Prospero, J.M., Pilinis, C., 2000. Aerosol physical and optical properties and their relationship to aerosol composition in the free troposphere at Izana, Tenerife, Canary Islands, during July 1995. *Journal of Geophysical Research* 105(D11), 14677-14700.
- Mejia-Velaquez, G.M., Rodriguez-Gallejos, M., 1997. Characteristics and estimated air pollutant emissions from fuel burning by the industry and vehicles in the Matamoros-Reynosa border region. *Environment International* 23, 733-744.
- Miranda, J., Cahill, T., Morales, R., Aldape, F., Flores, J., Diaz, R., 1994. Determination of elemental concentrations in atmospheric aerosols in Mexico City using Proton Induced X-ray Emission, Proton Elastic Scattering and Laser Absorption. *Atmospheric Environment* 28, 2299-2306.
- Molina, L.T., Molina, M.J., Air Quality in the Mexico Megacity: An Integrated Assessment. Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002.
- Motallebi, N., Croes, B.E., Taylor Jr., C.A., Turkiewicz, K., 2003a. Intercomparison of selected PM_{2.5} samplers in California. *Journal of the Air and Waste Management Association*, In press.
- Motallebi, N., Croes, B.E., Taylor Jr., C.A., Turkiewicz, K., 2003b. Spatial and temporal patterns of PM_{2.5}, coarse PM, and PM₁₀ in California. *Journal of the Air and Waste Management Association*, In press.
- Mukerjee, S., 2001. Selected air quality trends and recent air pollutant investigations in the US-Mexico border region. *The Science of the Total Environment* 276, 1-18.
- Pitchford, M., Green, M., Kuhns, H., Farber, R., 2000. Characterization of regional transport and dispersion using Project MOHAVE tracer data. *Journal of the Air and Waste Management Association* 50, 733-745.
- Price, J., Dattner, S., Lambeth, B., Kamrath, J., Aguirre, M., McMullen, G., Loos, K., Crow, W., Tropp, R., Chow, J., 1998. Preliminary results of early PM_{2.5} monitoring in Texas: separating the impacts of transport and local contributions. In: J Chow and P Koutrakis, eds. PM_{2.5}: A Fine Particle Standard. Proceedings of a Specialty Conference, January 28-30, 1998. Pittsburgh PA: Air & Waste Management Association.
- Pun, B.K., Seigneur, C., 1999. Sensitivity of PM Nitrate Formation to Precursor Emissions in the California San Joaquin Valley. San Ramon CA: Pacific Gas & Electric Company.

CHAPTER 6

- Schreffler, J.H., Barnes Jr., H.M., 1996. Estimation of trends in atmospheric concentrations of sulfate in the northeastern United States. *Journal of the Air and Waste Management Association* 46, 621-630.
- Shannon, J.D., 1999. Regional trends in wet deposition of sulfate in the United States and SO₂ emissions from 1980 through 1995. *Atmospheric Environment* 35, 807-816
- Sirois, A., 1993. Temporal variation of sulphate and nitrate concentrations in precipitation in Eastern North America: 1979-1990. *Atmospheric Environment* 27A, 945-963.
- Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., Sylte, W.W., 2000. The ammonium nitrate particle equivalent of NO_x in Central California's San Joaquin Valley. *Atmospheric Environment* 34, 4711-4717.
- U.S. EPA, 1999. Clean Air Status and Trends Network (CASTNet), 1998 Annual Report. Research Triangle Park NC: U.S. Environmental Protection Agency.
- U.S. EPA, 2000. Clean Air Status and Trends Network (CASTNet), 1999 Annual Report. Research Triangle Park NC. U.S. Environmental Protection Agency.
- U.S. EPA, 2000b. National Air Quality and Emissions Trends Report, 1998. Research Triangle Park NC. U.S. Environmental Protection Agency.
- U.S. EPA, 2002. Latest Findings on National Air Quality: 2001 Status and Trends Report. EPA 454/K-02-001. Research Triangle Park NC. U.S. Environmental Protection Agency. www.epa.gov/airtrends
- Vega, E., Reyes, E., Oritz, E., Ruiz, E., Chow, J.C., Watson, J.G., Edgerton, S.A., 2002. Basic statistics of PM_{2.5} and PM₁₀ in the atmosphere of Mexico City. *The Science of the Total Environment* 287: 167-176.
- Vet, R., Brook, J., Dann, T., Dion, J., 2001. The Nature of PM_{2.5} Mass, Composition and Precursors in Canada. In: JR Brook, PA Makar, MD Moran, MF Shepherd, RJ Vet, TF Dann, and J Dion. *Precursor Contributions to Ambient Fine Particulate Matter in Canada*. Toronto, Ontario: Meteorological Service of Canada.
- Weatherhead, E.C., Reinsel, G.C., Tiao, G.C., Meng, X.L., Choi, D., Cheang, W.K., Keller, T., DeLuisi, J., Wuebbles, D.J., Kerr, J.B., Miller, A.J., Oltmans, S.J., Frederick, J.E., 1998. Factors affecting the detection of trends: Statistical considerations and applications to environmental data. *Journal of Geophysical Research* 103, 17149-17161.
- White, W., 2001. Inter-annual variations in the composition of North American haze. Washington University, St. Louis MO.
- Zheng, M., Cass, G.R., Schauer, J., Edgerton, E., 2002. Source apportionment of fine particle air pollutants in the southeastern United States using solvent extractable organic compounds as tracers. *Environmental Science and Technology* 36, 2361-2371.

APPENDIX C. MONITORING DATA: AVAILABILITY, LIMITATIONS, AND NETWORK ISSUES

C.1. MONITORING PROGRAMS AND OBJECTIVES

PM data are currently available from a variety of monitoring programs and databases, which include

1. Global Atmosphere Watch (GAW) [global]
2. Interagency Monitoring of Protected Visual Environments (IMPROVE) [United States]
3. National Air Pollution Surveillance (NAPS) network [Canada]
4. Canadian Aerosol and Precipitation Monitoring Network (CAPMoN) [Canada]
5. Guelph Aerosol and Visibility Monitoring Network (GAViM) [Canada]
6. Federal Reference Method (FRM) fine particle monitoring network and U.S. National PM_{2.5} speciation network [United States]
7. National PM Research Monitoring Network [United States]
8. Red Automatica de Monitoreo Atmosferico (RAMA) [Mexico City]
9. Clean Air Status and Trends Network (CASTNet) [United States]
10. U.S. National Park Service data [United States]
11. California Air Resources Board databases [United States]
12. U.S. EPA Aerometric Information Retrieval System (AIRS) databases [United States]
13. Special studies.

Different PM monitoring networks have been designed for different purposes. Any one or more of the following objectives may be of principal importance:

1. Determine PM levels
2. Monitor exposure to some size fraction of PM or to one or more components
3. Monitor visibility impairment
4. Ascertain compliance with regulatory standards
5. Develop estimates of source contributions
6. Evaluate how well control strategies are achieving goals
7. Provide information needed to advance scientific understanding.

In practice, monitoring networks are resource limited and cost considerations typically limit their ability to address multiple objectives.

GAW sites are operated by individual investigators for scientific research purposes. Efforts are under way to establish an integrated archive of data.

The IMPROVE network was designed to monitor visibility impairment, with additional goals related to improving scientific understanding of the physical and chemical processes affecting visibility. Much of the nonurban data for the United States are from the IMPROVE network. IMPROVE fine-particle measurements are made in U.S. national parks and other locations that are typically representative of regional background particulate concentrations. The IMPROVE network collected aerosol samples at ~30 sites since the mid-1980s, and was recently expanded to over 100 locations. Because of its focus on providing data related to visibility in Class I and other areas where visibility is protected, the IMPROVE network is concentrated in the western United States, but future measurements will provide broader geographical coverage.

The Canadian NAPS was designed to provide a large and geographically diverse database for

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characterizing PM. It presently covers all main urban areas of Canada and includes 15 urban and four rural locations. Sampling has been conducted using dichotomous samplers, and data collection commenced as early as the mid-1980s at some sites. Samples are normally collected over a 24-hour period once every six days. Both the coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) fractions are analyzed for mass and over 50 elements.

The CAPMoN is a regional-scale air and precipitation monitoring network with multiple objectives. These objectives are to measure regional-scale spatial and temporal variations and long-term trends in the chemical composition of air and precipitation, to provide data for use in model development and testing, to provide data for process studies, and to provide a set of standard monitors across Canada. Sites are located outside urban areas and away from point or transportation emission sources and agricultural activities. The types of measurements made vary among sites, with, for example, 10 sites currently measuring SO_2 and 18 sites sampling precipitation chemistry. Data records extend back to the late 1970s for some sites. PM samples are collected daily. The size cutoff for particulate samples is not well defined, but is estimated to be about $8 \mu m$ (Nejedly et al., 1998).

The GAViM network is intended to improve scientific understanding of the physical and chemical processes affecting visibility in Canada. It has made speciated aerosol and optical measurements at five urban and rural locations across Canada twice per week, beginning in 1994. Measurements are made using IMPROVE-protocol samplers. Particle size cutoffs are 2.5 and $10 \mu m$.

The new U.S. fine particulate FRM network is primarily a compliance-monitoring network, and numbers roughly 1000 sites nationwide. These sites are concentrated in urban areas. The U.S. National $PM_{2.5}$ Speciation Trends Network was designed to develop estimates of source contributions, monitor exposure to PM components, and track trends.

The RAMA network consists of 32 stations in Mexico City and has operated since 1986. Types of measurements vary among sites, but typically include surface meteorological parameters, gas-phase species

(ozone, CO, SO_2 , and NO_x), and PM_{10} mass. A variety of special studies provide additional data for Mexico City over a forty-year period (Raga et al., 2000), but present measurements of PM composition are limited to a one-month period in 1997 (Edgerton et al., 1999).

The U.S. EPA CASTNet network was designed to provide estimates of dry deposition rates of sulfur and nitrogen compounds, which are combined with precipitation-chemistry measurements to estimate total sulfur and nitrogen loading rates. The standard CASTNet sites do not select a specific size aerosol, and they collect samples over a one-week time period. CASTNet sites are concentrated in the eastern United States, where IMPROVE coverage is limited. Eight eastern CASTNet sites have been instrumented with samplers operated according to the IMPROVE protocols (U.S. EPA, 2000).

An important ongoing special study is the Southeastern Aerosol Research and Characterization (SEARCH) project (Hansen et al, 2003). It began operating four urban-nonurban site pairs in mid-1998 in the southeastern United States (with urban sites in Atlanta GA, Birmingham AL, Gulfport MS, and Pensacola FL). Primary goals of the SEARCH network include aerosol research, measurement evaluation, characterization of urban-rural contrasts, and improved understanding of atmospheric processes. Both particulate and gas-phase species are measured, and particulate sampling includes continuous as well as filter-based methods.

C.2 NETWORK DESIGN

Network design begins with specification of network objectives. Contemporary networks emphasize different objectives, leading to a variety of general design specifications (Table C.1). Some of the specific key dimensions of PM monitoring programs include:

1. Size fractions
2. Chemical species
3. Sampling duration
4. Sampling frequency

5. Number and location of monitors

7. Instrumentation required to accomplish each of the above accurately and affordably.

6. Length of monitoring program

Size fractions and species measured, sampling duration and frequency, site location, sampler design,

Table C.1 General specifications for PM observation and monitoring networks.

Objective	Measurements	Spatial Resolution	Temporal Duration and Resolution	Design Procedure	Comments
What's there	FRM ^a or other prescribed methods; specialized instruments	Variable targets-ground and aloft	Variable; usually short term campaign	Subjective-targets of opportunity	Historical guidance and direction from air chemistry; later, regulatory motivation
Exposure/Dose	FRM and speciation measures	Mainly urban population oriented	Long term-multiyear	Relies on existing compliance networks or special process studies	Only considered explicitly in a few recent short term studies; e.g., PTEAM (Riverside, CA) and ARIES (Atlanta)
Visibility Variation	Optical properties or surrogate for human optical response	Designated air quality related value for pristine areas ^b	Prescriptive: linked with daytime visual perception.	Subjective with constraints on visual range	Recently driven by need to document light extinction combined with PM mass concentration and composition.
Compliance	FRM or other prescribed methods	Mainly urban/some regional non-urban	Prescriptive: long-term and linked with PM standards	Subjective or prescriptive (e.g. population based) ^c	Driven by regulatory needs for reporting community conditions-mostly urban focus. ^d
Source-Receptor Model	Specialized ground PM/precursor instrumentation supplemented with compliance networks; intermittent measures aloft; coupled with meteorological data.	Urban/regional scales covered by ground network, included nested grid for multiple spatial scale study.	Variable depending on model character; ranges from daily events to annual average considerations.	Subjective but recent objective concepts developed	Design varies with model methods; two regional studies followed semi-objective design; formal objective design approach attempted in concept.
Trends	FRM or other prescribed methods	Mainly urban/some regional non-urban	Long term-multi-year	Subjective; guided in U.S. as part of NAMS	Tied to emissions change; generally relies on compliance observations.
Processes	Specialized PM-precursor	Variable targets/designs range in scales from <1km-100km; aloft	Variable; usually short term campaign	Subjective-process specified	Highly focused; hypothesis generated; attention to secondary PM

^a U.S. Federal Reference Method for PM.

^b See, for example, the IMPROVE network.

^c e.g., U.S. guidelines.

^d For example, the NAMS, SLAMs networks in the U.S., NAPS in Canada, the RAMA network in Mexico City, or the California-Mexico border study.

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and other variables are typically optimized for the purpose of each network, and these differences add to uncertainty in the use of the data when applied for different purposes. An ongoing need is to provide complete documentation on network methods and comparability of data across networks.

Monitoring networks fill a variety of needs including the measurement of long-term trends, the measurement of baseline pollutant levels, the assessment of impacts, and the acquisition of data for model validation. The data set required typically varies with its application, and an effort should be made to ensure that existing monitoring networks meet diverse needs with maximum efficiency. Furthermore, North American networks should be harmonized to the extent possible to facilitate the sharing of data among Canada, the United States, and Mexico.

Objectives, measurements, and design criteria for existing national air quality networks in Canada and the United States, including those that monitor PM, are summarized by Demerjian (2000). The Demerjian (2000) review also identifies the types of data reports produced by each network as well as the additional types of data analyses of interest from the standpoints of science or of air quality management, delineates data analysis techniques of use for the analyses of interest, and characterizes data limitations. A key conclusion of the Demerjian (2000) review is that the differences between the types of monitoring information needed for scientific purposes compared with air quality management become critical for secondary pollutants. In the case of secondary pollutants, understanding the relative effectiveness of emission control strategies requires analyses of data that are capable of revealing the relations between the production of secondary species and their precursor concentrations.

The U.S. EPA has been an active participant in various attempts to apply network design methods to deposition-monitoring networks, including the National Atmospheric Deposition Program/National Trends Network (e.g., Seilkop and Finkelstein, 1987; Seilkop, 1987, Haas, 1990; Oehlert, 1993), the Environmental Monitoring and Assessment Program (Bromberg et al., 1989; U.S. EPA, 1989), the CASTNet, and, most recently, the networks included

within the National Ambient Air Monitoring Strategy (National Monitoring Strategy Committee, 2001; U.S. EPA, 2002). However, past efforts to establish scientific bases for network configuration have not always yielded results that were implemented or that affected network designs in significant ways.

The new National Air Monitoring Strategy offers the prospect of integrating current, single-pollutant monitoring approaches to better address the management of linked, multi-pollutant air quality issues (U.S. EPA, 2002). This monitoring strategy is specifically focused on the National Air Monitoring Stations (NAMS), the State and Local Air Monitoring Stations (SLAMS), Photochemical Air Monitoring Stations (PAMS), and IMPROVE. The National Air Monitoring Strategy is an initial step, and continuing efforts are needed to expand the focus of scientific network design and coordination to include air toxics and deposition networks. To date, analyses of ozone data from monitors nationwide have shown how to identify monitors that are effectively measuring the same ambient concentrations within local areas. This information will be used to redistribute monitors to use resources more efficiently. Completion of these types of analyses required the availability of an existing database. In addition, the National Air Monitoring Strategy outlines a plan for developing a national core network of up to just under one hundred locations where a number of air pollutants would be monitored in a coordinated manner.

In California, the results of ozone and PM field studies and modeling have been used to design enhancements to the routine monitoring network that could reduce future reliance on major field programs (Sweet et al, 2002). A critical component of this design effort was the use of twenty years of air quality studies to identify the numbers of monitoring locations and types of measurements needed for providing ongoing data that will characterize mesoscale meteorological features of importance to air quality. Examples of such features include onshore and offshore coastal flows, mixing depths, upslope and downslope flows, and eddies and jets. A network capable of resolving such features could routinely provide the data needed for operating and evaluating three-dimensional Eulerian air-quality models for any set of days. This capability would then permit assessment of pollutant transport,

emission control measures, and other questions of importance for air quality management for all days of interest, thus addressing continuing concerns about the representativeness of special field study periods.

The problem of characterizing the spatial field, or the spatial-temporal field, of one or more measurements has in fact attracted a great deal of attention over the years in several areas of study. Much of this attention has focused on network design, specifically on the placement of monitoring sites. Examples from the study of precipitation amount (rainfall) include Rodriguez-Iturbe and Mejia (1974) and Bras and Rodriguez-Iturbe (1976). Such network design techniques yield the number and configuration of monitoring stations that minimize an objective function of estimation error and cost. A significant body of literature on the design of air quality networks exists and dates back many years (e.g., Seinfeld, 1972; Noll et al, 1977; Nakamori and Sawaragi, 1984; Liu et al, 1986; Langstaff et al., 1987).

C.3 NETWORK NEEDS

Specific instrumentation requirements are discussed in Chapter 5. Specification of instrumentation should ensure that the key measurements are made with necessary accuracy and time resolution. Recent developments in semi-continuous monitoring for mass and chemical components of PM should be pursued so these methods become usable routinely in air monitoring and research programs.

The variety of types of measurement techniques currently in use raises questions about the accuracy and comparability of data obtained from different networks. These questions can only be addressed if adequate funding is devoted to comparisons (for comparisons of U.S. and Canadian data, see, e.g., Brook et al., 1997, Brook and Dann, 1999, Nejedly et al., 1998). Comparison of data from IMPROVE and nearby CASTNet sites indicate that the IMPROVE and CASTNet sulfate measurements are comparable, but nitrate measurements are not (Malm, 2000). The differences in nitrate concentrations stem from the presence of coarse particle nitrate and nitrate volatilization in the CASTNet samples. It has also been shown that the dichotomous samplers used in

the Canadian NAPS experience losses of particulate nitrate (Brook and Dann, 1999). The U.S. EPA Federal Reference Method suffers from loss of ammonium nitrate and semi-volatile organic compounds. Losses can be significant and at times may represent over half the collected mass (Hering and Cass, 2000).

Measurements that are representative of both the mass and composition of particles in the ambient air are difficult to obtain with either filter-based or semi-continuous methods. Much of the fine PM mass is composed of secondary species (those formed in the air or condensed from the gas phase onto existing particles). Such species often have significant vapor pressures, and thus exist in both the gas and particle phases in quasi-equilibrium. Depending on the filter material used, collection of PM by filters is plagued by both positive and negative sampling artifacts that are exacerbated by the need to transport, store, and analyze the filter some time after collection. Since the composition of particulate matter varies with location, season, and time of day, it is difficult to quantify the sampling artifacts. Denuders and reactive filters can be successfully used to obtain nitrate and ammonium with minimal bias. These data can be used to correct the collected mass, but significant uncertainty still exists in the mass value. Organic species are even more difficult to collect and no method to date exists for collecting a relatively bias-free organic sample (see Chapter 5). Recent results from the 1999 Atlanta Supersite Project suggest lower interferences from sampling artifacts are observed with semi-continuous methods than with filter-based integrated methods.

Many networks measure a suite of PM components, including sulfate, nitrate, ammonium, organic carbon, black carbon, and a variety of elements that represent crustal contributions. However, apart from limited special studies, virtually no speciated carbon measurements exist. Measurement of a variety of PM carbon compounds at emission sources and receptor locations holds the potential for substantially improving current knowledge of source contributions to ambient organic and black carbon concentrations. Similarly, gas-phase measurements are usually not included within most PM networks, yet they are necessary for fully understanding the behavior of

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semi-volatile compounds (e.g., ammonium nitrate and semi-volatile organics). Because many networks make the same types of measurements, it is likely that duplication of effort exists in some specific locales. With appropriate harmonization of operating schedules and methods, more data could be shared across networks, freeing resources for measurements that are not now made by any network. *It is unlikely that techniques will be available in the near future to provide complete chemical characterizations of carbonaceous aerosols with the frequency that would be required for air quality studies, so improved techniques for OC/BC measurements are needed for the near term. There is a need to learn more about the properties of organic compounds found in the gas and particulate phases. Moreover, an understanding of the behavior, lifetime, and effects of organic aerosols will require a better understanding of their tendency to absorb water.*

Continuing interaction with the health effects and visibility research communities is needed to ensure appropriate specification of PM size fractions and species of interest. In the case of health-effects research, this interaction needs to be ongoing and iterative. Health effects studies require monitoring information to conduct future epidemiological analyses, the conclusions from which may more fully identify the measurements of most importance. In contrast, the measurements needed for monitoring visibility impairment are generally well known as a result of past visibility studies.

REFERENCES

- Bras, R.L., Rodriguez-Iturbe, I., 1976. Network design for the estimation of areal mean of rainfall events. *Water Resources Research* 12, 1185-1196.
- Bromberg, S., Edgerton, E., Gibson, J., Holland, D., 1989. *Air/Deposition Monitoring for the Environmental Monitoring and Assessment Program (EMAP)*. Research Triangle Park: U.S. EPA, Atmospheric Research and Exposure Assessment Laboratory.
- Brook, J.R., Dann, T.F., 1999. Contribution of nitrate and carbonaceous species to PM_{2.5} observed in Canadian cities. *Journal of the Air and Waste Management Association* 49, 193-199.
- Demerjian, K.L., 2000. A review of national monitoring networks in North America. *Atmospheric Environment* 34, 1861-1884.
- Edgerton, S.A., Bian, X., Doran, J.C., Fast, J.D., Hubbe, J.M., Malone, E.L., Shaw, W.J., Whiteman, C.D., Zhong, S., Arriaga, J.L., Ortiz, E., Ruiz, M., Sosa, G., Vega, E., Limon, T., Guzman, F., Archuleta, J., Bossert, J.E., Elliot, S.M., Lee, J.T., McNair, L.A., Chow, J.C., Watson, J.G., Coulter, R.L., Doskey, P.V., Gaffney, J.S., Marley, N.A., Neff, W., Petty, E., 1999. Particulate air pollution in Mexico City: a collaborative research project. *Journal of the Air and Waste Management Association* 49, 1221-1229.
- Haas, T.C., 1990. Kriging and automated variogram modeling within a moving window. *Atmospheric Environment* 24A, 1759-1769.
- Hansen, D.A., Edgerton, E.S., Hartsell, B.E., Jansen, J.J., Hidy, G.M., Kandasamy, K., 2003. The Southeastern Aerosol Research and Characterization Study (SEARCH): 1. Overview. *Journal of the Air and Waste Management Association*, In press. <http://www.atmospheric-research.com/searchhome.htm>
- Hering, S., Cass, G., 2000. The magnitude of bias in the measurement of PM_{2.5} arising from volatilization of particulate nitrate from Teflon filters. *Journal of the Air and Waste Management Association* 49, 725-733.
- Hidy, G.M., 1994. *Atmospheric Sulfur and Nitrogen Oxides: Eastern North America Source-Receptor Relationships*. Academic Press, San Diego, CA.
- Langstaff, J.E., Seigneur, C., Liu, M.K., Behar, J.V., McElroy, J.L., 1987. Design of an optimum air monitoring network for exposure assessments. *Atmospheric Environment* 21, 1393-1410.
- Liu, M.K., Arvin, J., Pollack, R.I., Behar, J.V., McElroy, J.L., 1986. Methodology for designing air quality monitoring networks. I. Theoretical aspects. *Environ. Monitoring and Assessment* 6: 1-11.

- Malm, W.C., 2000. Spatial and seasonal patterns and temporal variability of haze and its constituents in the United States. National Park Service, Washington, DC.
- Nakamori, Y., Sawaragi, Y., 1984. Interactive design of urban level air quality monitoring network. *Atmospheric Environment* 18, 793-799.
- National Monitoring Strategy Committee, 2001. National Ambient Air Monitoring Strategy. U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Nejedly, Z., Campbell, J.L., Teesdale, W.J., Dlouhy, J.F., Dann, T.F., Hoff, R.M., Brook, J.R., Wiebe, H.A., 1998. Inter-laboratory comparison of air particulate monitoring data. *Journal of the Air and Waste Management Association* 48, 386-397.
- Noll, K.E., Miler, T.L., Norco, J.E., Raufer, R.L., 1977. An objective air monitoring site selection methodology for large point sources. *Atmospheric Environment* 11, 1051-1059.
- Oehlert, G.W., 1993. Regional trends in wet sulfate deposition. *Journal of the American Statistical Association* 88, 390-399.
- Raga, G.B., Baumgardner, D., Castro, T., Martinez-Arroyo, A., Navarro-Gonzalez, R., 2000. Mexico City air quality: a qualitative review of gas and aerosol measurements (1960-2000).
- Rodriguez-Iturbe, I., Mejia, J.M., 1974. The design of rainfall networks. *Water Resources Research* 10, 713.
- Seilkop, S., 1987. Evaluation of the National Trends Network's Site Placement Design. Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA, Research Triangle Park, NC.
- Seilkop, S.K., Finkelstein, P.L., 1987. Acid precipitation patterns and trends in eastern North America, 1980-84. *Journal of Climate and Applied Meteorology* 26, 980-994.
- Seinfeld, J.H., 1972. Optimal location of pollutant monitoring stations in an airshed. *Atmospheric Environment* 6, 847-858.
- Sweet, J.W., Shipp, E., Tanrikulu, S., DeMandel, R., Ziman, S., 2002. Conceptual design of an enhanced multipurpose aerometric monitoring network in central California. Air Waste Management Assoc. Symposium on Air Quality Measurement Methods and Technology – 2002. San Francisco CA, November 13-15, 2002.
- U.S. EPA. 1989. Design Report for the Environmental Monitoring and Assessment Program. U.S. EPA, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC. .
- U.S. EPA. 2002. National Ambient Air Monitoring Strategy: Summary Document.: U.S. EPA., Office of Air Quality Planning and Standards. Research Triangle Park, NC. www.epa.gov/ttn/amtic/stratdoc.html and www.epa.gov/ttn/amtic/monitor.html .

APPENDIX C

APPENDIX D. GLOBAL AEROSOL TRANSPORT

This appendix* describes some of the key features of the global aerosol pattern. The most prominent aerosol plume is seen over the Atlantic, originating from West Africa and crossing the tropical Atlantic (Figure D.1). It clearly reaches the Caribbean Sea and Amazon delta, 6,000 km away. Measurements indicate that the plume is dominated by crustal material (soil or dust). The dust plume is most intense during the warm season (March-August) as shown in Figure D.1. In the winter, the West African dust plume is shifted south toward the Gulf of Guinea by the prevailing winds. Airborne sampling of cross-sections of the Atlantic aerosol plumes has provided clear evidence that a significant amount of aerosol is transported above and well separated from the boundary layer.

Particulate levels over Asia show extreme variations between the pristine clean air over the Tibet Plateau and the hazy low-lying valleys of the Indian subcontinent, Indochina and China and the dusty regions of the Arabian Peninsula. The specific sources of the aerosol on the fringes of India, Indochina, and China are not known, but the hazy region is adjacent to the highest regional population density in the world. Continental Eastern Asia is known for its springtime dust sources, sulfur and other emissions from industrial sources, and for significant biomass burning.

Deforestation and agricultural burning produce thick layers of haze in the interior of South America. The PM levels are most pronounced over western Brazil and Bolivia, during the dry August, September, and October season when the biomass burning is most significant. Other aerosols of continental origin are evident off the coasts of Central America, from Mexico to Venezuela. They are most significant during the spring and summer and virtually disappear during fall and winter. These areas are also known for strong seasonal biomass burning.

A diffuse aerosol plume extends across the North Atlantic from eastern North America during the spring and summer seasons (Figure D.1). Measurements indicate the presence of small particles associated with the known sulfate-organic haze from urban industrial sources (e.g., Banic et al., 1996; Daum et al., 1996). Compared to other continents, North America and Europe show relatively low levels of aerosol optical thickness near their shores. Satellite imagery of the North African plume indicates transport reaching Central America and the U.S. Gulf Coast states, with the time of maximum impact occurring in July (Figure D.2). Measurements at surface sites along the transport path (e.g., Canary Islands, Bermuda) reveal that the dominant component of the North African PM plume is crustal material, also known as soil or dust. Surface-monitoring data from the IMPROVE network also show seasonal maximum dust concentrations in July (Figure D.3) and the plume is evident in daily PM₁₀ concentrations, whose 90th percentile values in the southeastern United States occur during July.

The transported component may be more significant to the daily average concentrations during summer episodes, possibly representing about 5 to 10 $\mu\text{g}/\text{m}^3$ on some days and up to 20 $\mu\text{g}/\text{m}^3$ at some locations (Figure D.3). For example, analyses by the Texas Natural Resource Conservation Commission indicate that the North African plume contributed as much as 15 to 20 $\mu\text{g}/\text{m}^3$ at sites in the Houston area on two days in June and August, 1997 (Price et al., 1998).

The transport of dust from Asia to North America also has been documented (e.g., Jaffe et al., 1999). For example, during April 1998, satellite data provide evidence of an aerosol plume reaching into North America (Figure D.4). Over the Pacific Ocean, the dust cloud followed the path of the springtime East-Asian aerosol plume shown by the optical thickness data. The PM_{2.5} dust concentration data from the

* Material in this Appendix was contributed by R. Husar.

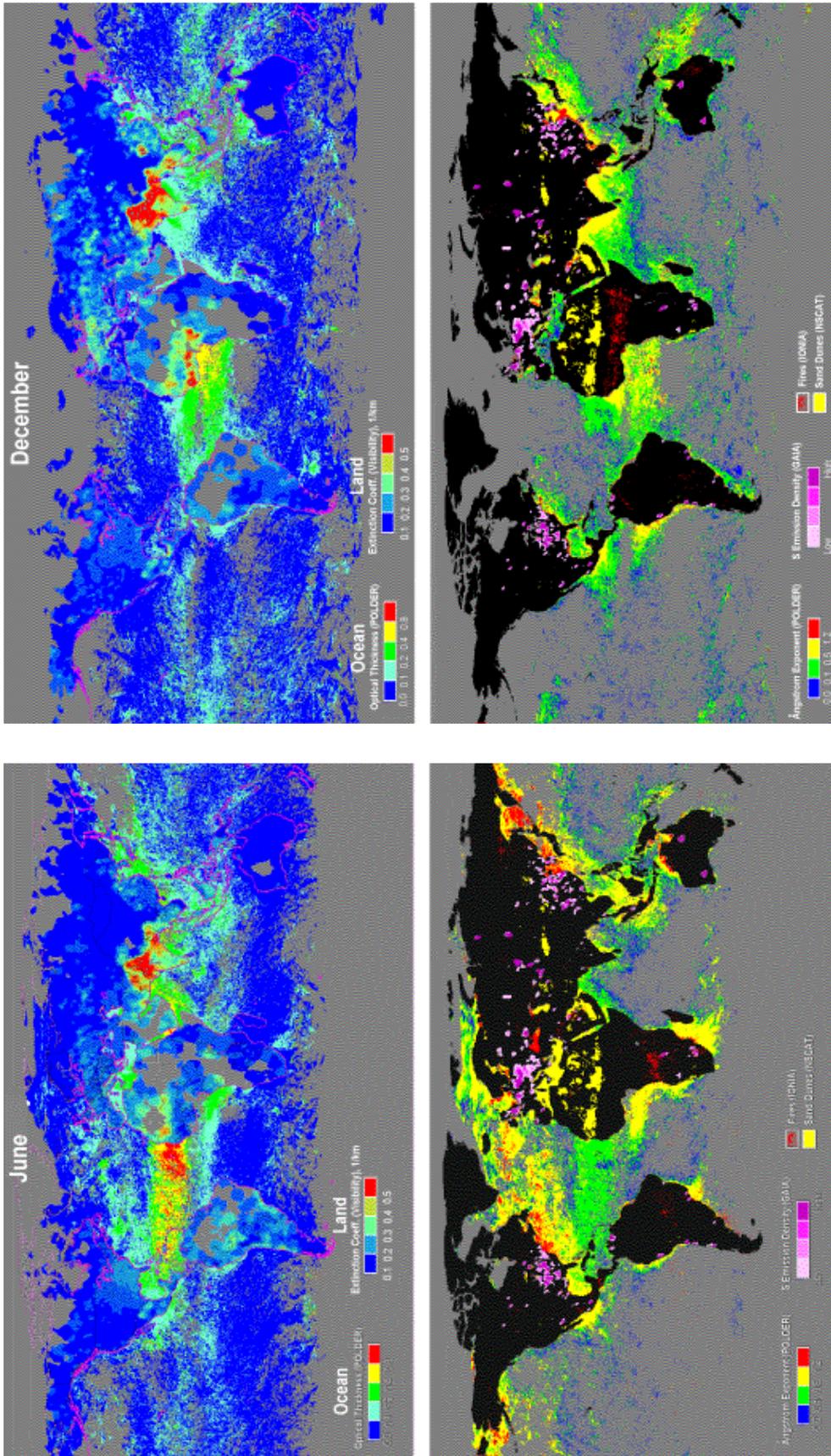


Figure D.1. Global distribution of aerosols and their likely source regions during June and December. (Source: R. Husar, pers. comm.).

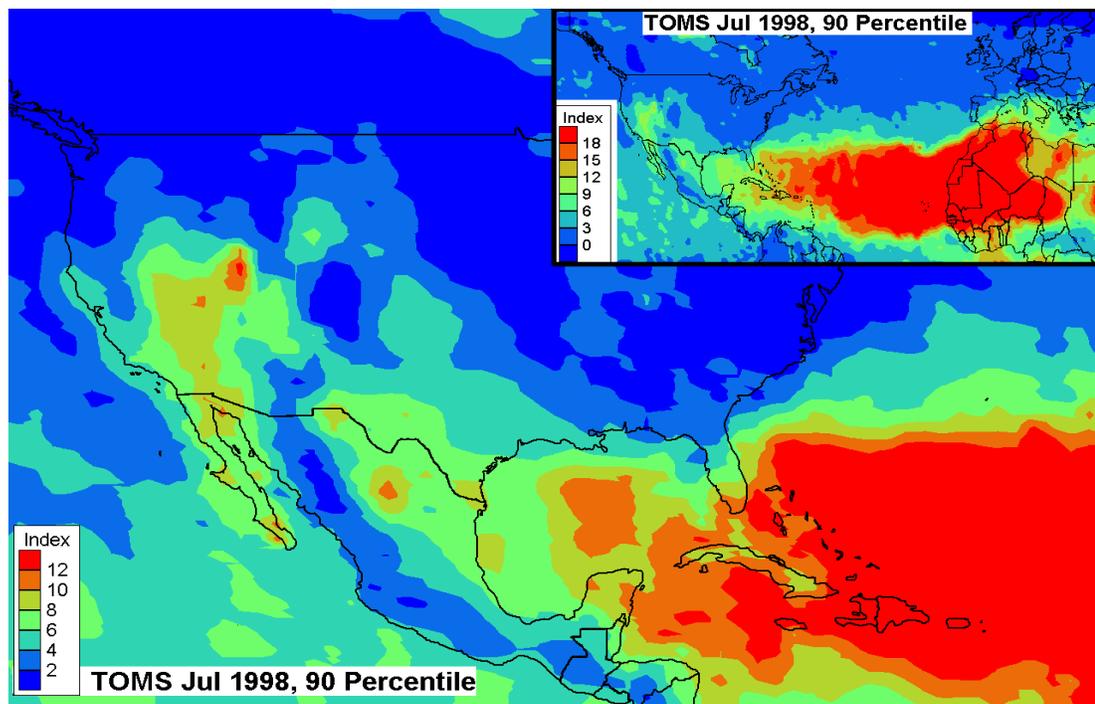


Figure D.2. Satellite data from July 1998 illustrating the extent of the Sahara dust plume. (Source: R. Husar, pers. comm.).

IMPROVE speciated aerosol network showed virtually no dust on April 25th, suggesting that the dust cloud had not reached the surface (Figure D.5). Higher $PM_{2.5}$ values then occurred over the West Coast on April 29 and further inland on May 2 (Figure D.5). Presently available data suggest that this event had an unusually strong effect on surface PM concentrations. For example, over the period 1988-98, the average $PM_{2.5}$ dust concentrations at three northern IMPROVE monitoring sites (Mt Rainier in WA, Crater Lake in OR, and Boundary Waters in MN) were well below $1 \mu\text{g}/\text{m}^3$, with occasional peaks of 1 to $3 \mu\text{g}/\text{m}^3$. On April 29, 1998, these sites showed a simultaneous sharp rise to 3 to $11 \mu\text{g}/\text{m}^3$. Evidently, the April 1998 Asian dust event caused dust concentrations 2 to 3 times higher than any other event during 1988-1998. Transport episodes of the magnitude of the April 1998 event therefore appear to occur less frequently than once per year and perhaps no more often than the order of once per ten years.

In April and May of 1998, satellite data showed the presence of large numbers of fires in Central America and prominent aerosol clouds (Figure D.6). Such

fires represent a significant source of internationally transported fine PM affecting considerable portions of Mexico. Typically, transport moves these aerosol clouds northward along the coastal areas, with the central mountain regions less affected (Figure D.6). During the PM episodes of April and May 1998, PM_{10} concentrations at locations in Texas and the southeastern United States all increased (Figure D.7), indicating the presence of a regional aerosol affecting sites across a broad area. Speciated PM measurements from the IMPROVE site at Big Bend, Texas, indicated that about half the fine particulate mass consisted of organic carbon. On average days, organic carbon may be one-fourth to one-third of PM mass.

As each of these examples of long-range transport indicates, the combined use of satellite and surface measurements provides evidence linking changes in surface PM concentrations to transported aerosol plumes. Further characterization of the frequency and magnitude of long-range aerosol transport requires systematic analysis of long-term databases of both satellite and surface measurements.

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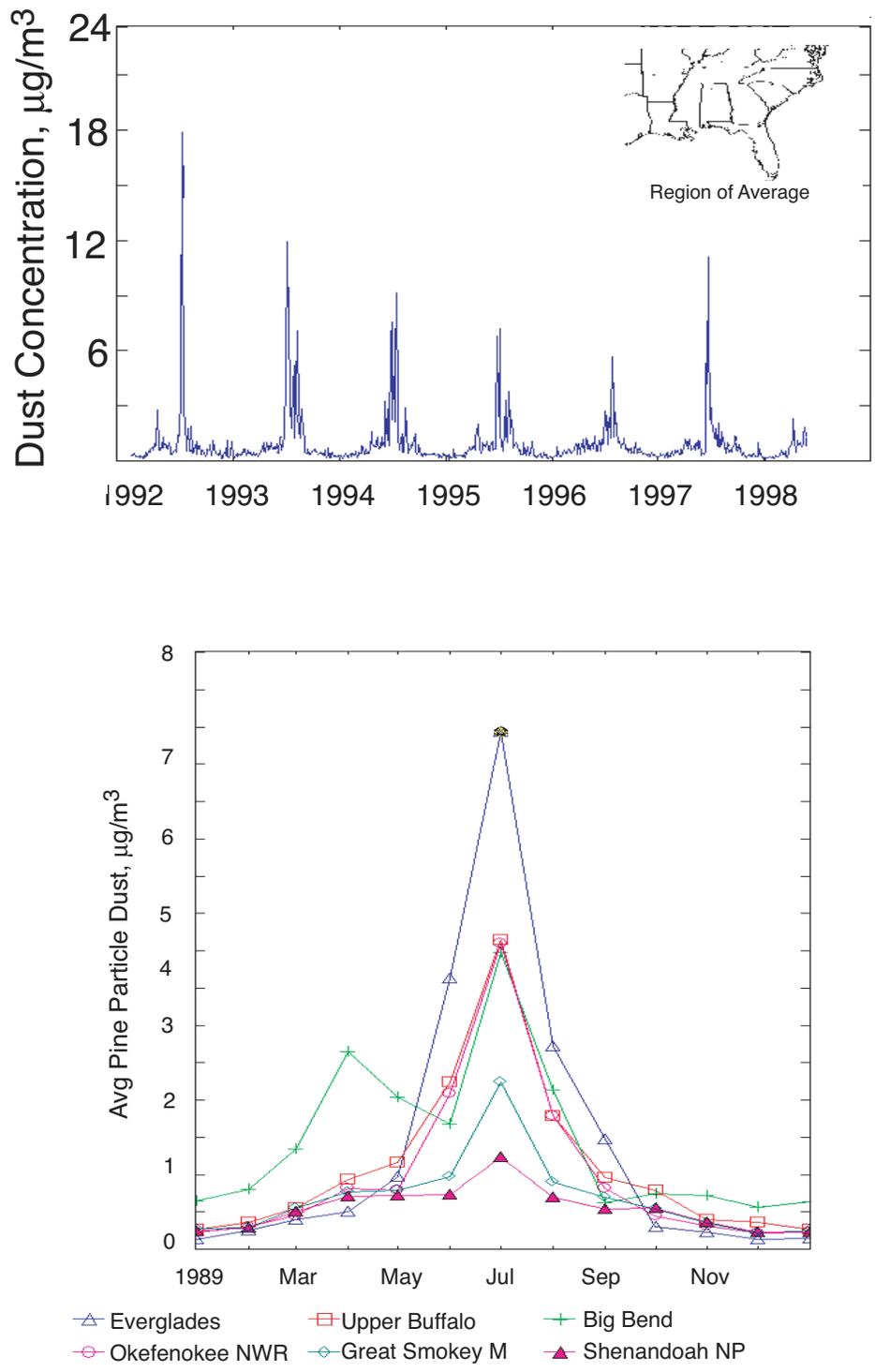


Figure D.3. Seasonal pattern of fine particulate soil (dust) concentration at IMPROVE monitoring sites in the southeastern United States. Top: Average of all sites versus date. Bottom: Monthly averages for six sites. (Source: R. Husar, pers. comm.).

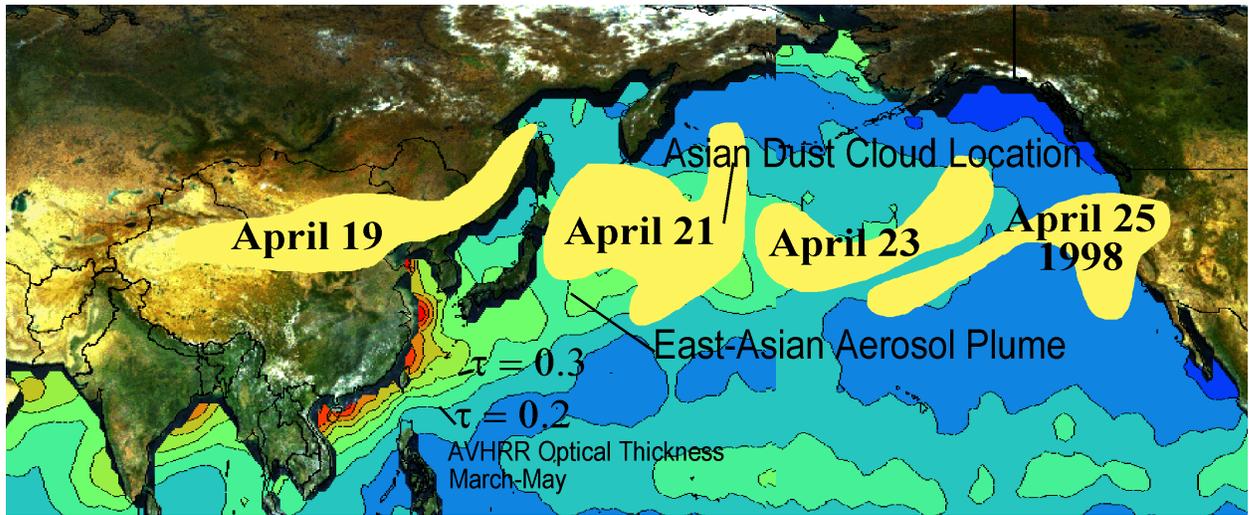


Figure D.4. Aerosol optical thickness and illustration of the positions of a dust plume during April 1998. (Source: R. Husar, pers. comm.).

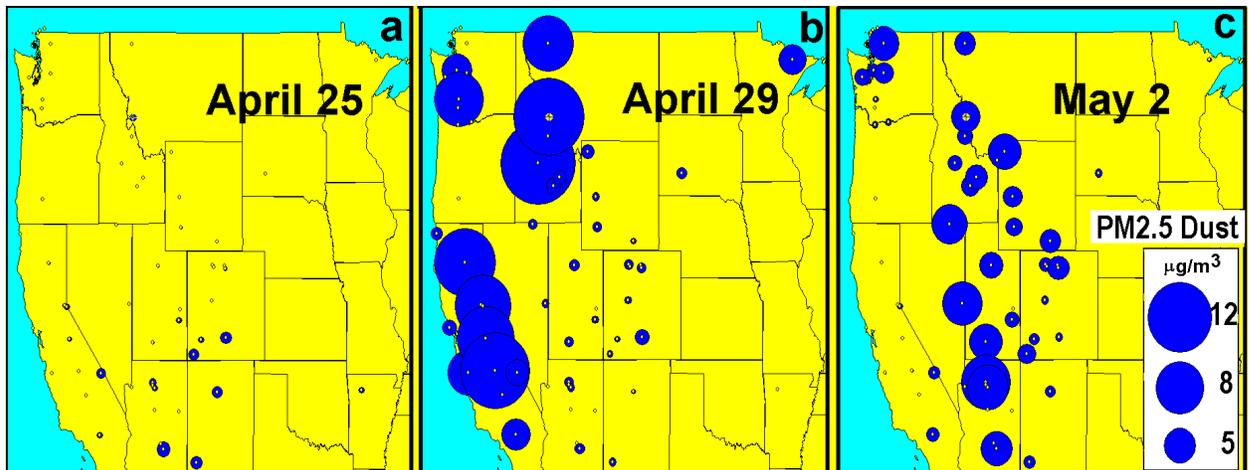


Figure D.5. PM_{2.5} dust concentrations at IMPROVE monitoring sites on three dates during April and May of 1998. (Source: R. Husar, pers. comm.).

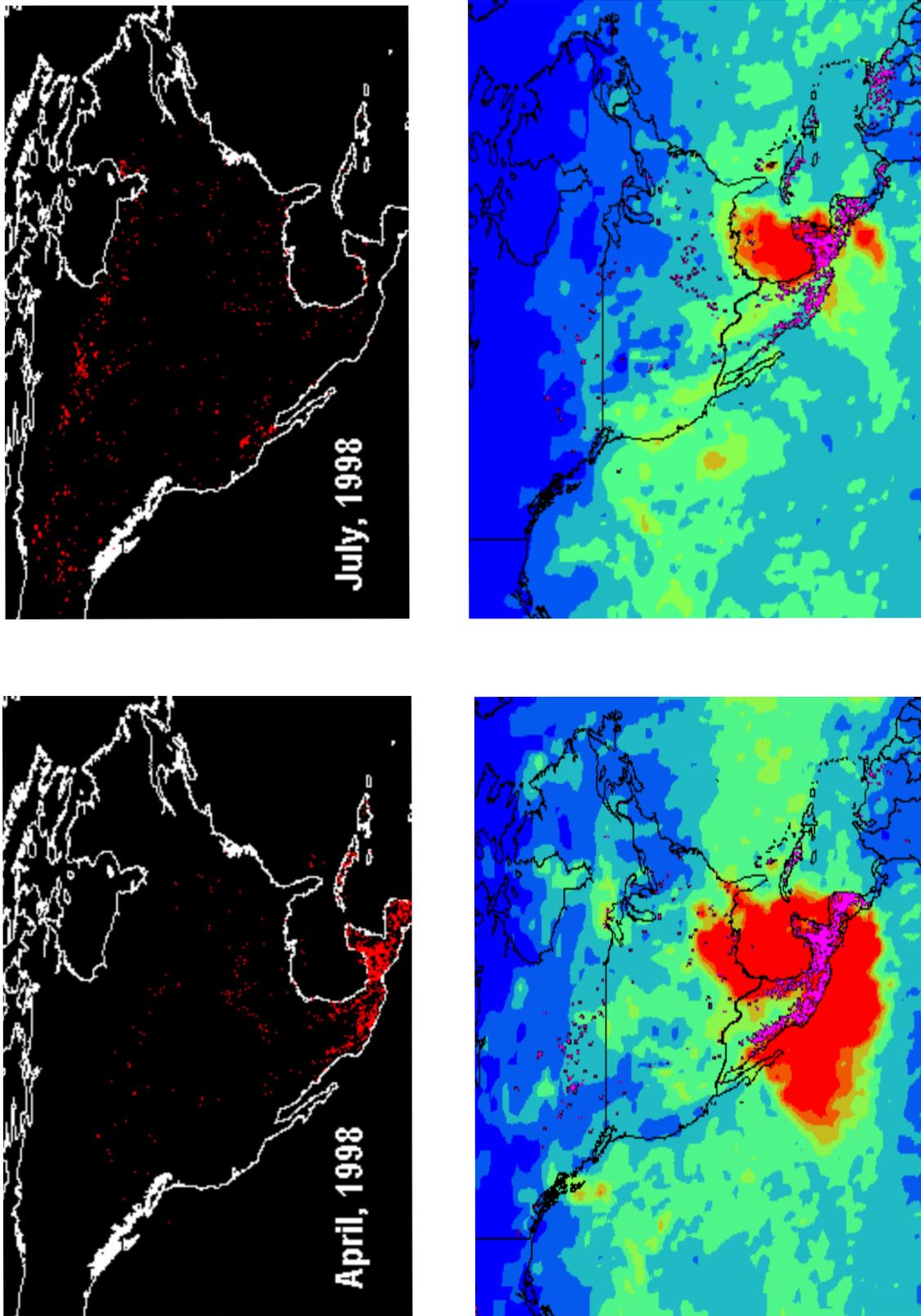


Figure D.6. Satellite imagery indicating the locations of major fires during April and July 1998 (top) and aerosol optical thickness during April and May 1998 (bottom). (Source: R. Husar, pers. comm.).

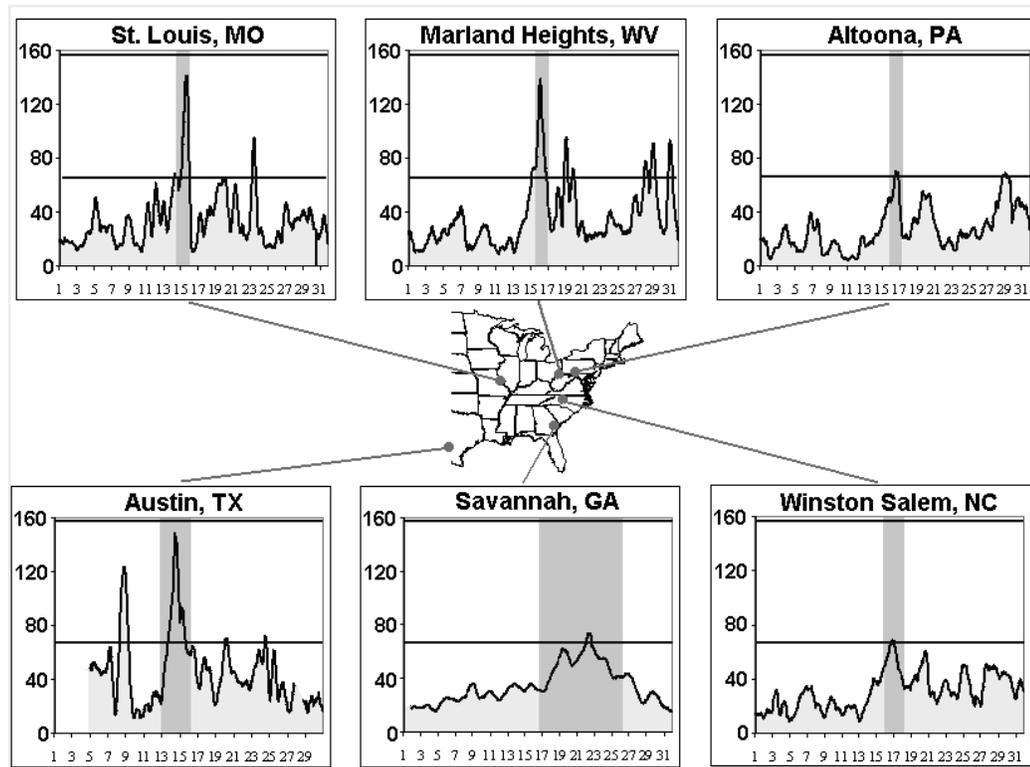


Figure D.7. Hourly PM_{10} concentrations at six locations during May 1998. (Source: R. Husar, pers. comm.).

REFERENCES

- Banic, C.M., Leaitch, W.R., Isaac, G.A., Couture, M.D., Kleinman, L.I., Springston, S.R., MacPherson, J.I., 1996. Transport of ozone and sulfur to the North Atlantic atmosphere during the North Atlantic Regional Experiment. *Journal of Geophysical Research* 101, 29091-29104.
- Daum, P.H., Kleinman, L.I., Newman, L., Luke, W.T., Weinstein-Lloyd, J., Berkowitz, C.M., Busness, K.M., 1996. Chemical and physical properties of plumes of anthropogenic pollutants transported over the North Atlantic during the North Atlantic Regional Experiment. *Journal of Geophysical Research* 101, 29029-29042.
- Husar, R.B., Tratt, D.M., Schichtel, B.A., et al., 2001. Asian dust events of April 1998. *Journal of Geophysical Research* 106, 18317-18330.
- Jaffe, D. et al., 1999. Transport of Asian air pollution to North America. *Geophysical Research Letters* 26, 711-714.
- Price, J., Dattner, S., Lambeth, B., Kamrath, J., Aguirre, M., McMullen, G., Loos, K., Crow, W., Tropp, R., Chow, J., 1998. Preliminary results of early $PM_{2.5}$ monitoring in Texas: separating the impacts of transport and local contributions. In: J Chow and P Koutrakis, eds. *$PM_{2.5}$: A Fine Particle Standard*. Proceedings of a Specialty Conference, January 28-30, 1998. Pittsburgh PA: Air & Waste Management Association.

APPENDIX D