

California Environmental Protection Agency



Air Resources Board

Staff Report:

**Public Hearing to Consider Amendments to the
Ambient Air Quality Standards for
Particulate Matter and Sulfates**

**Prepared by the Staff of
the Air Resources Board and
the Office of Environmental Health Hazard Assessment**

Release Date:

May 3, 2002

**State of California
California Environmental Protection Agency
AIR RESOURCES BOARD**

**STAFF REPORT: INITIAL STATEMENT OF REASONS
FOR PROPOSED RULEMAKING**

**PUBLIC HEARING TO CONSIDER AMENDMENTS TO THE
AMBIENT AIR QUALITY STANDARDS FOR
PARTICULATE MATTER AND SULFATES**

To be considered by the Air Resources Board on June 20, 2002, at:

California Environmental Protection Agency
Air Resources Board
9530 Telstar Avenue
El Monte, California 91731

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Acknowledgements

Staff wishes to acknowledge the following individuals in particular:

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Staff also wishes to acknowledge the following Air Resources Board staff for their expert assistance in preparing this report:

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Disclaimer

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Glossary and Abbreviations

AAQS	ambient air quality standard(s)
Aethelometer	an instrument to measure light absorption
AL	alveolar
ARB	Air Resources Board
BAM	beta attenuation monitor
CAAM	continuous ambient air monitor
CAC	correlated acceptable continuous
CAS	California approved sampler
CFR	Code of Federal Regulations
C.I.	confidence interval, a statistical measure of the interval in which the true value of an estimate is likely to be found
Coarse Particles	particles with an aerodynamic diameter between 2.5 and 10 micrometers (microns), also referred to as the coarse fraction, or PM10-PM2.5
COH	coefficient of haze, a measurement of particle light absorption that was historically used as a surrogate for suspended particle mass. A COH instrument draws a known volume of air through a paper filter, then reports the change in light transmittance between a clean filter and the filter with aerosol deposit as though it were a transmittance measurement over a path, equal to the filtered volume divided by the filter area. $COH / 1000 \text{ ft} = (\log_{10} (I_0/I_1) * 10,000) / L$ where I_0 is the clean filter transmittance, I_1 is the transmittance of the filter with aerosol deposit, and L equals the filtered volume divided by the filter area expressed in feet.
COPD	chronic obstructive pulmonary disease
DEP	diesel exhaust particle
DOP	dioctyl phthalate
ESP	electrostatic precipitator
ETS	environmental tobacco smoke
ET	extrathoracic, referring to the upper respiratory tract
Extinction	the reduction of the intensity of a beam of light as it propagates through a transmitting medium: $(I_0 - I_1) / I_0$ where I_0 and I_1 are the beam intensity at the beginning and end, respectively, of the transmittance path
Extinction Coefficient	natural logarithm of extinction per unit distance. The Extinction Coefficient is defined as B_{ext} in the following equation: $B_{\text{ext}} = - \ln ((I_0 - I_1) / I_0) / d$ where I_0 and I_1 are beam intensity at the beginning and end, respectively, of the transmittance path and d is the length of the path
FDMS	filter dynamics measurement system
FEM	federal equivalent method
FEV ₁	forced expiratory volume in one second, a measure of lung function

Fine Particles	PM _{2.5} , or particulate matter with a mean aerodynamic diameter of 2.5 micrometers (microns) or less
FRM	federal reference method
FVC	forced vital capacity, a measure of lung function
HRV	heart rate variability, a measure of the heart's ability to respond to stress
ICAM	intercellular adhesion molecule, involved in directing movement of immune cells to the site of injury or inflammation
lpm	liters per minute
LRS	lower respiratory symptoms
Mie Scattering	light scattering by particles with diameters near the wavelength of the light (0.1 μm to 10 μm). Mie scattering is the dominant cause of visible atmospheric haze.
MMEF	mid-maximal expiratory flow, a measure of lung function
NAAQS	National Ambient Air Quality Standard
Nephelometer	an instrument to measure light scattering in air.
nm	nanometer, or one billionth of a meter
NO ₂	nitrogen dioxide
NO _x	oxides of nitrogen, which includes nitric oxide (NO), nitrogen dioxide (NO ₂), and other oxides of nitrogen
NO _y	total reactive nitrogen
Odds Ratio (OR)	a measure of association between an exposure and disease. An odds ratio of one indicates no association, while odds ratios greater than one or less than one indicate positive and negative associations between the exposure and disease, respectively
OEHHA	California Office of Environmental Health Hazard Assessment
PEF	peak expiratory flow, a measure of lung function
PM	particulate matter
PM ₁₀	particulate matter with an aerodynamic diameter of 10 micrometers (microns) or less
PM _{2.5}	particulate matter with an aerodynamic diameter of 2.5 micrometers (microns) or less, also referred to as fine particles
PMNs	polymorphonuclear cells, a class of white blood cells involved in acute inflammatory response
RAAS	reference ambient air monitor
Rayleigh Scattering	light scattering by atmospheric gases. Rayleigh scattering decreases as the fourth power of wavelength. In pure air, blue light ($\lambda = 400 \text{ nm}$) is scattered 9 times more efficiently than red light ($\lambda = 700 \text{ nm}$).
Relative Risk (RR)	a measure of association between an exposure and disease. A relative risk of one indicates no association, while relative risks greater than one

or less than one indicate positive and negative associations between the exposure and disease, respectively.

REM	regional equivalent monitor
RMSSD	root mean square successive differences, a measure of heart rate variability. More specifically, this measure is the square root of the mean of the sum of squares of differences between adjacent normal beats over the whole electrocardiographic recording.
SBP	systolic blood pressure
scc	sharp cut cyclone
SDNN	standard deviation of all normal R-R intervals, a measure of heart rate variability
SDANN	standard deviation of all normal R-R intervals of successive 5-minute periods, a measure of heart rate variability
SES	sampler equilibration system
SO ₂	sulfur dioxide
SO _x	oxides of sulfur, which includes sulfur dioxide (SO ₂) and sulfur trioxide (SO ₃)
SSI	size selective inlet
TB	tracheobronchial, referring to the conducting airways from the trachea through the bronchioles
TEOM	tapered element oscillating microbalance
Transmissometer	an instrument to measure light extinction in air
TSP	total suspended particles, a measure of airborne particles of all sizes
Ultrafine Particles	particles with an aerodynamic diameter less than 0.1 micrometer (100 nanometers)
Visual Range (V _r)	the greatest distance at which a black target can be distinguished from the background sky around the majority of the horizon circle
vsc	very sharp cut cyclone
U.S. EPA	United States Environmental Protection Agency
µg	microgram, or one millionth of a gram
µg/m ³	micrograms per cubic meter
µm	micrometer (micron), or one millionth of a meter

1. Executive Summary

In this report, the staff of the Air Resources Board proposes amendments to the state Ambient Air Quality Standards (AAQS) for particulate matter. The potential health impacts from exposure to particulate matter (PM) air pollution are significant. Health effects associated with PM exposure include: premature mortality, increased hospital admissions for cardiopulmonary causes, acute and chronic bronchitis, asthma attacks and emergency room visits, respiratory symptoms, and days with some restriction in activity. These adverse health effects have been reported primarily in infants, children, the elderly, and those with pre-existing cardiopulmonary disease.

The Children's Environmental Health Protection Act (Senate Bill 25, Senator Martha Escutia; Stats. 1999, Ch. 731, Sec. 3) requires the Air Resources Board (ARB or Board), in consultation with the Office of Environmental Health Hazard Assessment (OEHHA), to "review all existing health-based ambient air quality standards to determine whether, based on public health, scientific literature, and exposure pattern data, these standards adequately protect the health of the public, including infants and children, with an adequate margin of safety" (Health & Safety Code section 39606(d)(1)). In December 2000, as a result of that requirement, the ARB approved a joint ARB/OEHHA staff report (ARB and OEHHA, 2000) that contained preliminary reviews of all of the health-based California ambient air quality standards. These reviews were not exhaustive, but were narrowly targeted to two purposes: (1) to determine whether the existing ambient air quality standards adequately protect the health of the public, including infants and children, with an adequate margin of safety; and (2) to prioritize for full review those standards determined not to adequately protect public health (Health & Safety Code section 39606(d)(1) and (2)).

The staff recommended, and the Board concurred, that among several standards deemed possibly inadequate, the existing standards for particulate matter less than 10 micrometers in aerodynamic diameter (PM₁₀) should be the first to undergo full review. This recommendation was based on the assessment that almost everyone in California is exposed to levels at or above the current State PM₁₀ standards during some parts of the year, and that the statewide potential for significant health impacts associated with PM exposure was determined to be large and wide-ranging. Finally, the staff recommended, and the Board concurred, that the standard for sulfates be reviewed concurrently with the PM₁₀ standards since sulfates are a component of particulate matter.

This report presents the findings and recommendations of a joint ARB/OEHHA review of the health and scientific literature on PM and sulfates, as well as exposure pattern data for PM and sulfates in California. The proposed amendments to the AAQS for particulate matter are based on a health effects review and recommendations from OEHHA. The scientific review suggests the need for separate standards for PM_{2.5} (particulate matter less than 2.5 micrometers in aerodynamic diameter) in addition to revising the standards for PM₁₀ to make them more health protective. The review also concluded that the standard for sulfates should be retained.

In accordance with Health & Safety Code section 57004, the proposed amendments were peer reviewed by the Air Quality Advisory Committee (AQAC), an external scientific peer review committee, comprised of world-class scientists in the PM field and appointed by the Office of the President of the University of California.

As part of the review process, a joint ARB/OEHHA staff report entitled "Review of the California Ambient Air Quality Standards for Particulate Matter and Sulfates" was submitted to the AQAC for their review. This report, containing recommendations for revising the PM

standards, was released to the AQAC and the public on November 30, 2001. Public workshops to receive community input on the proposal to review the standards were held during December 2001 in Sacramento, Oakland, Bakersfield, El Monte, Mira Loma, and Huntington Park.

The AQAC met on January 23 and 24, 2002, to review the scientific basis of the recommendations and comments received from the public. The AQAC's major findings were that the recommendations for amending the PM standards in the November 30, 2001 report were based upon sound scientific knowledge, methods, and practices and supported by the scientific literature. However, the AQAC did not concur with the lack of a recommendation for a 24-hour standard for PM_{2.5}. The AQAC concluded that there was adequate information in the scientific literature and in the studies reviewed in the November 30, 2001 report to support a 24-hour standard for PM_{2.5}. The AQAC requested staff to develop a proposal to establish a 24-hour PM_{2.5} standard and to incorporate it into the overall staff recommendation. In response, staff from ARB and OEHHA developed a proposal entitled "Draft Proposal to Establish a 24-hour Standard for PM_{2.5}, Report to the Air Quality Advisory Committee." This draft proposal and associated public comments were reviewed and approved by the AQAC at its meeting on April 3, 2002. Following that AQAC meeting, the staff report was revised to incorporate the proposal to establish a 24-hour PM_{2.5} standard along with written and oral comments received from the AQAC and the public.

Proposed Amendments to the Ambient Air Quality Standards for Particulate Matter:

The proposed amendments to the standards are largely based on results from epidemiological studies in hundreds of cities. These studies indicate strong associations between both long- and short-term exposure to PM and a variety of adverse health effects, as described above. California ambient air quality standards have four elements (see Health and Safety Code section 39014, and title 17, California Code of Regulations, sections 70100 and 70200): (1) definition of the air pollutant, (2) an averaging time, (3) a pollutant concentration, and (4) a monitoring method to determine attainment of the standard. Staff's recommendations for amending the ambient air quality standards for PM and sulfates are summarized below.

Pollutant, Concentrations and Averaging Times:

- PM₁₀ Annual-Average Standard – Lower the annual-average standard for PM₁₀ from 30 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) to **20 mg/m³, not to be exceeded**. Revise the averaging method from an annual geometric mean to an annual arithmetic mean. This recommendation is based on the results of numerous epidemiological studies which have found associations between long-term PM₁₀ exposure and adverse health effects, such as mortality and morbidity from cardiopulmonary causes.
- PM₁₀ 24-hour-Average Standard – Retain the 24-hour-average standard for PM₁₀ at **50 mg/m³, not to be exceeded**.
- PM_{2.5} Annual-Average Standard – Establish a new annual-average standard for PM_{2.5} at **12 mg/m³, not to be exceeded**. Establish the new PM_{2.5} standard as an annual arithmetic mean. This recommendation is based on a growing body of epidemiological and toxicological studies showing significant toxicity (resulting in mortality and morbidity) related to exposure to fine particles.
- PM_{2.5} 24-hour-Average Standard – Establish a new 24-hour-average standard for PM_{2.5} at **25 mg/m³, not to be exceeded**. This recommendation is based on epidemiological

studies showing associations between ambient PM_{2.5} levels and mortality and morbidity resulting from cardiopulmonary causes.

- Sulfates 24-hour-Average Standard – Retain the 24-hour-average standard for sulfates at **25 mg/m³**.

Monitoring Methods, Samplers, and Instruments:

- PM₁₀ Monitoring Method – Adopt the Federal Reference Method (FRM) for PM₁₀ as the method for California.
- PM_{2.5} Monitoring Method – Adopt the Federal Reference Method (FRM) for PM_{2.5} as the method for California.
- Continuous PM Samplers – Adopt those continuous PM samplers which have been found to be suitable for determining compliance with the state PM₁₀ and PM_{2.5} AAQS, and designate them as California approved samplers (CAS).
- Sulfates Monitoring Method – Revise the sulfates monitoring method by deleting the current total suspended particle (TSP) sulfates method, ARB method MLD 033, and replacing it with the existing ARB method for PM₁₀ sulfates, ARB method MLD 007.

Health Benefits:

The health benefits from attaining the proposed standards are substantial. For example, a quantitative risk assessment estimated that attainment of the proposed annual PM₁₀ standard from current ambient levels would result in a reduction of approximately 6,500 cases (3,200 – 9,800 for a 95 percent confidence interval (95% CI)) of premature mortality per year. This estimate is based on the assumption that mortality is primarily associated with exposure to PM_{2.5} rather than with the coarse PM fraction. Estimated annual reductions in hospitalizations related to attaining the proposed PM₁₀ standards are 1,200 (66-2,300, 95% CI) for chronic obstructive pulmonary disease, 1,700 (760-2,600, 95% CI) for pneumonia, 3,100 (2,500-3,600, 95% CI) for cardiovascular causes, and 960 (400-1,500, 95% CI) for asthma. Among children ages 7 to 14, attainment of the PM₁₀ standard is estimated to result in about 389,000 (161,000 –573,000, 95% CI) fewer days of lower respiratory symptoms per year. Of these, approximately half of the days of lower respiratory symptoms may be associated with attainment of the proposed PM_{2.5} standard.

Other Recommendations:

- Staff recommends that the standards for PM and sulfates be revisited within five years, to evaluate new evidence regarding the health effects associated with averaging time, particle size, chemistry, and concentration.
- Staff also recommends that further scientific information be gathered and research be conducted into the health effects of short-term exposures to PM, especially effects from less than 24-hour exposures. This information should be considered when staff revisits the PM standards to determine if AAQS with averaging times of less than 24 hours would be appropriate.

Environmental and Economic Impacts:

The proposed ambient air quality standards will in and of themselves have no environmental or economic impacts. Standards simply define acceptable air quality. Local air pollution control or air quality management districts (Districts) are responsible for the adoption of rules and regulations to control emissions from stationary sources, while the Board is responsible for controls related to mobile sources. A number of different control measures are possible,

and each will have its own environmental and economic impacts. These impacts will be evaluated when specific control measures are proposed by the ARB or the Districts.

Environmental Justice Concerns:

State law defines environmental justice as the fair treatment of people of all races, cultures, and incomes with respect to the development, adoption, implementation, and enforcement of environmental laws, regulations, and policies. Ambient air quality standards define clean air, therefore, all of California's communities will benefit from the proposed health-based standards.

Comment Period and Board Hearing:

Release of this staff report opens the official 45-day comment period required by the Administrative Procedure Act. Please direct all comments to either the following postal or electronic mail address:

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To be considered by the Board, written submissions not physically submitted at the hearing must be received at the ARB no later than 12:00 noon, June 19, 2002.

Public workshops are scheduled for June 2002 to present the recommendations and receive public input on the Report. Information on these workshops, as well as summaries of the presentations from past workshops and meetings are available by calling (916) 445-0753 or at the following ARB website: www.arb.ca.gov/research/aaqs/std-rs/std-rs.htm.

The final recommendations for revising the PM and sulfate standards will be presented to the Board at a public hearing scheduled for June 20, 2002.

The staff recommends that the Board adopt the proposed amendments to the Ambient Air Quality Standards for Particulate Matter and Sulfates. The proposed amendments and their basis are described in detail in this staff report.

1.1 References

Air Resources Board and Office of Environmental Health Hazard Assessment (2000). Adequacy of California Ambient Air Quality Standards: Children's Environmental Health Protection Act. Staff Report. Sacramento, CA. Available at <http://www.arb.ca.gov/ch/ceh/airstandards.htm>.

2. Introduction and Overview

Particulate matter (PM) is a complex mixture of suspended particles and aerosols composed of small droplets of liquid, dry solid fragments, and solid cores with liquid coatings. Particles vary widely in size, shape and chemical composition, and may contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and compounds from the earth's crust. PM may be either directly emitted into the atmosphere (primary particles) or formed there by chemical reactions of gases (secondary particles) from natural or man-made (anthropogenic) sources such as SO₂, NO_x, and certain organic compounds. PM is a public health concern because it can be inhaled into the upper airways and lungs, with the amount inhaled directly related to size and shape. Detailed discussions on exposure and associated adverse human health effects are presented in Sections 6 and 7, respectively.

To protect public health, the Air Resources Board (ARB or Board) previously adopted three ambient air quality standards for particulate matter: an annual-average standard for particulate matter less than 10 micrometers in diameter (PM₁₀), a PM₁₀ 24-hour-average standard, and a sulfates 24-hour-average standard. This report presents the findings and recommendations of a joint review by the ARB and the Office of Environmental Health Hazard Assessment (OEHHA) of the health and scientific literature on PM and sulfates, as well as exposure pattern data for PM and sulfates in California. Based on the results of that review, staff proposes amendments to the PM standards to ensure that they continue to adequately protect public health. The proposed amendments to the PM standards are based on recommendations from OEHHA. The scientific review suggests the need for separate annual and 24 hour standards for PM_{2.5} (particulate matter 2.5 micrometers or less in aerodynamic diameter) in addition to revising the annual standard for PM₁₀ to ensure public health protection. The review concludes that the standard for sulfates should be retained, although staff recommends a change in the monitoring method to expand monitoring capabilities in the State.

2.1 Setting California Ambient Air Quality Standards

Section 39606(a)(2) of the Health and Safety Code authorizes the ARB to adopt standards for ambient air quality "in consideration of public health, safety, and welfare, including, but not limited to, health, illness, irritation to the senses, aesthetic value, interference with visibility, and effects on the economy".

Ambient air quality standards (AAQS) represent the legal definition of clean air. They specify concentrations and durations of exposure to air pollutants that reflect the relationships between the intensity and composition of air pollution and undesirable effects (Health and Safety Code section 39014). The objective of an AAQS is to provide a basis for preventing or abating adverse health or welfare effects of air pollution (title 17, California Code of Regulations, section 70101).

Ambient air quality standards should not be interpreted as permitting, encouraging, or condoning degradation of present air quality that is superior to that stipulated in the standards. Rather, standards represent the minimum acceptable air quality. An AAQS adopted by the Board is implemented, achieved, and maintained by the adoption and implementation of control measures through rules and regulations that are separate from the standard itself. These rules and regulations are primarily, though not exclusively, emissions limitations that apply to specific source categories of pollutants established by the regional and local air pollution control and air quality management districts for stationary sources, and

by the Board for vehicular sources (see generally, Health and Safety Code sections 39002, 40000, and 40001).

California law specifies that standards be health based, although welfare effects are also considered. Health-based standards are predicated on a review of health science literature, and are to be based on the recommendation of OEHHA (Health and Safety Code section 39606(a)(2)). Standards are set to ensure that sensitive population sub-groups are protected from exposure to levels of pollutants that may cause adverse health effects. In addition, OEHHA is to assess the following considerations for infants and children in its recommendation (Health and Safety Code section 39606(b)):

- Exposure patterns among infants and children that are likely to result in disproportionately high exposure to ambient air pollutants in comparison to the general population.
- Special susceptibility of infants and children to ambient air pollutants in comparison to the general population.
- The effects on infants and children of exposure to ambient air pollutants and other substances that have a common mechanism of toxicity.
- The interaction of multiple air pollutants on infants and children, including the interaction between criteria air pollutants and toxic air contaminants. OEHHA's assessment of these considerations is to follow current principles, practices, and methods used by public health professionals.

In accordance with Health & Safety Code section 57004, the proposed amendments were peer reviewed by the Air Quality Advisory Committee (AQAC), an external scientific peer review committee, comprised of world-class scientists in the PM field and appointed by the Office of the President of the University of California. Under Health and Safety Code section 57004(d)(2), the committee prepares a written evaluation of the staff report that describes the scientific basis of the proposed ambient air quality standard. A description of the AQAC review of the proposed standards for particulate matter and sulfates follows later in this chapter. The findings of the Air Quality Advisory Committee can be found in Appendix 2.

2.2 Current California Ambient Air Quality Standards for Particulate Matter and Sulfates

2.2.1 Particulate Matter, 24-hour and Annual Averages

The current California ambient air quality standards for PM₁₀ are 50 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) for a 24-hour average and 30 $\mu\text{g}/\text{m}^3$ for an annual geometric mean. Both values are not to be exceeded. Both standards were adopted by the ARB in 1982 (ARB 1982). They were based on recommendations from the Department of Health Services (at the time, the Department of Health Services fulfilled the role in ambient air quality standard setting now assigned to the OEHHA). The standards were based on studies indicating a significant association between particulate pollution and excess mortality, increased symptoms of respiratory disease in persons with chronic bronchitis and asthma, respiratory functional impairment, and increases in respiratory illness among school children. Evidence from short-term exposure studies indicated that effects were evident at concentrations as low as 70 $\mu\text{g}/\text{m}^3$ total suspended particulate (TSP) and at 60 $\mu\text{g}/\text{m}^3$ British smoke. These concentrations are equivalent to PM₁₀ concentrations of approximately 41 to 60 $\mu\text{g}/\text{m}^3$, respectively. The Department recommended a 24-hour standard of 50 $\mu\text{g}/\text{m}^3$, which was approximately the mid-point of the range of values noted above. It was also essentially neither

a relaxation nor tightening of the previous 24-hour TSP standard when converted to an equivalent PM10 concentration.

The range of values at which long-term effects (effects on pulmonary function and increased respiratory illness) were observed was approximately 50 to 177 $\mu\text{g}/\text{m}^3$ when TSP was converted to PM10. Another chronic health effect of concern was cancer. The epidemiological studies reviewed did not establish a relationship between cancer and community air pollution, although known carcinogens were recognized in community air at that time. The Department of Health Services concluded that a particle standard should not only protect the public against pulmonary function health effects, but also to some degree serve as a surrogate measure for protection against cancer. Until more substantial evidence concerning cancer was available, the Department of Health Services believed that the long-term standard should not be a relaxation of the TSP standard. An annual geometric mean of 30 $\mu\text{g}/\text{m}^3$ (10 μm diameter) was approximately equivalent to the former annual TSP standard when corrected to PM10.

2.2.2 Sulfates, 24-hour Average

The current California ambient air quality standard for sulfates was established in 1976 at 25 $\mu\text{g}/\text{m}^3$ as a 24-hour average (ARB, 1976). The need for a sulfates standard was based on concern that a natural gas shortage would lead to greater use of fuel oil containing higher levels of sulfur, which would result in increases in ambient sulfate levels, particularly in the South Coast Air Basin. The small body of scientific literature available suggested that the projected concentrations of sulfates posed health risks, further raising concerns.

The 1976 sulfates standard was based on a critical harm value methodology so that public health could be protected, even though there was insufficient information available at the time to set a standard according to the usual threshold model. The concentration selected, 25 $\mu\text{g}/\text{m}^3$, was the midpoint between an upper bound of 33 $\mu\text{g}/\text{m}^3$ based on analysis of industrial exposures, and a lower bound of 10 $\mu\text{g}/\text{m}^3$ derived from the few epidemiological studies available. The midpoint of the range was selected as opposed to the lower bound because of uncertainties in the epidemiological data related to the adequacy of the statistical models used for the analyses, and whether potential confounding factors had been adequately controlled.

At the time the sulfates standard was promulgated, in 1976, it was known that there were differences in the sulfate concentrations reported from collocated samplers that used different methods of collection and analysis (ARB, 1976). The Board decided the use of glass filters to collect 24-hour high-volume total suspended particle samples was the most practical method to use. They were also unable to identify a suitable size-segregating collection device.

In 1977, the ARB conducted a subsequent review of the sulfate standard and monitoring methodology (ARB 1977). The review indicated that the variability of sulfate data between different types of glass-fiber filters may be due in part to a sulfate artifact which ranged from 1 to 8 $\mu\text{g}/\text{m}^3$, depending on which filter types were used. After the review in 1977, and because other methodologies based on respirable particles (e.g. PM10) were not yet developed, no changes were recommended to the monitoring methods and the level of the standard was also reaffirmed (ARB, 1977). It should be noted that the uncertainty of the exposure estimates does not impact the sulfate standard. The 1976 standard recommendation, affirmed by the 1977 review, was neither directly based on industrial health nor epidemiologic studies. Rather, since the standard was based on a critical harm level methodology, the uncertainties in the monitoring data did not enter into selection of the concentration for the standard.

2.3 Review of the California Ambient Air Quality Standards

2.3.1 Review Schedule

The Children's Environmental Health Protection Act (Senate Bill 25, Escutia, Stats. 1999, Ch. 731 section B; Health and Safety Code section 39606) required the Board, in consultation with the OEHHA, to evaluate all health-based standards by December 31, 2000, to determine whether the standards were adequately protective of the health of the public, including infants and children (Health and Safety Code section 39606(d) and (e)). Standards deemed possibly not protective were prioritized for full review. If the standard is found during the full review to be inadequate, the standard will be revised. The Act requires that the highest priority standard be reviewed and, if necessary, revised no later than December 31, 2002. Additional standards where health protection, particularly for infants and children, may not be sufficient are to be reviewed, and revised as necessary, at the rate of at least one standard per year (Health and Safety Code section 39606(d)(2)). Regulations also require the review of standards whenever substantial new information becomes adopted by the ARB pertaining to ambient air quality standards available, and at least once every five years (title 17, California Code of Regulations, section 70101).

In the report on the adequacy of the standards (ARB and OEHHA, 2000), the Board found that health effects may occur in infants, children, and other groups of the population exposed to several pollutants at or near levels corresponding to current standards. The standard with the highest priority for review is PM₁₀ including sulfates. Other standards with a high priority for review include ozone and nitrogen dioxide. Standards with a lower priority for review are carbon monoxide, sulfur dioxide, hydrogen sulfide, and lead.

After extensive review of the scientific literature, ARB and OEHHA staff developed the staff report titled "Review of the California Ambient Air Quality Standards for Particulate Matter and Sulfates, Report to the Air Quality Advisory Committee" (ARB, 2001a). This report, which was released November 30, 2001, contained the proposed PM and sulfate standards. As described in the following section, the public was afforded an opportunity to comment on and participate in the standard setting process.

2.3.2 Public Outreach

Public outreach for the standard review involved dissemination of information through various outlets to include the public in the regulatory process. In an ongoing effort to include the public in the review of the PM standards, the ARB and OEHHA integrated outreach into public meetings, workshop presentations, electronic "list serv" notification systems, and various web pages. Notification of release of the staff report, the schedule for public meetings and workshops, and invitations to submit comments on the staff report were made through the "list serv" notification system. The notices gave information on where, when and how materials relating to the PM and sulfates standards reviews was available, and how interested persons could participate in the standards review process. Public workshops on the proposed PM and sulfates standards were held in December 2001 in Oakland, Sacramento, Bakersfield, Mira Loma, El Monte, and Huntington Park. Additional public workshops on the proposed standards are scheduled for June 2002.

In addition, public meetings of the Air Quality Advisory Committee (AQAC) were held in Berkeley on January 23 and 24, 2002, and in Oakland on April 3, 2002 (described below). The public was invited to submit comments to the committee before and during these meetings.

Individuals or parties interested in signing up for an electronic e-mail "list-serv" notification on the PM standards, as well as any air quality-related issue, may self-enroll at the following

location: www.arb.ca.gov/listserv/aaqs/aaqs.htm. Additional information on the standards review process is also available at the PM standards review schedule website at: www.arb.ca.gov/research/aaqs/std-rs/std-rs.htm.

2.3.3 Air Quality Advisory Committee Review and Public Comments

The Air Quality Advisory Committee, an external scientific peer review committee that was appointed by the President of the University of California, met January 23 and 24, 2002 to review the initial staff report and public comments, and to ensure that the scientific basis of the recommendations for the annual PM₁₀ and PM_{2.5} standards and the 24-hour PM₁₀ standard are based upon sound scientific knowledge, methods, and practices. Although the AQAC approved the scientific underpinning of the recommendations, finding that the changes proposed for the AAQS were appropriate, the AQAC also concluded that the staff report, which lacked a recommendation for a 24-hour PM_{2.5} standard, needed to be revised to incorporate such a recommendation. In response, staff from ARB and OEHHA released an update to the staff report titled "Draft Proposal to Establish a 24-hour Standard for PM_{2.5}, Report to the Air Quality Advisory Committee." This proposed recommendation and associated public comments were reviewed and approved by AQAC on April 3, 2002.

Following the April 3rd AQAC meeting, the draft report was revised to reflect comments received from AQAC and to address comments made by the public. These comments, both written and oral, have been summarized, responded to and incorporated when appropriate into this Staff Report. A summary of the comments, and ARB/OEHHA responses is provided in Appendices 2 and 3. The comments ranged in scope and detail, and included procedural issues related to the standards-setting process, editorial issues, and requests that a particular reference be included. Other concerns related to control issues, natural PM background, the statistical form of the standards, and attainment designations. Another group of questions addressed the epidemiological models used, and the interpretation and application of the scientific literature. Each comment was considered in the process of revision of the draft report, and a response to the comment has been prepared (see Appendices 2 and 3). The comments were accommodated in the revised draft report in various ways, including correction of errors, expanded discussion, clarification of explanation, consideration and inclusion of additional material, and addition of references, as described in the responses to the public comments. Comments that staff disagreed with or which addressed issues that were not part of the standards or the standard setting process were not incorporated into the report. In these cases, an explanation for not incorporating the comment is provided in the responses to comments (Appendices 2 and 3).

2.4 Recommendations

The proposed amendments to the standards are largely based on results from epidemiological studies in hundreds of cities. These studies indicate strong associations between both long- and short-term exposure to PM and a variety of adverse health effects, as described above. California Ambient Air Quality Standards have four elements (Health and Safety Code section 39014, and title 17, California Code of Regulations, Article 2, section 70200): (1) definition of the air pollutant, (2) an averaging time, (3) a pollutant concentration, and (4) a monitoring method to determine attainment of the standard. A summary of staff's proposed recommendations for amending the PM and sulfates standards is listed below.

2.4.1 Pollutant, Concentrations and Averaging Times

- PM₁₀ Annual-Average Standard – Lower the annual-average standard for PM₁₀ from 30 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) to **20 mg/m^3 , not to be exceeded**. Revise the averaging method from an annual geometric mean to an annual arithmetic mean.

This recommendation is based on the results of numerous epidemiological studies of mortality and morbidity, which have found associations between adverse health effects and PM₁₀ when the long-term (i.e., months to years) study mean concentrations are at or below the current annual average standard of 30 µg/m³. The recommendation is primarily based on the Harvard Six-Cities data (Dockery et al., 1993) and the American Cancer Society (ACS) study (Pope et al., 1995), both reanalyzed by Krewski et al. (2000). Other investigations, including the Children's Health Study (McConnell et al., 1999) and the Harvard Six-Cities Study (Dockery et al., 1989), have also reported associations between long-term PM exposures and morbidity outcomes, including bronchitis, exacerbation of asthma, and reductions in lung function. In these studies, the long-term (one- or multi-year) mean PM₁₀ concentrations ranged from about 21 to 35 µg/m³.

- PM₁₀ 24-hour-Average Standard – Retain the 24-hour-average standard for PM₁₀ at **50 mg/m³, not to be exceeded.**

Staff recommends that the 24-hr standard for PM₁₀ at 50 µg/m³, not to be exceeded, be retained. The recommendation is based on time series studies of daily mortality and morbidity.

- PM_{2.5} Annual-Average Standard – Establish a new annual-average standard for PM_{2.5} at **12 mg/m³, not to be exceeded.** Establish the new PM_{2.5} standard as an annual arithmetic mean.

This recommendation is based on a growing body of epidemiological and toxicological studies showing significant toxicity related to exposure to fine particles. The ACS and Harvard Six-Cities long-term exposure studies (Dockery et al., 1993; Pope et al., 1995; Krewski et al., 2000) reported robust associations between long-term exposure to PM_{2.5} and mortality. The mean PM_{2.5} concentrations for all the cities studied were 18 and 20 µg/m³ in the Six-Cities and the ACS studies, respectively. In the ACS study, the relative risks are similar in cities at the lowest long-term PM_{2.5} concentrations of 11 and 12.5 µg/m³. Larger increases in risk do not occur until the long-term PM_{2.5} mean equals 14.9 µg/m³. Therefore, an annual standard of 12 µg/m³ would be below the mean of the most likely effects level and would provide a margin of safety. Additional evidence comes from other epidemiological studies that examined the relationships between multiple daily exposures of PM_{2.5} and adverse health outcomes. These studies have long-term (three- to four-year) means in the range of 13 to 18 µg/m³.

- PM_{2.5} 24-hour-Average Standard – Establish a new 24-hour-average standard for PM_{2.5} at **25 mg/m³, not to be exceeded.**

This recommendation is based on studies showing associations between ambient PM_{2.5} levels and mortality and morbidity when the 98th percentile of the study PM_{2.5} concentration ranged between 28 and 55 µg/m³. The methodology used to derive the standard is based on setting the level of the standard at a concentration below the 98th percentile observed in studies consistently associated with adverse health effects. The underlying principle is to reduce not only the mean concentration (represented by the annual average), but specifically the upper tail of the distribution, described by the 98th percentile of the distributions of published studies. For this standard staff has relied primarily on studies relating fine particle concentrations with daily mortality, the most serious irreversible health impact. Ultimately, additional protection will be provided by expressing the standard in a “not to be exceeded” form.

- Sulfates 24-hour-Average Standard – Retain the 24-hour-average standard for sulfates at **25 mg/m³**.

Exposure to ambient sulfates has been associated with mortality and the same range of morbidity effects as PM10 and PM2.5, although the associations have not been as consistent as with PM10 and PM2.5. These effects have been particularly noted in areas rich in strongly acidic sulfates, such as the eastern United States and Canada. In contrast, controlled exposure studies involving high levels (up to 1,000 µg/m³) of strongly acidic sulfates have demonstrated little, if any, effect on volunteer subjects, (e.g., Aris et al., 1991). Furthermore, in California, acidic sulfates (principally sulfuric acid and ammonium sulfate) constitute a small fraction of the PM mass relative to the areas in which sulfates have been found to be associated with adverse health impacts. Also, sulfate concentrations in California have been far lower during the past few years than the level of the existing standard. In view of the mixed evidence on sulfates and health in California, the low likelihood of health risks in relation to ongoing reduction trends in sulfate emissions and ambient levels, staff recommends that the current standard be retained until the next review of the PM standard, if not earlier. However, staff is making recommendations to change the monitoring method for sulfates.

2.4.2 Monitoring Methods, Samplers, and Instruments

- PM10 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM10 as the method for California. This proposal allows for alignment of the State method for PM monitoring with all federal high-volume and low-volume samplers, and thereby will eliminate confusion of having two methods (State and federal) for the same parameter.
- PM2.5 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM2.5 as the method for California. This proposal allows for alignment of the State method for PM monitoring with all federal high-volume and low-volume samplers, and thereby will eliminate confusion of having two methods (State and federal) for the same parameter.
- Continuous PM Samplers – Adopt those continuous PM samplers which have been found to be suitable for determining compliance with the state PM10 and PM2.5 AAQS, and designate them as California approved samplers (CAS). This proposal allows for the use of continuous PM sampler technology. Continuous monitoring for either PM10 or PM2.5 has many advantages over traditional filter based sampling techniques. A continuous method is an in-situ, automatic measurement method of suspended particle mass with varied averaging time (minutes to hours) that provides an instantaneous result. Their 24 hour/day, 7day/week sampling schedule will further our understanding of PM emission patterns and exposure, and can be used to enhance public health research into short-term peak exposure. They can provide more data for model validation, to aid in identifying air pollution source(s), and to reflect dispersion patterns. Official approval of continuous instruments/methods will promote further development of continuous samplers and potentially reduce the cost of the air monitoring network.
- Sulfates Monitoring Method – Revise the sulfates monitoring method by deleting the current total suspended particle (TSP) sulfates method, ARB method MLD 033, and replacing it with the existing ARB method for PM10 sulfates, MLD 007. This proposal allows the ARB to use its existing PM10 network to greatly expand its monitoring network capabilities for sulfates. By doing so, the ARB greatly expands its ability to better understand sulfate air quality in the state. This method changes allows for the minimization of any artifact-forming potential through the use of alkalinity-controlled filters.

The staff also proposes to maintain the regulatory language that permits other samplers deemed to give equivalent results to be approved by the ARB at a subsequent time.

This action is intended to eliminate the ambiguity that currently exists between the acceptable use of samplers for State and federal programs and to respond to the need for continuous samplers to meet a variety of needs. It will also greatly expand the database of information that will be available to decision-makers. Adopting the specific samplers into the regulation will make information about appropriate monitoring methods and samplers accessible, standard and enforceable.

2.4.3 Other Recommendations:

Further, in light of the adverse health effects observed at current ambient concentrations and the lack of a demonstrated threshold, staff makes the following recommendations for Board approval:

- Staff recommends that the standards for PM and sulfates be revisited within five years, to evaluate new evidence regarding the health effects associated with, particle size, chemistry, concentration, and averaging time.
- Staff also recommends that further scientific information be gathered and research be conducted into the health effects of short-term exposures of PM, especially effects from less than 24-hour exposures. This information should be considered when staff revisits the PM standards to determine if AAQS with averaging times of less than 24 hours would be appropriate.

2.5 Health Benefits

Although a precise measure of risk is difficult to determine, staff performed a quantitative risk assessment based on attainment of the recommended annual average standards of $12 \mu\text{g}/\text{m}^3$ and $20 \mu\text{g}/\text{m}^3$ for PM_{2.5} and PM₁₀, respectively. The results of this assessment are summarized in Tables 9.4 and 9.6, respectively. The assessment applied concentration – response functions from available epidemiologic studies to California by using California-specific PM, mortality and morbidity data (see Chapter 9 for a full discussion).

The quantitative risk assessment estimated that attainment of the proposed annual PM₁₀ standards would result in a reduction of approximately 6,500 cases of premature mortality per year (3,200 – 9,800, 95 percent confidence interval (CI)). This estimate is based on the assumption that mortality is primarily associated with exposure to PM_{2.5} rather than with the coarse PM fraction. Estimated mean annual reductions in hospitalizations related to attaining the proposed PM₁₀ standards are 1,200 cases for Chronic Obstructive Pulmonary Disease (COPD) (66 – 2,300, CI), 1,700 cases for pneumonia (760 – 2,600, CI), 3,100 cases for cardiovascular causes (2,500 – 3,600, CI), and 960 cases for asthma (400 – 1,500, CI). Among children ages 7 to 14, attainment of the PM₁₀ standard is estimated to result in about 390,000 fewer days of lower respiratory symptoms per year (160,000 – 570,000, CI). Of these, approximately half of the days of lower respiratory symptoms may be associated with attainment of the proposed PM_{2.5} standard.

Use of the concentration-response functions from short-term exposure studies, which only capture part of the total effects on mortality, generates an estimate of 1,900 fewer premature deaths per year (2,200 – 3,100, CI) based on attainment of a standard of $12 \mu\text{g}/\text{m}^3$ for PM_{2.5}. Attainment of the recommended PM_{2.5} standards is estimated to result in up to about 11,000 fewer cases of chronic bronchitis among people over age 27. Estimated reductions in hospitalizations are 600 (33 – 1,200, CI) for COPD, 860 (390 – 1,300, CI) for pneumonia, and 470 (86 – 850, CI) for asthma.

In summary, the epidemiologic evidence and risk assessment support the likelihood of significant reductions in mortality and morbidity effects with attainment of the recommended annual and 24-hour PM standards.

2.6 Environmental and Economic Impacts

The proposed ambient air quality standards will in and of themselves have no environmental or economic impacts. Standards simply define clean air. Once adopted, local air pollution control or air quality management districts are responsible for the adoption of rules and regulations to control emissions from stationary sources to assure their achievement and maintenance. The Board is responsible for adoption of emission standards for mobile sources. A number of different control measures are possible, and each will have its own environmental and economic impact. These impacts must be evaluated when any control measure is proposed. Environmental or economic impacts associated with the imposition of future control measures will be considered when specific measures are proposed.

2.7 Environmental Justice

State law defines environmental justice as the fair treatment of people of all races, cultures, and incomes with respect to the development, adoption, implementation, and enforcement of environmental laws, regulations, and policies (Senate Bill 115, Solis; Stats 1999, Ch. 690; Government Code § 65040.12(c)). The Board recently established a framework for incorporating environmental justice into the ARB's programs consistent with the directives of State law (ARB, 2001b). The policies developed apply to all communities in California, but recognize that environmental justice issues have been raised more in the context of low-income and minority communities, which sometimes experience higher exposures to some pollutants as a result of the cumulative impacts of air pollution from multiple mobile, commercial, industrial, areawide, other sources. Because ambient air quality standards simply define clean air, all of California's communities will benefit from the proposed health-based standards, as progress is made to attain the standards. Over the past twenty years, the ARB, local air districts, and federal air pollution control programs have made substantial progress towards improving the air quality in California. However, some communities continue to experience higher exposures than others as a result of the cumulative impacts of air pollution from multiple mobile and stationary sources and thus may suffer a disproportionate level of adverse health effects (see section 7.7.2 of this report). Since the same ambient air quality standards apply to all regions of the State, these communities will benefit by a wider margin and receive a greater degree of health improvement from the revised standards than less affected communities, as progress is made to attain the standards. Moreover, just as all communities would benefit from new, stricter standards, alternatives to the proposed recommendations, such as recommending no change to the PM10 standards, or not proposing standards for PM2.5, would adversely affect all communities. Once ambient air quality standards are adopted, the ARB and the local air districts will propose emission standards and other control measures to reduce emissions from various sources of PM. The environmental justice aspects of each proposed control measure will be evaluated in a public forum at this time.

As additional relevant scientific evidence becomes available, the PM standards will be reviewed again to make certain that the health of the public is protected with an adequate margin of safety. To ensure that everyone has an opportunity to stay informed and participate fully in the development of the PM standards, ARB and OEHHA staff have held (and will continue to conduct) workshops in a number of communities across the State and have distributed information by mail and through the internet, as described in section 2.3.2 in this chapter.

2.8 Research Needs

Available evidence indicates that significant adverse health effects may occur among both children and adults when ambient PM concentrations exceed current State standards or become elevated above those proposed in this report. The foundation for revising California PM standards is based primarily on numerous epidemiological studies conducted throughout the world which yielded remarkably consistent results, despite local differences in PM sources and types of co-pollutants. Although this consistency was sufficient to guide staff in proposing new, more stringent standards, several data gaps were identified during the preparation of this document. Moreover, many questions about the mechanisms by which particles adversely affect health remained unanswered. Results from research designed to address these questions would refine knowledge and reduce uncertainties in various aspects of the PM literature and should be ongoing at the State, federal, and international level. Specific areas of research that would assist the Board with subsequent revisions of the standards include:

- health impacts of short-term exposures to PM and sulfates
- health impacts of long-term exposures to PM and sulfates
- health impacts of ultrafine PM
- relationship between community and individual exposures to PM
- factors contributing to sensitivity in individuals and groups
- health effects of PM related to physical properties and/or chemical constituents
- physiological mechanisms of PM and sulfates effects
- how PM interacts with other air pollutants to harm health
- health impacts of PM at low concentrations
- role of PM in causing new disease
- impacts of PM and sulfates on children including neonates
- environmental justice and its relationship to PM health effects

Development and application of improved study methodologies will require research in several areas, including improvements in air monitoring and exposure assessment methodologies. As ambient air monitoring for PM expands to include time-resolved data reporting, it would be useful to incorporate this new data into community health investigations. Further, studies are needed to determine how community and indoor levels of PM relate to actual human exposures.

Development and application of improved statistical methodologies, particularly for epidemiological studies, are needed to improve the analytical tools available to health investigators as they evaluate the health impacts of daily or multi-day observations collected over prolonged study periods. Improved identification of and control for potentially confounding factors in epidemiological studies are critically needed.

Review of the health effects literature undertaken for this document presented staff with a major challenge in determining safe levels of PM for short- or longer-term exposure. The epidemiological studies reviewed reported adverse effects even at the lowest levels of ambient PM present. The statistical methods available, as well as the sources and types of air quality and health data available for use in these studies, impose substantial limitations to identifying truly safe levels of these pollutants.

Crucial to answering the questions outlined above is an improved physical characterization (particle shape and aerodynamic diameter) and chemical speciation of PM and sulfate samples which will allow identification of the toxic components of the ambient mixture. Physical and chemical characterization data for sulfates and PM will likely become increasingly important in designing hypothesis-driven animal and controlled human exposure studies. Comparisons of the toxicity of different sized particles of the same chemical species are also needed (ultrafine vs. fine vs. coarse).

More information is needed to identify the physiological, genetic, medical and other factors that contribute to susceptibility to PM and sulfates health effects. Age appears to be one factor in susceptibility to adverse effects resulting from exposure to PM and sulfates. Studies on children and neonates are critically needed. Subjects at risk of PM and sulfates-induced health effects need to be incorporated into research on the health impacts of these pollutants. Hypothesis-driven animal toxicological experimental studies, as well as human clinical studies, offer especially valuable opportunities to investigate issues that are related to biological sensitivity. This information will be very useful in optimizing research protocols and refining subject selection criteria so that future research targets the most significant endpoints and most at-risk subpopulations.

2.9 References

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3. Physics and Chemistry of Particles

3.1 Introduction

Airborne particulate matter (PM) is not a single pollutant, but rather a mixture of many subclasses of pollutants with each subclass potentially containing many different chemical species. Particles may be either directly emitted into the atmosphere (primary particles) or formed there by chemical reactions of gases (secondary particles) from natural and anthropogenic sources such as SO₂, NO_x, and certain organic compounds. The relative importance of primary and secondary particles generally depends on the geographical location with precursor emissions, atmospheric chemistry, and meteorology all playing a role. Examples of PM include combustion-generated particles, such as those from automobiles or wood burning; photochemically-produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from resuspended dust.

In California, the proximity of a location to a variety of sources, in addition to the diurnal and seasonal variations in meteorological conditions, causes the size, composition, and concentration of particulate matter to vary in space and time. PM pollution is the most serious and complex air pollution problem facing both scientific communities and regulatory agencies, and reducing particulate pollution is one of the most difficult environmental challenges facing California because of the great diversity of sources and chemical species involved.

Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds of organic compounds. The particle formation process includes nucleation of particles from low-vapor-pressure gases emitted from sources or formed in the atmosphere by chemical reactions; condensation of low vapor pressure gases on existing particles; and coagulation of particles. Thus, any given particle may contain PM from many sources. The composition and behavior of airborne particles are fundamentally linked with those of the surrounding gas. An aerosol may be defined as a suspension of solid or liquid particles in air. The term aerosol includes both the particles and all vapor or gas-phase components of air. However, while this is the rigorous definition of aerosols, the term is often used in the atmospheric chemistry literature to denote just the particles.

A complete description of the atmospheric aerosol would include an accounting of the chemical composition, optical properties, morphology, and size of each particle, and the relative abundance of each particle type as a function of particle size. However, most often the physical and chemical characteristics of particles are measured separately. Size distributions by particle number, from which surface area and volume distributions are calculated, often are determined by physical means, such as electrical mobility or light scattering of suspended particles. Chemical composition usually is determined by analysis of collected samples. The mass and average chemical composition of particles, segregated according to aerodynamic diameter by cyclones or impactors, can also be determined. This chapter provides general information on the physics and chemistry of atmospheric particles that may be useful in reading subsequent sections. For a more extensive review of the physics and chemistry of PM, the reader is referred to Finlayson-Pitts and Pitts (1999), Warneck (1999), and Seinfeld and Pandis (1998).

3.2 Physical Properties

3.2.1 Definition

Particulate matter can exist in the liquid or solid phase and its size can span several orders of magnitude, from a molecular cluster of 0.002 μm in aerodynamic diameter to coarse particles on the order of 100 μm . The lower end of the size range is not sharply defined because there is no accepted criterion at which a cluster of molecules becomes a particle. The upper end corresponds to the size of fine drizzle or very fine sand; these particles are so large that they quickly fall out of the atmosphere and hence do not remain suspended for significant periods of time. The most important particles with respect to atmospheric chemistry and physics are generally in the 0.002 to 10 μm range.

Atmospheric particles are usually referred to as having a radius or diameter, implying they are spherical. However, many particles in the atmosphere have quite irregular shapes for which geometrical radii and diameters are not meaningful. Hence, the size of such irregularly shaped particles is expressed in terms of equivalent diameter that depends on a physical, rather than a geometrical, property. One of the most commonly used term is the aerodynamic diameter, which is defined as the diameter of a sphere of unit density (1 g/cm^3) that has the same terminal falling speed in air as the particle under consideration. The aerodynamic diameter of particles is important because it determines the residence time in the air, and it reflects the various regions of the respiratory system in which particles of different sizes become deposited.

3.2.2 Particle Size Distributions

The atmosphere, whether in urban or remote areas, contains significant concentrations of aerosol particles, sometimes as high as 10^7 to 10^8 particles/ cm^3 . The aerodynamic diameter of these particles span over four orders of magnitude, from a few nanometers to around 100 μm . Because the size of the atmospheric particles plays such an important role in both their chemistry and physics in the atmosphere, as well as their effects, it is important to know the distribution of particle sizes.

Urban aerosols are mixtures of both primary and secondary particles. The number distribution is dominated by particles smaller than 0.1 μm , while most of the surface area is in the 0.1 to 0.5 μm size range. The aerosol size distribution is quite variable in an urban area. Extremely high concentrations of very fine particles (less than 0.1 μm) are found close to sources such as highways, but their concentrations decrease rapidly with distance from their source. Figure 3.1 (Seinfeld and Pandis, 1998) describes the number of particles as a function of their diameter for rural, urban-influenced rural, urban, and freeway-influenced urban aerosols. There is roughly an order of magnitude more particles close to the freeway compared to the average urban concentration.

An important feature of atmospheric aerosol size distribution is the tri-modal character: (1) nuclei, (2) accumulation, and (3) coarse. As the technology for measuring small particles has improved, ultrafine particles (with diameters less than .01 μm , i.e., <100 nm) have also been increasingly studied. Particles in the atmosphere are now frequently treated in terms of the four modes summarized in Figure 3.2 (Finlayson-Pitts and Pitts 1999). This figure shows the mechanisms such as condensation and coagulation that transfer aerosol mass from one size range to another, and also shows the major sources and removal processes for each one. The number distribution is dominated by particles smaller than 0.1 μm , while most of the surface area is in the 0.1 to 0.5 μm size range. The mass distribution has usually two distinct modes, one in the submicrometer regime (referred to as accumulation mode) and the other in the coarse particle regime.

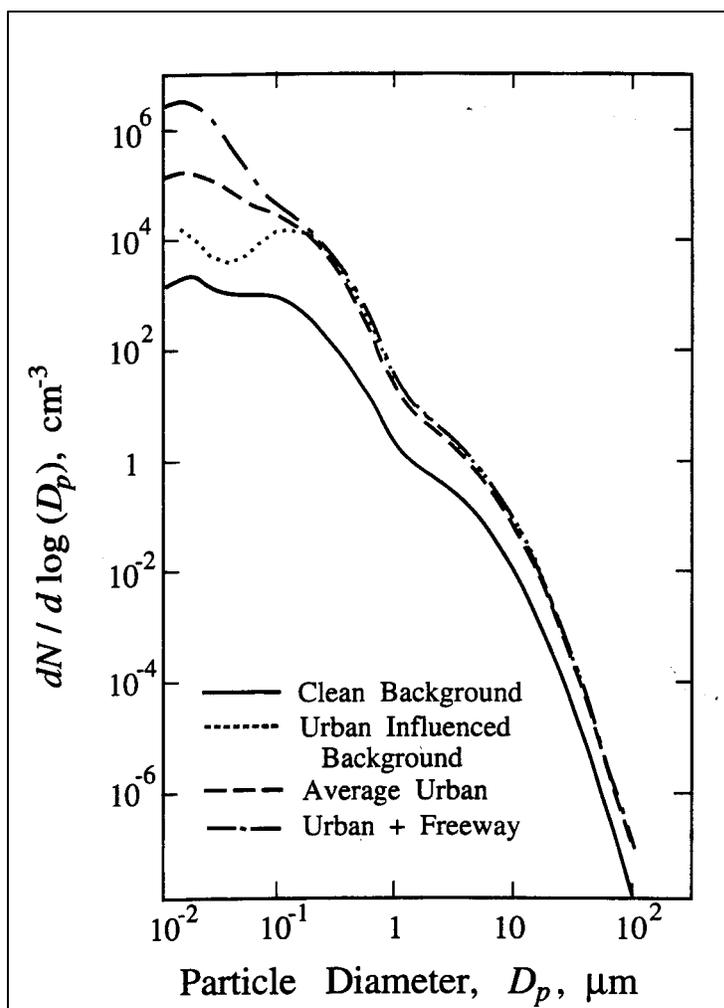


Figure 3.1. Aerosol number distribution for the average urban, for urban influenced by background, and for background (adapted from Seinfeld and Pandis, 1998). Number concentrations are shown on logarithmic scale to display the wide range by site and size, where N is the number concentration and D_p is the mean diameter.

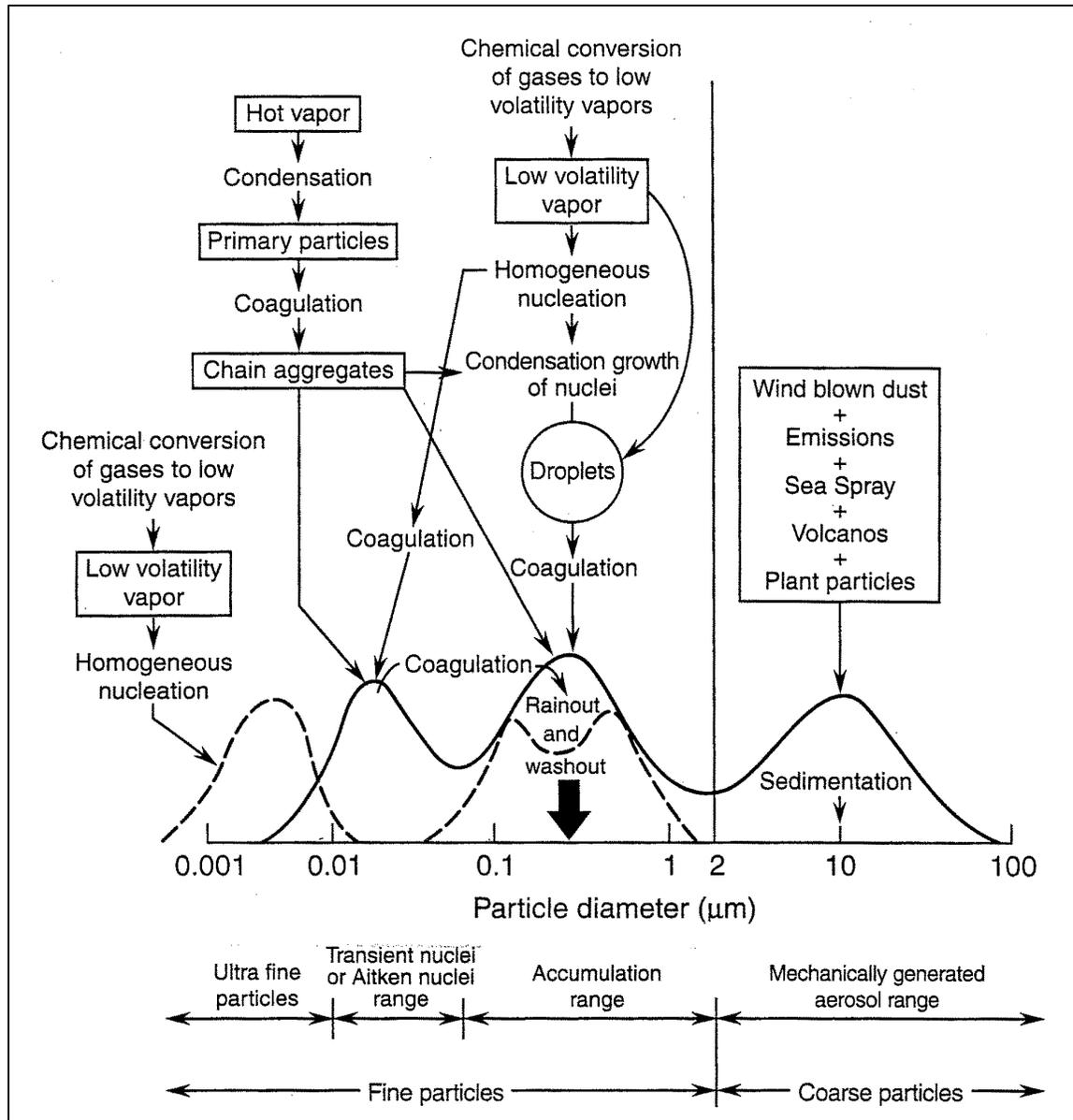


Figure 3.2. Schematic of an atmospheric aerosol size distribution showing four modes (adapted from Finlayson-Pitts and Pitts, 1999).

The nuclei mode, corresponding to particles below about 0.1 μm, may not be noticeable in volume or mass distributions. Nuclei mode particles are the result of nucleation of gas phase species to form condensed phase species with very low equilibrium vapor pressure. As an example, metallic ultrafine particles may be formed from metals in lubricating oil or fuel additives that are vaporized during combustion of gasoline or diesel fuels (Kittelson 1998). Recent smog chamber studies and indoor experiments show that atmospheric oxidation of certain organic compounds found in the atmosphere can produce highly oxidized organic compounds with an equilibrium vapor pressure sufficiently low to result in nucleation (Kamens et al. 1999; Weschler and Shields 1999). Some scientists argue that ultrafine particles pose potential health problems and that some health effects may be more closely associated with particle number or particle surface area than particle mass. Because nuclei-mode particles

contribute the major portion of particle number and a significant portion of particle surface area, further attention to nuclei-mode particles is justified.

The size range from 0.1 to 2.5 μm , is the accumulation mode. Fine particles include both the accumulation and the nuclei modes. Nuclei-mode particles may be removed by dry deposition or by growth into the accumulation mode. This growth takes place as other low vapor pressure material condenses on the particles or as nuclei-mode particles coagulate with themselves or with accumulation mode particles. The coagulation rates for particles in the nuclei range with the larger particles in the accumulation range are usually larger than for self-coagulation of the small particles. This occurs because of the high mobility of the small particles combined with the larger target area of the bigger particles.

Particles in accumulation mode tend to represent only a small fraction of the total particle number, but a significant portion of the aerosol mass. Because they are too small to settle out rapidly, they have much longer lifetimes than coarse particles. This long lifetime, combined with their effects on visibility, cloud formation, and health, makes them of great importance in atmospheric physics and chemistry. Because of the nature of their sources, particles in the accumulation mode generally contain organic compounds as well as soluble inorganic compounds such as ammonium nitrate and ammonium sulfate.

The third mode, containing particles larger than 2.5 μm , is known as the coarse particle mode. Coarse particles are usually produced by mechanical processes such as grinding, wind, or erosion. As a result, they are relatively large and hence settle out of the atmosphere by sedimentation in a reasonably short time, except on windy days, where fallout is balanced by reentrainment. Chemically, their composition reflects their source, and hence it is predominantly inorganic such as sand and sea salt, although significant amounts of organic compounds have also been reported associated with them (Boon et al. 1998). Because the sources and sinks are different from those of the smaller modes, the occurrence of particles in this mode tends to be only weakly associated with the fine particle mode. The majority of biological particles, such as spores and pollens, tend to be in the coarse particle range.

While particles in the coarse particle mode are generally sufficiently large that they are removed relatively rapidly by gravitational settling, there are large-scale mechanisms of transport that can carry them long distances during some episodes. The results of several studies indicate the transport of dust in larger particles from the Sahara Desert to the northwestern Mediterranean, Atlantic Ocean, and the United States (Gatz and Prospero 1996). Similarly, dust transported from Asia has been reported on a regular basis over the Pacific (Zhang et al. 1997). Asian dust has been observed during the spring at the Mauna Loa Observatory in Hawaii (Zieman et al. 1995; Holmes et al. 1997). At this location, the elemental signature (in terms of silica to iron or titanium to iron ratios) in particles in the size range 0.5 to 3.5 μm is very similar to those measured during dust storms in Beijing, consistent with long-range transport of these particles.

The literature includes references to fine, coarse, suspended, respirable, inhalable, thoracic and other adjectives to indicate a size segregation of PM. Uniform criteria are not always employed in the application of these designations. Particles less than 2.5 μm in aerodynamic diameter are generally referred to as "fine" and those greater than 2.5 μm diameters as "coarse". The selection of PM₁₀ as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region. Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks (e.g., Seinfeld and Pandis 1998, Finlayson-Pitts and Pitts, 1999, Friedlander, 2000).

3.2.3 Particle Formation and Growth

The formation of particles in various size ranges in the atmosphere may occur by a number of mechanisms. These include reaction of gases to form low-vapor-pressure products followed by nucleation to form new particles or condensation on preexisting particles, along with some coagulation between particles. An important parameter in particle nucleation and in particle growth by condensation is the saturation ratio, which is defined as the ratio of the partial pressure of a species to its equilibrium vapor pressure above a flat surface. For either condensation or nucleation to occur, the species vapor pressure must exceed its equilibrium vapor pressure.

Nucleation can occur both in the absence or presence of foreign material (pre-existing particles, such as primary particles emitted by sources). Homogeneous nucleation is the nucleation of vapor on embryos comprised of vapor molecules only, in the absence of foreign substances. Heterogeneous nucleation is the nucleation on a foreign substance or surface, such as an ion or a solid particle. In addition, nucleation processes can be homomolecular (involving a single species) or heteromolecular (involving two or more species). Once the initial nucleation step has occurred, the nuclei of the new phase tend to grow rapidly. Nucleation theory attempts to describe the rate at which the first step in the phase transformation process occurs – the rate at which the initial very small nuclei appear. For a review of nucleation in the atmosphere, the reader is referred to literature on nucleation and atmospheric aerosols (Fukura and Wagner 1992; Seinfeld and Pandis 1998).

Condensation occurs when the vapor concentration of a species exceeds its equilibrium concentration (expressed as its equilibrium vapor pressure). Condensable species can either condense on the surface of existing particles or can form new particles. The relative importance of nucleation versus condensation depends on the rate of formation of the condensable species and on the surface or cross-sectional area of existing particles (McMurry and Friedlander 1979). In ambient urban environments, the available particle surface area is sufficient to rapidly scavenge the newly formed condensable species. Formation of new particles (nuclei mode) is usually not important except near sources of condensable species. The results of several studies report observations of the nuclei mode in traffic (Hildemann et al. 1991; Abdul-Khalek et al. 1998). New particle formation also can be observed in cleaner, remote regions. Bursts of new particle formation in the atmosphere under clean conditions usually occur when aerosol surface area concentrations are low (Covert et al. 1992). High concentrations of nuclei mode particles have been observed in regions with low particle mass concentrations, indicating that new particle formation is inversely related to the available aerosol surface area (Clarke 1992). For more detailed discussions of the quantitative treatment of condensation processes in the atmosphere, the reader is referred to articles by Pandis et al. 1995, and Kerminen and Wexler 1995.

Coagulation refers to the formation of a single particle via collision and adhesion of two smaller particles. Small particles undergo relatively rapid Brownian motion (i.e., constant random movement along an irregular path caused by the bombardment of surrounding air molecules), that leads to sufficient particle-particle collisions to cause such coagulation. Coagulation of smaller particles with much larger ones is similar to condensation of a gas on the larger particles and acts primarily to reduce the number of small particles, adding relatively little to the mass or size of the larger particles. Hence the larger mode will not show significant growth by such a mechanism. The rate of such processes depends on the diameter of the large particle, how rapidly the smaller particle is carried to it (i.e., the diffusion of the smaller particle), and the concentrations of the particles. Self-coagulation, where the particles are approximately the same size, can, however, lead to changes in the size

distribution of the aerosol particles. The rate of this process is a strong function of the particle concentration as well as the particle size (Pandis et al. 1995).

3.2.4 Removal Processes

Once particles are in the atmosphere, their size, number, and chemical composition are changed by several mechanisms until they are ultimately removed by natural processes. Some of the physical and chemical processes that affect the “aging” of atmospheric particles are more effective in one regime of particle size than another. The lifetimes of particles vary with size. Coarse particles can settle rapidly from the atmosphere within hours, and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized coarse-mode particles may have longer lives and travel distances. Nuclei mode particles rapidly grow into the accumulation mode. However, the accumulation mode does not grow into the coarse mode. Accumulation-mode fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. They can be transported thousands of kilometers and remain in the atmosphere for a number of days.

Atmospheric species removal processes can be grouped into two categories: dry deposition and wet deposition. Dry deposition denotes the direct transfer of species, both gaseous and particulate, to surfaces and proceeds without the aid of precipitation. Wet deposition, on the other hand, encompasses all processes by which airborne species are transferred to surfaces in aqueous form (i.e., rain, snow, or fog). Wet deposition include processes such as dissolution of atmospheric gases in airborne droplets (cloud droplets, rain, or fog), removal of atmospheric particles when they serve as nuclei for the condensation of atmospheric water to form a cloud or fog droplet, and removal of atmospheric particles when the particle collides with a droplet both within and below clouds.

Dry deposition rates are expressed in terms of a deposition velocity that varies with particle size, reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter. The wide ranges of reported dry deposition velocities for any given pollutant reflect a combination of experimental uncertainties as well as real differences due to meteorology, nature of the surface, diurnal variation, etc. The overall uncertainty in the appropriate value of the deposition velocity to use under a given set of circumstance can thus be quite large. A discussion of these issues can be found in articles by Gao and Wesley (1995) and Wesley and Hicks (1999).

Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Fine particles, especially particles with a hygroscopic component, grow as the relative humidity increases, serve as cloud condensation nuclei, and grow into cloud droplets. If the cloud droplets grow large enough to form rain, the particles are removed in the rain. Falling rain drops impact coarse particles and remove them. Ultrafine or nuclei mode particles are small enough to diffuse to the falling drop, be captured, and removed in rain.

3.2.5 Meteorology and Particles

Meteorological conditions are, generally, the biggest factor influencing the temporal variation in pollutant concentrations. Weather plays a major role in what primary particles are emitted, and to what degree. “Background” aerosol (e.g., sea spray, volcanic dust) concentrations are affected by wind transporting material or by “stirring up” local natural aerosols. Rain suppresses dust from both natural and manmade sources. Seasonal and daily variations in weather influence the production of biogenic pollutants (gases, pollen, etc.). Primary emissions from human activities will be similarly influenced, both directly, as with wind and rain on dust, and indirectly through changes in human activity (e.g., residential wood burning increases in colder weather, and agricultural activity peaks during planting and harvesting).

Secondary particle formation is influenced by a combination of precursor pollutant concentrations and weather conditions. Conversion of SO_x to sulfate aerosols is accelerated by the presence of oxidants and OH radicals in the air (as during ozone episodes) and is accelerated even more under humid conditions when the conversion can occur inside water droplets. NO_x conversion to nitrate is even more sensitive to weather conditions, as formation rates must compete with dissociation back to gases, so that nitrate is generally a cool-wet (e.g., winter) weather phenomenon. Figure 3.3 represents a flowchart of actual linkages between particulate matter air pollution and controlling factors of weather and source activity. Due to the influences of these links, the same emissions can result in high PM concentrations on one occasion, and low concentrations on another. The purpose of detailed analysis is to refine our understanding of how the linkages shown in this chart act on pollutants so that we can accurately determine what portions of the measured concentrations are due to each of the various sources.

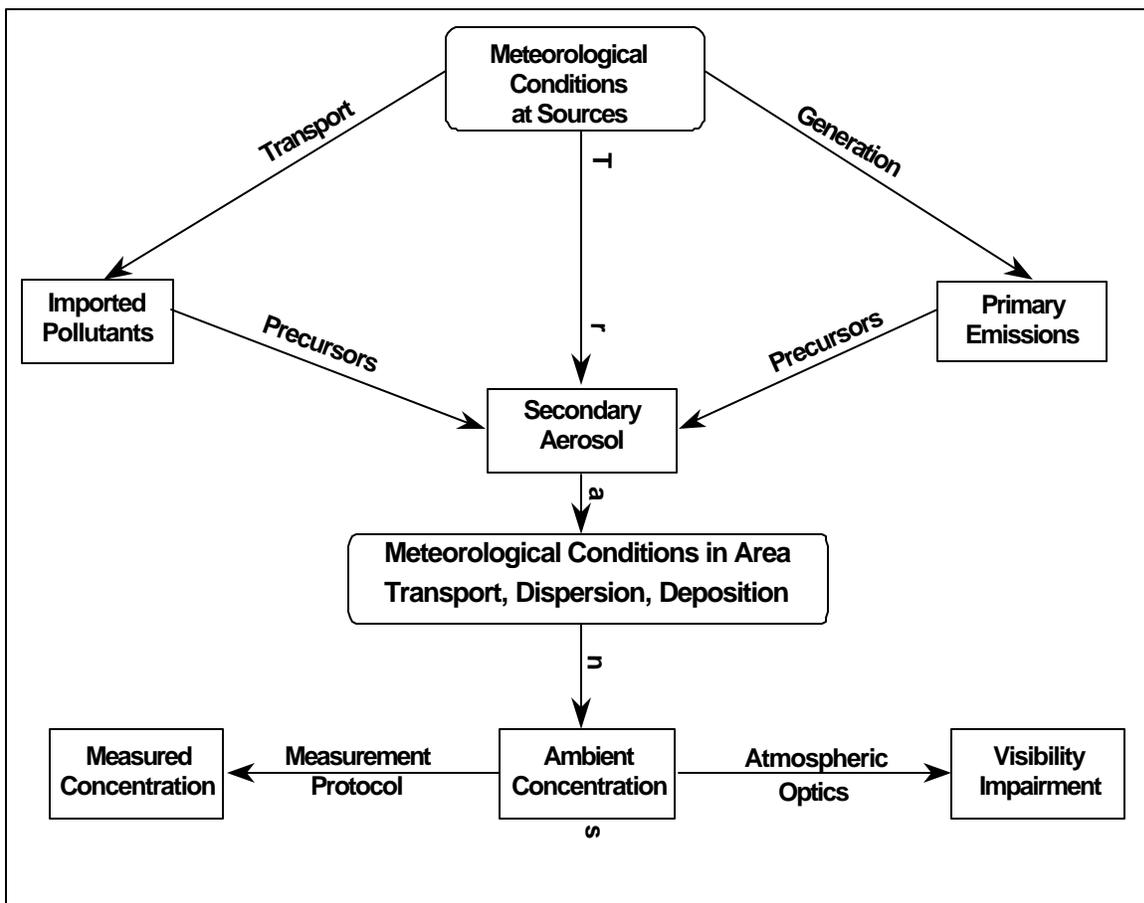


Figure 3.3. Flowchart of actual linkages between particulate matter air pollution and controlling factors of weather and source activity

Pollutant concentrations at measurement sites vary not only due to the various influences on local pollutants, but also due to the transport of material from upwind areas. In addition to variable local influences, occasional transport of PM can significantly influence concentrations, particularly at sites downwind of major urban centers. Different conditions not only cause different concentrations, they can also alter the mix of responsible sources; in other words, the sources identified for appropriate control can vary not only temporally but

also among monitoring sites. For example, in the San Joaquin Valley, PM₁₀ and PM_{2.5} episodes in the winter-time are often accompanied by light and variable winds, thus limiting horizontal transport. As a result, pollutants tend to accumulate in local areas; however, a uniform gradient of secondary aerosols was seen valley wide (nitrates in particular). Results of several data analyses, as to the cause of this smooth gradient in secondary particulate concentrations, revealed a shallow mixing layer near the surface with nearly calm winds, but winds of 4 to 8 m/s were observed about 100 meters above the surface. Thus, pollutants trapped near the surface when mixed into this fast moving upper layer, were transported large distances and reacted with sources such as ammonia to form the secondary aerosols.

3.2.6 Fine Mass and Aerosol Light Scattering Relationship

The aerosol parameter to be monitored must be a suitable causal measure of health effects, as well as effects on visibility, climate, etc. It can be presumed that, for health effects, penetration into the lung and toxicity of the aerosol chemical species are relevant. On the other hand, visibility effects are determined by the light extinction under atmospheric conditions. The direct aerosol effect on climate is due to scattering and absorption of sunlight while the indirect aerosol effect on climate is due to the aerosol interaction with cloud processes. Because each of the aerosol effects is associated with a specific size and/or chemical composition, it is not likely that a single monitoring variable would be equally suitable as a surrogate for all of the effects. Thus, a choice in the measurement technique requires a value judgment as to which effect (health, visibility, or climate) matches most closely with exposure.

Depending on their size and composition, particles can scatter or absorb light. Coefficient of haze (COH) and nephelometer (B_{scat} , or scattering coefficient) measurements provide an indication of the relative contributions of light absorption and light scattering. The COH is a direct measure of the light-absorbing ability of the particles. Light absorption is primarily due to elemental carbon from combustion. The nephelometer roughly measures all scattering by fine particles. The characteristics of scattering light are extremely sensitive to the size of the scattering particles. Light scattering by the large particles (>10 μm diameter) is generally not significant. As particle sizes approach the range of light wavelengths (0.1-1 μm) they become significantly more efficient in light scattering. COH units are defined as the quantity of particulate matter that produces an optical density of 0.01 on a paper filter tape. A photometer detects the change in the quantity of light transmitted through the spot as the particulate matter collects on the paper filter tape and produces an electrical signal proportional to the optical density. A COH of less than 1.0 represents relatively clean air while a COH of greater than 2.0 represents air with a relatively high concentration of primary combustion-generated particles and/or secondary aerosols formed in the atmosphere.

As was noted earlier in this chapter, the aerosol population is a mixture of different particle sizes, and each size class is composed of an internal and/or external mixture of chemically diverse particles. Hence, it is not possible to express the aerosol concentration as a single number, as is the case for gaseous pollutants. On the other hand, practical considerations dictate that the number of aerosol parameters to be monitored has to be limited. Routine monitoring of aerosol chemical composition in many size classes does not appear to be practical for regulatory purposes. Rather, the aerosol size - chemical composition distribution function needs to be monitored using integral measures such as fine mass concentration (PM_{2.5}) and/or total (or size segregated) light scattering coefficient. PM_{2.5} is the integral of the aerosol mass - size distribution up to about 2.5 μm . The total light scattering is also an integral of the aerosol mass size distribution but also weighted by the size-dependent scattering efficiency factor.

Numerous field investigations have been performed on the correlation between scattering coefficient and particulate volume and mass concentration. Most of the earlier studies (1970s) were based on “high volume” (non-particle size selective sampler) total suspended particle (TSP) mass concentration measurements whose uncertainties and ill-defined upper particle size limits resulted in questionable data. As attention focussed on fine particle monitoring during the 1980s, similar comparison field tests restricted to smaller particles were conducted. It is well established that the fine particle mass concentration measured by size segregated filter sampling has a strong statistical correlation with total aerosol light scattering. The main reason for this relationship is that both the fine particle mass as well as the light scattering efficiency factor have a peak in the size range 0.3 - 0.6 μm . Exception to this relationship occurs when the characteristic aerosol size is either smaller (e.g., primary automobile exhaust) or larger (wind blown dust) than the above size range.

Husar and Falke (1996) conducted a comparative study of the aerosol light scattering and fine particle mass data. A comparison of the light scattering coefficient and PM_{2.5} was performed for fourteen different sites in the western U.S. (including six sites in California). The scatter charts of daily PM_{2.5} and scattering data included the slope (m^2/g) of the relationship as well as the correlation, R^2 . The data for the fourteen sites indicate a good correlation, with half of the sites exhibiting R^2 above 0.8. A notable exception is Azusa, CA, ($R^2 = 0.61$). The slope, i.e., the light scattering PM_{2.5} ratio, ranges between 4.1 and 11.9 with an average of 7.4 m^2/g .

Groblicki et al. (1981) presented the light scattering coefficient observed in studies in Denver, Colorado as a function of the observed mass in the fine and coarse particle ranges, respectively. It has been seen that a good linear relationship exists between scattering coefficient and the fine mass, but not between scattering coefficient and coarse particle mass. A good linear relationship has been observed in a number of areas ranging from pristine to urban sites with scattering coefficient to fine particle mass concentration ratio of approximately 3 (Waggoner et al. 1981; Conner et al. 1991).

Light scattering dominates light absorption except where there are light absorbing particles or gases present. Graphitic or elemental carbon (commonly known as soot) is very efficient at absorbing light. Particle light absorption is about 10% of particle scattering in rural areas, but can be nearly equal to particle light scattering in urban areas where elemental carbon is present (Waggoner and Weiss 1981). Because of the nature of its sources, the elemental carbon contribution to light extinction varies geographically and temporally. For example, wood-burning fireplaces and diesel engines are major sources of elemental carbon, and areas with large numbers of these sources generally have more elemental carbon in the atmospheric aerosol, hence more light absorption.

The results of several studies of the contribution of various particle components to light scattering and light absorption suggest that sulfate and organic species are major contributors to light scattering, with the contribution of nitrate being more variable. Relative humidity influences particle light extinction strongly when relative humidity exceeds 70%. The effect of humidity on light scattering properties is also very dependent on chemical and microphysical variables, as components of fine particles (hygroscopic fraction of aerosol) will vary in their ability to absorb water.

Finally, although results of several studies are strongly suggestive of common optical properties for the fine particle fraction, it would be disingenuous to claim that PM_{2.5} mass and light scattering coefficient are always equivalent, either temporally and spatially. The high-time resolution (i.e., hourly measurements) light scattering data clearly indicate that aerosol variation is significant in both seasonal and monthly time scales. There is also a measurable

diurnal variation of up to 50% of the daily average values where primary particle emissions are significant. The light scattering-humidity relationship depends on the particle composition, microstructure (i.e., internally or externally mixed aerosols) as well as the history of relative humidity values previously experienced by the particles. Hence the relationship between fine particle mass and light scattering can be obscured by many physical/ chemical factors and sampling errors. All of these factors should be examined carefully before the use of any scattering data for estimating fine mass concentration.

3.3 Chemical Properties of Particles

Generally, atmospheric PM can be divided into fine (<2.5 μm) and coarse particles (>2.5 μm). Fine and coarse particles differ in formation mechanisms, chemical composition, sources, and exposure relationships. Figure 3.4 represents a schematic diagram of both primary and secondary particles formation.

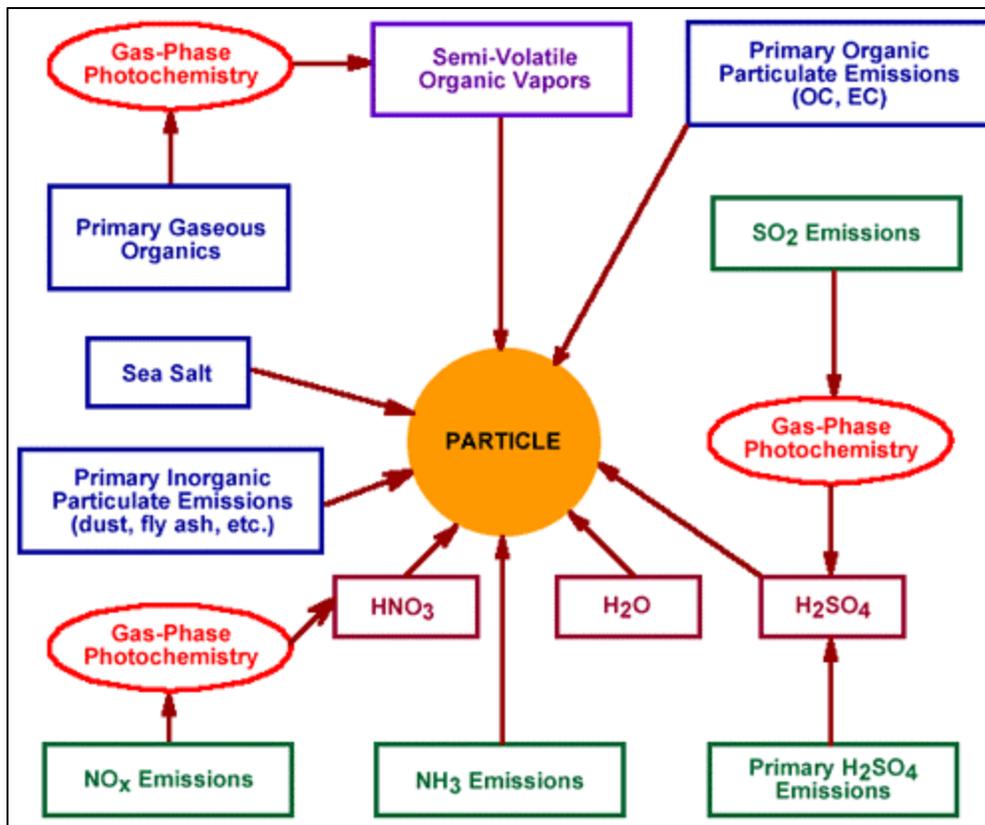


Figure 3.4. Schematic diagram of particle formation (adapted from Meng et al 1997).

Fine PM is derived from combustion material that has volatilized and then condensed to form primary PM, or from precursor gases (such as sulfur dioxide, nitrogen oxides, and certain organic compounds) reacting in the atmosphere to form secondary PM. Fine particles typically are comprised of sulfate, nitrate, ammonium, elemental carbon, organic compounds, and a variety of other compounds.

Coarse particles, in contrast, are formed by crushing, grinding, and abrasion of surfaces, which breaks large pieces of material into smaller pieces. These particles are then suspended by wind or by anthropogenic activity such as construction, mining, and agricultural activities.

As the particles respond to conditions in their atmospheric environment, their chemical and physical properties - and hence their characteristics, such as light scattering and toxicity - can change by accumulation of atmospheric gas-phase chemical reaction products or through heterogeneous reactions with gas-phase species.

3.3.1 Nitrate Chemistry

The atmospheric chemistry leading to formation of particulate nitrate is fairly complicated. Fresh NO_x emissions, which consist primarily of nitric oxide (NO) undergo reactions with ozone and peroxy radicals to form nitrogen dioxide (NO_2), via the reactions shown below.



The NO_2 can be directly converted to nitric acid via the homogenous gas phase reaction with the hydroxyl radical (OH).



This is the principal formation mechanism for nitric acid in the daytime (Finlayson-Pitts and Pitts, 1999). Modeling calculations suggest that more than 90% of the daylight HNO_3 formation occurs via this reaction. It involves the OH radical, which is the key species in the photochemical oxidation cycle. The OH radical concentration is controlled by the amount of sunlight and the ambient concentrations of ozone, water vapor, NO, NO_2 , and reactive organic compounds.

NO_2 reacts with O_3 forming nitrate radical (NO_3). An important reaction of NO_3 is with NO_2 to form N_2O_5 . The second major formation pathway for nitric acid is the reaction of N_2O_5 with water vapor and liquid water.



The rate of reaction will only be significant when the liquid water content of the atmosphere is high, i.e., when clouds and fog are present.

There is a wide range of conversion rates for nitrogen dioxide to nitric acid, ranging from less than 1 percent per hour to 90 percent per hour. Although they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours. This is in contrast to the gas-phase sulfate chemistry, which is most active during daylight hours.

The principal chemical loss process for gas-phase nitric acid is its reaction with gaseous ammonia to form ammonium nitrate (NH_4NO_3).



This reversible reaction is believed to be the primary source of fine (<2.5 μm diameter) nitrate aerosol in California's urban air. The equilibrium constant for the reaction is both temperature- and relative humidity-dependent. High humidity and low temperature favor NH_4NO_3 formation. Aqueous NH_4NO_3 is formed at relative humidities above the relative humidity of deliquescence (62%).

Another pathway for the formation of nitrate aerosol is a heterogeneous chemical reaction between sea-salt particles and gas-phase nitric acid, leading to thermally stable sodium nitrate production in the particle phase accompanied by liberation of gaseous hydrochloric acid (HCl) from the particles. Gard et al. (1998) focussed their study on the replacement of chloride by nitrate in sea-salt particles (reaction 3.6) at Long Beach.



Reaction (3.6) may be the principal source of coarse (2.5 to 10 μm) nitrate, and plays an important role in atmospheric chemistry because it is a permanent sink for gas-phase nitrogen oxide species. This reaction is one of the most extensively studied heterogeneous chemical reactions in the laboratory, and the extent to which this occurs is affected by many factors, including gas-phase and particle-phase concentrations, temperature, relative humidity, and reaction time.

Significant amounts of NO_x can be converted to organic nitrates, such as peroxyacetyl nitrate (PAN) which is the most abundant organic nitrate in urban air. The thermal decomposition of PAN is very temperature sensitive. As temperature rises, PAN decomposes back to NO_2 and methyl peroxyacetyl. A deficit exists in observable NO_y species in ambient air, and it is thought that PAN-analog compounds could comprise a significant part of the missing nitrogen species. Nitric acid and ammonia are believed to be deposited on surfaces very rapidly, while sulfate deposits relatively slowly. NO_x , ammonium, and nitrate aerosol deposit at rates in between these two extremes.

The atmospheric chemistry leading to formation of particulate nitrate is complicated. The rate of formation depends on the concentrations of many intermediate species (including ammonia and radical species) involved in the reactive organic gases and NO_x photochemical system. Figure 3.5 summarizes chemical pathways involving nitrogen oxides in the atmosphere (Warneck 1999). Photochemically induced reaction pathways are indicated by bold arrows. These processes are active only during the day, whereas the others occur at all times.

Until recently it was assumed that the end product of tropospheric NO_x was nitric acid. However, a recent research project conducted under ARB sponsorship (Mochida and Finlayson-Pitts 2000) has shown that nitric acid on a surface can react with NO to regenerate NO_2 which can then form ozone and particulate nitrate. Preliminary modeling studies suggest that this reaction may increase the formation of particulate nitrate and that existing models underestimate the benefit of NO_x controls for reducing PM and ozone. This finding may have very serious implications as to the effectiveness of control strategies for both ozone and PM. An additional research contract is continuing with a focus on providing a more complete understanding of the effect of heterogeneous nitrogen chemistry on ozone and particle formation. The information gained in this project may have very serious implications as to the effectiveness of control strategies for both ozone and PM.

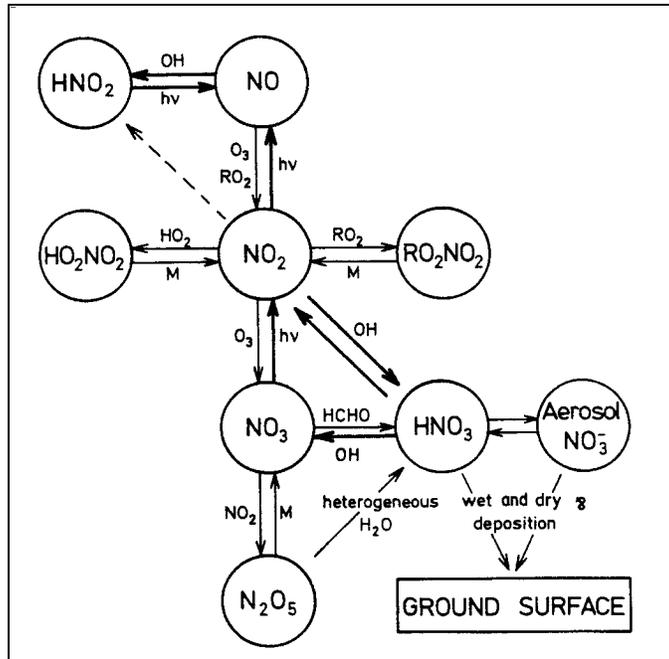


Figure 3.5. Oxidation scheme for nitrogen oxides and related compounds (adapted from Warneck 1999).

Ambient concentrations of secondary particles are not necessarily proportional to the quantities of their precursor emissions, since the rates at which they form and their gas/particle equilibria may be controlled by factors other than the concentration of the precursor gases. The rate of NO_x oxidation and the branching ratio between inorganic and organic nitrates depends on the specific environmental conditions in addition to reactant concentrations (Seinfeld and Pandis 1998). The partitioning of inorganic nitrate between gaseous nitric acid, ammonium nitrate, and nonvolatile nitrate is known to depend on a number of factors, such as relative humidity, temperature, and ammonia, in a nonlinear manner.

Secondary ammonium nitrate is generally the largest contributor to the PM_{2.5} mass during the winter at most of the urban sites in California. The results of several studies (Magliano et al., 1999; Kim, et al. 2000) indicate that during some episodes of high particle concentrations in California, ammonium nitrate – formed secondarily from NO_x and ammonia emissions – can account for over half of the PM_{2.5} mass. The formation of secondary particles, which are a major contributor to the fine PM levels in California, from gas-phase precursors is a complex, nonlinear process. Consequently, a one-to-one relationship between precursor emissions and ambient secondary PM concentrations is not expected. Understanding how particulate ammonium nitrate is formed and how to effectively reduce it through controls on NO_x and/or ammonia sources is a critical part of California's PM_{2.5} program.

3.3.2 Sulfate Chemistry

Sulfur dioxide emissions result almost exclusively from the combustion of sulfur-containing fuels. Other sulfur compounds, such as sulfur trioxide (SO₃), sulfuric acid (H₂SO₄), and sulfates (SO₄²⁻), may also be directly emitted during combustion of sulfur-containing fuels, although usually only in small amounts. In the atmosphere, sulfur dioxide is chemically transformed to sulfuric acid, which can be partially or completely neutralized by ammonia and

other alkaline substances in the air to form sulfate salts (Warneck 1999; Seinfeld and Pandis 1998).

The oxidation of sulfur dioxide to sulfuric acid can occur in the gas phase, in or on particles, and in the aqueous phase (i.e., in droplets of rain, clouds, or fogs). Sunlight intensity, the presence of oxidants and oxidant precursors, relative humidity, and the presence of fogs and clouds all appear to be related to the observed high oxidation rates. Results of several studies show that aqueous-phase oxidation of SO₂ is a significant pathway for the total transformation of SO₂.

3.3.2.1 Aqueous-Phase Sulfur Dioxide Reactions

Oxidation of sulfur dioxide can also occur in the aqueous phase via reactions of dissolved sulfur constituents (hydrated SO₂, sulfite, and bisulfite; collectively called S(IV)) with hydrogen peroxide (H₂O₂), ozone, and oxygen catalyzed by iron and manganese (Kleinman 1984; Seigneur et al. 1984). Ozone is an important oxidant for sulfur dioxide at high pH, but its effect becomes negligible at pH levels less than 4. The extent of S(IV) oxidation is primarily limited by the availability of H₂O₂ and the low solubility of sulfur dioxide at low pH. When fog droplets form on acidic nuclei, the low initial pH prevents oxidation of S(IV) other than by H₂O₂.

The effects of season and time of day suggest the importance of photochemistry, and perhaps temperature, in the oxidation rate of SO₂. This does not necessarily imply that oxidation reactions themselves are photochemical in nature, but rather they may involve oxidants such as H₂O₂ which are formed through photochemical processes.

The fastest atmospheric reactions of SO₂ believed to be with H₂O₂, and with O₃ at higher pH values. Under extreme conditions of large droplets (>10 μm) and very high oxidant concentrations, the chemical reaction times may approach those of diffusion, particularly in the aqueous phase. However, it is believed that under most conditions typical of the troposphere, this will not be the case and the chemical reaction rate will be rate determining in the S(IV) aqueous phase oxidation.

In heavily polluted atmospheric water droplets, such as those found in urban fogs, metal-catalyzed S(IV) oxidation is a significant contributor to formation of S(VI) in the liquid phase, and apparently is more important than oxidation by H₂O₂.

3.3.2.2 Gas-Phase Sulfur Dioxide Reactions

Sulfur dioxide is converted to sulfuric acid in the gas phase during daylight hours, primarily by reaction with hydroxyl radical (OH). (See reaction sequence below.)



The SO₃-H₂O adduct may dissociate back to reactants with about the same probability as it rearranges to sulfuric acid. Thus, the kinetics of sulfuric acid formation in reaction (3.9) may be considerably more complex than if it were a simple bimolecular reaction as written above.

Because of its extremely low vapor pressure (<10⁻⁷ atmospheres), sulfuric acid quickly adheres to existing particles. Sulfuric acid reacts irreversibly with ammonia to form ammonium bisulfate, NH₄HSO₄ and ammonium sulfate, (NH₄)₂SO₄. Since the sedimentation velocity of these submicrometer particles is very low, sulfate can be transported long distances. In the absence of precipitation or fog, the typical atmospheric lifetime of fine particulate sulfate is on the order of several days. Washout by precipitation and accelerated

sedimentation resulting from incorporation of sulfate particles into fog droplets are important sinks.

In power-plant or smelter plumes containing SO_2 and NO_x , the gas-phase chemistry depends on plume dilution, sunlight, and volatile organic compounds, either in the plume or in the ambient air mixing into and diluting the plume. For the conversion of SO_2 to H_2SO_4 , the gas-phase rate in such plumes during summer midday conditions in the eastern United States typically varies between 1 and 3% h^{-1} but in the cleaner western United States rarely exceeds 1% h^{-1} . For the conversion of NO_x to HNO_3 , the gas-phase rates appear to be approximately three times faster than the SO_2 conversion rates. During the winter, rates for SO_2 conversion are approximately an order of magnitude lower than during the summer.

The contribution of aqueous-phase chemistry to particle formation in point-source plumes is highly variable, depending on the availability of the aqueous phase (wetted aerosols, clouds, fog, and light rain) and the photochemically generated gas-phase oxidizing agents, especially H_2O_2 for SO_2 chemistry. The in-cloud conversion rates of SO_2 to SO_4^{2-} can be several times larger than the gas-phase rates. Overall, it appears that SO_2 oxidation rates to SO_4^{2-} by gas-phase and aqueous-phase mechanisms may be comparable in summer, but aqueous phase chemistry may dominate in winter.

Nationwide, large reductions in ambient SO_2 concentrations have resulted in reductions in sulfate formation that would have been manifest in $\text{PM}_{2.5}$ concentrations on the regional scale in the eastern and central United States, where sulfate has historically constituted a larger fraction of $\text{PM}_{2.5}$ than in the west. Likewise, reductions in NO_2 concentrations would have had a more noticeable impact on $\text{PM}_{2.5}$ concentrations in the western United States than in the eastern United States because nitrate is a larger component of the aerosol in the western United States. Trends in aerosol components (i.e., nitrate, sulfate, carbon, etc.) are needed for a more quantitative assessment of the effects of changes in emissions of precursors. Measurements of aerosol nitrate and sulfate concentrations have been obtained at North Long Beach and Riverside, CA, since 1978 (Dolislager and Motallebi, 1999). Downward trends in aerosol nitrate have tracked downward trends in NO_x concentrations, and SO_2 and sulfate concentrations have both decreased. However, the rate of decline of sulfate has been smaller than that of SO_2 , indicating that long-range transport of sulfate from outside the air shed may be an important source in addition to the oxidation of locally generated SO_2 . There are a number of reasons why pollutant concentrations do not track estimated reductions in emissions. Some of these reasons are related to atmospheric effects, such as meteorological variability and changes in the rates of photochemical transformations and deposition. Other reasons are related to uncertainties in ambient measurements and in emissions inventories.

3.3.3 Organic Particles

Atmospheric particulate carbon consists of both elemental carbon (EC) and organic carbon (OC). Elemental carbon has a chemical structure similar to impure graphite and is emitted directly by sources. Organic carbon can either be emitted directly by sources (primary OC) or can be the result of the condensation of low-vapor-pressure products of the gas-phase reactions of hydrocarbons onto the existing aerosol (secondary OC). Atmospheric carbon particles are emitted from more than 70 different types of air pollution sources (Gray and Cass 1998). Obvious sources include gasoline-powered motor vehicles, heavy-duty diesel vehicles, railroad engines, boilers, aircraft and many other combustors that burn fossil fuel. To the emissions from fuel combustion are added carbon particles from woodsmoke, food cooking operations, and even an ambient concentration increment from such minor sources

as cigarette smoke. In addition, there are fugitive sources including the organic carbon content of paved road dust, tire dust and vehicular brake wear particles.

Although the mechanisms and pathways for forming inorganic secondary particulate matter are fairly well known, those for forming secondary organic PM are not as well understood. Ozone and the hydroxyl radical are thought to be the major initiating reactants. Pandis et al. (1992) identified three mechanisms for formation of secondary organic PM: (1) condensation of oxidized end-products of photochemical reactions (e.g., ketones, aldehydes, organic acids, hydroperoxides), (2) adsorption of organic gases onto existing solid particles (e.g., polycyclic aromatic hydrocarbons), and (3) dissolution of soluble gases that can undergo reactions in particles (e.g., aldehydes). The first and third mechanisms are expected to be of major importance during the summertime when photochemistry is at its peak. The second pathway can be driven by diurnal and seasonal temperature and humidity variations at any time of the year. With regard to the first mechanism, Odum et al. (1996) suggested that the products of the photochemical oxidation of reactive organic gases are semivolatile and can partition themselves onto existing organic carbon at concentrations below their saturation concentrations. Thus, the yield of secondary organic PM depends not only on the identity of the precursor organic gas but also on the ambient levels of organic carbon capable of absorbing the oxidation product.

The formation of atmospheric aerosols from biogenic emissions has been of interest for many years. Recent laboratory and field studies support the concept that nonvolatile and semivolatile oxidation products from the photo-oxidation of biogenic hydrocarbons could contribute significantly to ambient PM concentrations in both urban and rural environments. A number of multifunctional oxidation products have been identified in laboratory studies (Yu et al. 1998; Glasius et al. 2000; Koch et al. 2000). Many of these compounds have subsequently been identified in field investigations (Kavouras et al. 1998, 1999b). However, further investigations are needed to accurately assess their overall contributions to fine PM concentrations.

Generally, organic PM concentrations, composition, and formation mechanisms are poorly understood. Particulate organic matter is an aggregate of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties (Saxena and Hildemann, 1996). Some of the organic compounds are "semivolatile" such that both gaseous and condensed phases exist in equilibrium in the atmosphere. The presence of semivolatile or multiphase organic compounds complicates the sampling process. Understanding the mechanisms of formation of secondary organic PM is important because secondary organic PM can contribute in a significant way to ambient PM levels, especially during photochemical smog episodes. Experimental studies of the production of secondary organic PM in ambient air have focused on the Los Angeles Basin. Turpin and Huntzicker (1994, 1995) provided strong evidence that secondary PM formation occurs during periods of photochemical ozone formation in Los Angeles and that as much as 70% of the organic carbon in ambient PM was secondary in origin during a smog episode in 1987. Schauer et al. (1996) estimated that on an annually averaged basis, 20 to 30% of the total organic carbon PM in the <2.1 μ m size range in the Los Angeles airshed was secondary in origin.

A high degree of uncertainty is associated with all aspects of the calculation of secondary organic PM concentrations. Currently, it is not possible to fully quantify the concentration, composition, or sources of the organic components. Many of the secondary organic aerosol components are highly oxidized, difficult to measure, multifunctional compounds. This is compounded by the volatilization of organic carbon from filter substrates during and after sampling as well as potential positive artifact formation from the absorption of gaseous hydrocarbon on quartz filters. In addition, no single analytical technique is currently capable of

analyzing the entire range of organic compounds present in the atmosphere in PM. Even rigorous analytical methods are able to identify only 10 to 20% of the organic PM mass on the molecular level (Rogge et al. 1993a; Schauer et al. 1996).

Environmental smog chambers can be useful in elucidating the chemical mechanisms associated with the formation of compounds found in organic PM; however, significant uncertainties always arise in the interpretation of smog chamber data because of wall reactions. Limitations also exist in extrapolating the results of smog chamber studies to ambient conditions found in urban airsheds. Additional laboratory studies are needed to comprehensively identify organic compounds, strategies need to be developed to sample and measure such compounds in the atmosphere, and models of secondary organic aerosol formation need to be improved and added to air quality models in order to address compliance issues related to reducing PM mass concentrations that affect human exposure.

3.3.4 Particle-Vapor Partitioning

Several atmospheric aerosol species, such as ammonium nitrate and certain organic compounds, are semivolatile and are found in both gas and particle phases. A variety of thermodynamic models have been developed to predict the temperature and relative humidity dependence of the ammonium nitrate equilibria with gaseous nitric acid and ammonia. The gas-particle distribution of semivolatile organic compounds depends on the equilibrium vapor pressure of the compound, total particle surface area, particle composition, atmospheric temperature, and relative humidity. Although it generally is assumed that the gas-particle partitioning of semivolatile organics is in equilibrium in the atmosphere, neither the equilibria nor the kinetics of redistribution are well understood. Diurnal temperature fluctuations, which cause gas-particle partitioning to be dynamic on a time scale of a few hours, can cause semivolatile compounds to evaporate during the sampling process. The pressure drop across the filter can also contribute to loss of semivolatile compounds. The dynamic changes in gas-particle partitioning, caused by changes in temperature, pressure, and gas-phase concentration, both in the atmosphere and after collection, cause serious sampling problems.

A recent ARB-funded final research report (Ashbaugh et al. 1998) describes analysis of three data sets to evaluate the extent of mass loss on polytetrafluoroethylene (PTFE or Teflon[®]) filters due to ammonium nitrate volatilization. The results indicated that the effect on measured mass is site-dependent, and depends on the meteorological conditions and the fraction of PM mass that consists of ammonium nitrate particles. There is no straightforward method to correct for the mass loss without measuring it. The highest mass loss occurred during summer daytime in southern California, amounting to 30-50% of the gravimetric mass. This study of ammonium nitrate suggests potentially significant nitrate or semivolatile organic compounds loss using the Federal Reference Method sampler for fine particle sampling because it uses PTFE filters for mass concentrations. This may lead to control strategies that are biased toward sources of fugitive dust and other primary particle emission sources.

3.4 Summary

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Atmospheric size distributions show that most atmospheric particles are quite small, below 0.1 μm , whereas most of the particle volume (and therefore most of the mass) is found in particles greater than 0.1 μm . Several processes influence the formation and growth of particles. New particles may be formed by nucleation from gas phase material. Existing particles may grow by condensation as gas phase material condenses onto existing particles. Particles may also grow by coagulation as two particles combine to form one. Gas phase material condenses preferentially on smaller particles and the rate constant for coagulation of two particles

decreases as the particle size increases. Therefore, nuclei mode particles grow into the accumulation mode but accumulation mode particles do not grow into the coarse mode.

The lifetimes of particles vary with particle size. Coarse particles can settle rapidly from the atmosphere within minutes or hours, and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized, coarse-mode particles may have longer lives and travel greater distances. Accumulation-mode fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. They can be transported thousands of kilometers and remain in the atmosphere for a number of days. Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Coarse mode particles of less than 10 μm diameter as well as accumulation-mode and nuclei-mode (or ultrafine) particles all have the ability to penetrate deep into the lungs and be removed by deposition in the lungs.

The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. Particulate material can be primary or secondary. PM is called primary if it is in the same chemical form in which it was emitted into the atmosphere. PM is called secondary if it is formed by chemical reactions in the atmosphere. Primary coarse particles are usually formed by mechanical processes. Primary fine particles are emitted, either directly as particles or as vapors that rapidly condense to form particles.

Most of the sulfate and nitrate and a portion of the organic compounds in atmospheric particles are secondary. Secondary aerosol formation depends on numerous factors including the concentrations of precursors; the concentrations of other gaseous reactive species such as ozone, hydroxyl radical, peroxy radicals, or hydrogen peroxide; atmospheric conditions, including solar radiation and relative humidity; and the interactions of precursors and preexisting particles within cloud or fog droplets, or on or in the liquid film on solid particles. As a result, it is considerably more difficult to relate ambient concentrations of secondary species to sources of precursor emissions than it is to identify the sources of primary particles.

Finally, current filter-based mass measurements lead to significant evaporative losses, during and possibly after collection, of a variety of semivolatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase). Important examples include ammonium nitrate and semivolatile organic compounds. Loss of these components may significantly impact the quality of the measurement, and can lead to both positive and negative sampling artifacts. The systematic bias in the sampling method is likely to result in a bias in recommended control strategies. If the measured mass is under-represented by the semivolatile compounds in the atmosphere, other sources of particulate matter will be over-represented. Thus, control strategies developed from the biased data will tend to overemphasize controls on nonvolatile species.

3.5 References

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4. Sources and Emissions of Particles

Particulate matter is produced by emission sources either directly in particle form (primary PM), or as gases that react in the atmosphere to produce particulates (secondary PM). The emissions are produced by stationary, mobile, area-wide, and natural sources. For air pollution, the particulates of concern are those that are 10 micrometers or less in size (PM10), and, those that are 2.5 micrometers or less in size (PM2.5, which is a subset of PM10). This section discusses the characteristics of the major particulate matter sources.

PM emission levels are either measured, using monitoring equipment, or estimated, using emission inventory methods. Most of the information provided in this section is from estimated emission inventory data. This is currently the most reliable and comprehensive method of comparing PM emissions between sources and for evaluating regional emission sources.

4.1 Primary Particulate Sources

Primary particulate emission sources emit particulate matter directly to the air. Primary sources include stationary, mobile, area-wide, and natural particulate generating processes. Figure 4.1 summarizes the statewide directly emitted PM10 emission sources for California. Each of the major source categories depicted in the chart is discussed more fully below.

4.1.1 Stationary Sources

Stationary sources are generally small contributors to overall statewide primary particulate levels. The stationary source PM contribution is small because most major stationary source facilities have incorporated control equipment for decades and therefore are not large PM emitters. Some stationary sources of PM include industrial sources such as petroleum refining, wood and paper processing, food and agricultural processing, and sand, rock, and gravel mining and handling. Most stationary source facilities submit emission inventory reports to their air districts, so PM from these sources is typically well quantified. Most of the PM generated by combustion from stationary sources is PM2.5. Other stationary sources, such as those handling mineral products, emit relative greater proportions of PM10.

4.1.2 Mobile Sources

The contributions of directly emitted PM from mobile sources vary substantially within California. Sources of mobile emissions include gasoline and diesel powered vehicle exhaust emissions, tire wear, and break wear. Types of mobile sources include trucks, busses, heavy equipment, ships, trains, and aircraft. Like most combustion sources, the particulate emissions from mobile sources are nearly all in the PM2.5 size fraction. (This category does not include the road or soil dust created by car, truck, or equipment operations, which are included in the area-wide source category.)

4.1.3 Area-Wide Sources

Based on ambient measurements and emission inventory data developed by the ARB, area-wide sources contribute to a large fraction of the primary particulate emissions inventoried for the State. Area-wide sources are generally defined as sources that lack a definitive emissions point such as a stack or exhaust pipe, or sources which are relatively small, numerous, and geographically spread out.

For PM10, some of the most significant area-wide sources of directly emitted PM are geologic dust, such as windblown dust from disturbed lands, paved road dust, unpaved road dust, construction activities, and agricultural land preparation. Typical area-wide combustion sources, which predominantly produce particulates in the sub-2.5 micrometer size range,

include burning of agricultural debris, open burning, forest and range management burning, wildfires, fireplaces and wood stoves. The major PM sources vary from region to region in California, as well as by season.

4.1.4 Natural Sources

Most natural sources of PM are not currently included in the statewide emission inventory. These sources include marine-derived airborne salts, windblown dust from undisturbed lands, and biogenic emissions from plants. However, wildfires are currently included in emission inventory estimates.

4.2 Secondary Particulate Sources

Secondary particulate matter is typically 2.5 micrometers or less in size. Secondary PM is formed via atmospheric reactions of primary gaseous emissions. The gases that are the most significant contributors to secondary particulates in California are nitrogen oxides, ammonia, sulfur oxides, and certain organic gases.

The primary sources of nitrogen oxides and sulfur oxides include motor vehicle exhaust and stationary combustion sources such as boilers and other industrial equipment. Sources of ammonia include livestock operations such as dairies and feedlots, fertilizer application, some industrial sources, and biogenic sources. Organic gases are produced by both anthropogenic and natural sources.

Unlike direct emissions, it is not possible to develop an emission inventory for secondary particulates. This is because the particles form through various chemical pathways when gaseous emissions react in the atmosphere. So instead, the precursor gases are inventoried, and then location- and time-specific modeling is performed to estimate how much of each gas converts to particles.

Because a significant component of PM_{2.5} can be due to gaseous precursors, a pie chart that includes only the directly emitted PM_{2.5} emissions can be misleading, and is not included in this document. Such a chart would not give an accurate representation of which sources contribute to PM_{2.5} levels, especially in regions with high secondary particulate levels. For PM_{2.5}, chemically speciated air quality monitoring data often provides a more meaningful portrayal of the sources contributing to PM_{2.5} in the air.

4.3 Regional Dependence of Source Contributions

The contributors to primary PM vary regionally in the State. Urban areas are typically dominated by paved road dust and construction-related emissions for directly emitted PM. More rural regions include paved and unpaved road dust, farming operations, and windblown dust as major contributors. Desert regions often have some of the cleanest air in the State, but, when episodic windstorms occur, they also experience some of the most dramatic exceedances of the PM₁₀ standards. Unpaved road dust, paved road dust, and construction activities also contribute to PM₁₀ in the desert.

Regional meteorology also plays a part in PM concentrations in the State. As mentioned, high winds can contribute to PM in the drier areas of the State. In other areas, stagnant air can exacerbate PM levels. Moist, colder weather in the San Joaquin Valley during winter contributes to the formation of secondary nitrates, and nitrates also contribute to high particulate levels in Southern California. In regions that are relatively cold, wood burning can substantially increase regional PM₁₀ concentrations during the winter. In summary, the sources and quantities of PM emissions throughout the state are strongly affected by regional meteorology, geography, population, and land use.

4.4 Temporal Dependence of Source Contributions

Regional monitoring shows that many areas in the state show seasonal trends in ambient PM concentrations. For example, in the Sacramento Valley, PM values peak during October to January, and July to August. In the San Joaquin Valley, there are both winter and late fall peaks. The winter PM is predominantly fine particulate (PM_{2.5} and smaller secondary particulates), while the fall season PM has a more significant PM₁₀ emission component due to directly emitted geologic dust. In Southern California, high PM levels occur at several times of the year based on meteorological conditions. In the Owens Valley, windstorms create short-term episodic high PM concentrations. And in places like Mammoth Lakes and Lake Tahoe, high particulate levels typically occur in the winter due to woodstove emissions and application of anti-skid materials to icy roads.

There are substantial regional and seasonal variations in the quantities and types of PM emitted to the air. These variations are not fully captured through emission estimates, especially when trying to include secondary particulates. Therefore, chemically speciated air quality monitoring data is a more effective means to identify the sources and levels of particulate matter for specific regions and locations.

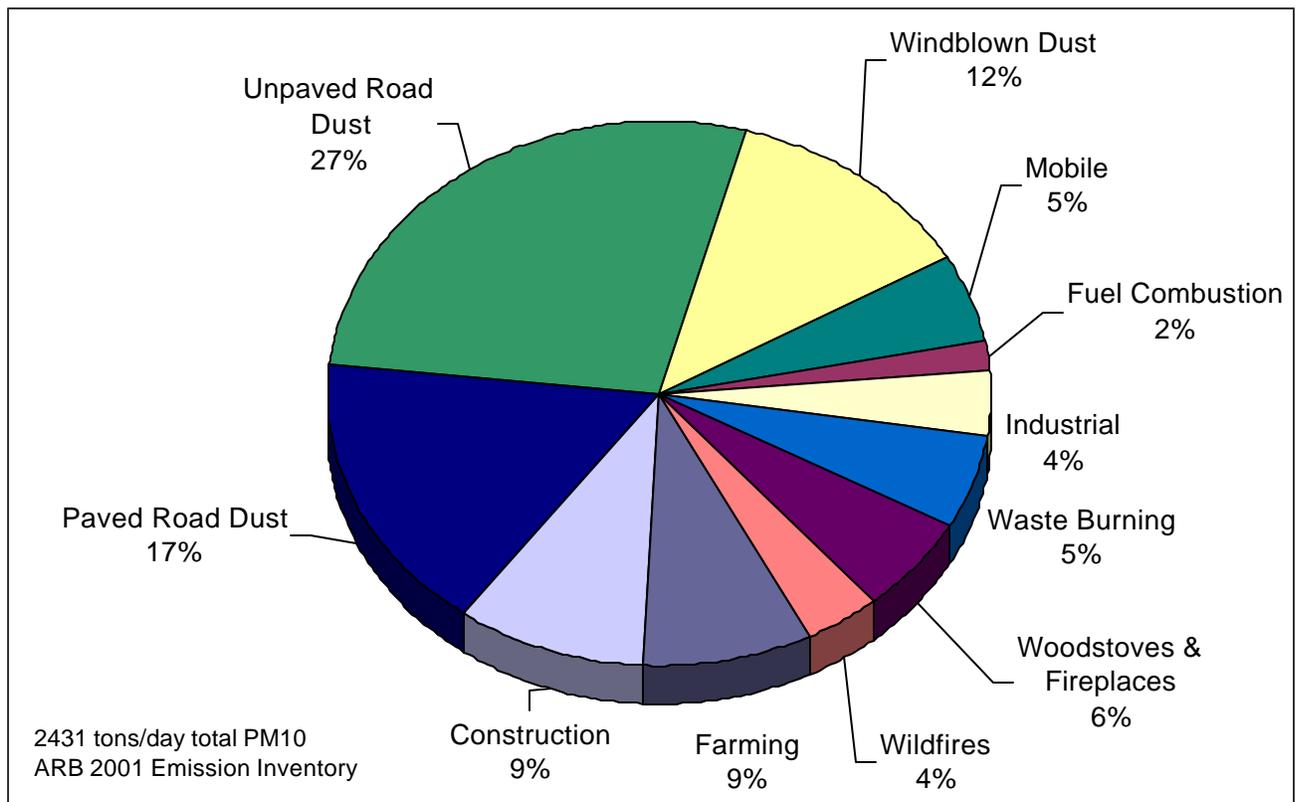


Figure 4.1. California Statewide PM₁₀ Emission Inventory, Direct Particulate Emissions, 2001

4.5 References

Emission Inventory, 2001. California Air Resources Board. August 2001. Available via website at: <http://www.arb.ca.gov/emisinv/eib.htm>

Emission Inventory Procedure Manual, Volume III, Methods for Assessing Area Source Emissions. Air Resources Board. October 1997. Available via website at <http://www.arb.ca.gov/emisinv/areasrc/areameth.htm>

5. Measurement of Particulate Matter

5.1 Introduction

On December 9, 1982, the California Air Resources Board (Board or ARB) replaced the total particulate matter ambient air quality standard with a standard that focused on particles of a smaller diameter. The Board approved amendments to the California Code of Regulations, title 17, section 70200, which modified the definition of suspended particulate matter (PM) to specifically include particulate matter with an aerodynamic diameter of 10 microns or less (PM10), and established PM10 ambient air quality standards. The Board included general reference to a PM10 measurement method in the standard and directed staff to establish more specific criteria for PM10 sampling equipment. Method P, adopted by the Board in 1985, established the State method for ambient PM10 measurement. In 1986, the State identified the size selective inlet (SSI) high volume (hi-vol) PM10 sampler as the PM10 sampler satisfying the requirements of Method P.

In December 2000, the Board determined that the state ambient air quality standards for PM10 and particulate sulfates should be reviewed to ensure they are protective of public health. The Board asked staff to provide this review and any recommendations for changes to the standards by 2002.

This chapter addresses the measurement methods that are required to be used to determine compliance with the newly proposed PM standards. At this time, the ARB proposes to align the state and federal requirements for PM samplers by adopting the Federal Reference Methods (FRMs) for PM10 and PM2.5 as the state's method. The FRMs specify performance characteristics and operational requirements applicable to PM10 and PM2.5 monitoring methods, and for PM2.5, specify sampler design characteristics. The associated samplers meet the requirements specified in the methods. The method and associated sampler are designated as a reference method. We are not proposing to adopt Federal Equivalent Methods, per se, given their history of poor performance in California. Continuous samplers will be addressed, however, and will be incorporated as California Approved Samplers based on their performance in a recently concluded study in Bakersfield, CA.

The reference methods (FRMs) are traditional, filter-based sampling methods with laboratory weighing of the filters before and after sampling. The sampling and analytical methods are both labor-intensive. Each sample is collected during a 24-hour period, and one sample typically is taken every six days throughout the year at each monitoring station. There is a time-lag of days to weeks from the date of sampling to the time results are available.

Continuous monitoring for either PM10 or PM2.5 has many advantages over traditional filter based sampling techniques. A continuous method is an in-situ, automatic measurement method of suspended particle mass with varied averaging time (minutes to hours) that provides an instantaneous result. Their 24/7 sampling schedule will further our understanding of PM emission patterns and exposure, and can be used to enhance public health research into short-term peak exposure. They can provide more data for model validation, to aid in identifying air pollution source(s), and to reflect dispersion patterns. Official approval of continuous instruments/methods will promote further development of continuous samplers and potentially reduce the cost of the air monitoring network.

5.2 Existing Monitoring Requirements

5.2.1 State Method P for PM10

Method P (cited in title 17, California Code of Regulations, sections 70100 and 70200) describes the design and performance requirements for the PM10 sampler to be used to determine compliance with the state ambient air quality standards. Method P is contained in Appendix 5 part A of this document and describes the operating principle and design of the samplers, which are in turn specified in proposed section 70100.1.

An “ideal” sampler should be designed to determine the mass concentration of ambient particulate matter of a mean aerodynamic diameter of 10 micrometer (μm) or less (PM10) to simulate particle penetration of the human respiratory system as described by the Chan-Lippmann model (1980). According to this model, PM10 particles are small enough to enter the thoracic region of the human respiratory tract. An ideal sampler is the one that collects 50 percent (referred as D50) of all particles of $10 \pm 1 \mu\text{m}$ aerodynamic diameter, and which collects a rapidly declining fraction of particles as their diameter increases and rapidly increasing fraction of particles of smaller particle diameters. Aerodynamic diameter is defined as the diameter of a spherical particle of a unit density with settling velocity equal to that of the particle in question. Particles with the same size and shape but with different densities will have different aerodynamic diameters.

Suspended particulate matter refers to atmospheric particles, solids, or liquids, except uncombined water. Dry, free-flowing particles should be sampled with the same efficiency as liquid, sticky particles. The expected mass concentrations of liquid particles should be within the limits of that predicted by the ideal sampler. For solid particles, the expected mass concentration should be no more than 5 percent above that obtained for liquid particles of the same size. The sampler must have less than 15 percent variation in the measurements produced by three collocated samplers.

Meteorology is one of several factors that can effect sampling efficiency. The performance of a PM10 sampler should be independent of wind speed to simulate human respiration. The inlet design and its internal configuration should be such that it shows no dependency on wind direction and wind speed when operated within 2 to 24 kilometers-per-hour wind speeds. To do this, the inlet should be omnidirectional, that is, the inlet should be symmetrical about the vertical axis.

A sampler must possess a sampling medium (filter) upon which the PM is collected without spattering and falling off. The sampler should be designed to hold and seal the filter in a horizontal direction so that the sample air is drawn uniformly downward through the filter to allow a uniform distribution of PM10 collected so as to permit subdivision of the filter for qualitative and quantitative analysis. Filters shall have a collection efficiency of more than 99 percent as measured by the dioctyl phthalate (DOP) test (ASTM-2986), with $0.3 \mu\text{m}$ particles at flow rates equal to the sampler’s operating face velocity. Filters must have mechanical and chemical stability and be stable in a wide temperature range to allow a variety of qualitative and quantitative analyses. Filters must minimize artifacts, that is, should not react with the deposit and must not absorb contaminant gases. They must be non-hygroscopic, and have high chemical purity with alkalinity of <5 microequivalents/gram. The filters must be equilibrated prior to use at constant temperature and humidity conditions.

The sampler must possess an automatic flow control device which maintains a constant flow rate to within ± 10 percent of the recommended range for the sampler inlet over normal variations in line voltage and filter pressure drop during the sampling period. Change in flow velocity will result in change in nominal particle size collected. Therefore, it is important that

the flow rate through the inlet be maintained at a constant value that is as close as possible to the inlet design flow rate.

A timing/control device should be capable of starting and stopping the sampler during a sample collection period of 24 ± 1 hr ($1,440 \pm 60$ min). An elapsed time meter, accurate to within 15 minutes, shall be used to measure sampling time. This meter is optional for samplers with continuous flow recorders if the sampling time measurement obtained by means of the recorder meets the ± 15 minutes accuracy specification. Using the total sampling time, the total volume of air sampled is determined. PM concentration is computed as the total mass of collected particles in PM₁₀ size range divided by the volume of air sampled. The particulate matter concentration is expressed as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) corrected to standard conditions (760 torr and 25 C).

5.2.2 State Method for Sulfates

State regulations (section 70200 of title 17, California Code of Regulations) contain an independent ambient air quality standard for particulate sulfates. The measurement method for sulfates described in this standard is high-volume TSP sampling, with filter analysis by Turbidimetric Barium Sulfate Spectrometry, AIHL Method 61, or “[a]ny equivalent procedure which can be shown to the satisfaction of the Air Resources Board to give equivalent results at or near the level of the air quality standard.”

The ARB’s current measurement method for sulfates is MLD Method 033, which uses TSP sampling followed by ion chromatography. However, adsorption of SO₂ with subsequent chemical reactions on the filter surface, can, at sufficient concentrations, lead to gas-to-particle conversion, and can create positive artifacts on the filter. These can be minimized with the use of alkalinity-controlled filters which are provided for in the current PM₁₀ network and PM₁₀ Federal Reference Methods.

5.2.3 Federal Methods for PM₁₀

Federal ambient measurement methods must be used to determine the attainment status of air basins nationwide. Federal Reference Methods (FRMs) use the measurement principles and specifications defined in U.S. EPA regulations. Provisions also allow for a Federal Equivalent Method (FEM) to be approved by the U.S. EPA and used for the same purpose. The requirements for an FRM for PM₁₀ are described in Appendix M, Title 40, Code of Federal Regulations Part 50, 1997, and are provided here as Appendix 5 part B to this document. These requirements are, for the most part, the same as the California Method P. This is understandable, as Method P was adopted by the ARB in consultation with the U.S. EPA as that agency was preparing to propose methods for the NAAQS for PM₁₀. A comparison of the two methods, item-by-item, is given in Appendix 5 part C. There are differences in a few specific requirements, which are highlighted in the table. The discussion below focuses only on those differences. The purpose of presenting this information is to highlight the need to update Method P.

- The FRM requires PM₁₀ sampler to simulate particle penetration of the human respiratory system as described by the Chan-Lippmann (1980), penetration model. The D50 cut-point of the sampler is 10 μm with a tolerance of ± 0.5 μm , compared to the tolerance of ± 1.0 μm for Method P.
- The alkalinity of filter medium should be less than 2.5 microequivalents/gram for FRM as opposed to less than 5 microequivalents/gram for Method P. The filters should be equilibrated at constant relative humidity of between 20 percent and 45 percent ± 5 percent for FRM instead of <50 percent relative humidity for Method P before weighing.

- The precision of collocated FRM samplers must be $5\ \mu\text{g}/\text{m}^3$ for PM concentration below $80\ \mu\text{g}/\text{m}^3$ and 7 percent for PM₁₀ concentration above $80\ \mu\text{g}/\text{m}^3$ for FRM, as opposed to 15 percent for all concentrations for Method P.
- The FRM requires the air flow rate through the sampler remain stable over a 24-hour period, regardless of filter loading; the specific requirements are ± 5 percent of the initial reading for the average flow, and ± 10 percent of the initial flow rate for any instantaneous flow measurement. For Method P, the flow rate should be within 10 percent at all times.
- Typically, an analytical balance with a sensitivity of 0.1 mg is required for hi-vol samplers (flow rates $>0.5\ \text{m}^3/\text{min}$, large filters). Lo-vol samplers (flow rates $<0.5\ \text{m}^3/\text{min}$, smaller filters) require a more sensitive balance, which is not indicated in Method P.
- The particulate matter concentration is expressed as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) at local temperature and pressure (LTP) as opposed to standard temperature and pressure (STP, 760 torr and 25 C) for Method P.

The other major difference between the State and federal method is the designation of FEM test protocols, not included in Method P, although method equivalency is referred to and accepted in general terms in State regulations.

The differences between the FRMs and state-approved samplers can generally be attributed to advancements and improvements in sampler flow control and filter medium technology that occurred since Method P was established. The PM₁₀ air monitoring network in California meets FRM requirements. Consequently, changing Method P to be consistent with the FRM will bring the criteria into line with both equipment and material specifications, and field and laboratory practices.

5.2.4 Federal Methods for PM_{2.5}

The U.S. EPA promulgated rigorous design and performance specifications for its PM_{2.5} FRM samplers (40 CFR part 50, Appendix L; 40 CFR part 53, Subpart E; and 40 CFR part 58, Appendix A, all dated July 18, 1997. These are set forth in Appendix 5, parts D, E and F, respectively, of this document). Only measurements made using U.S. EPA-designated FRM samplers may be used to determine an area's compliance status with the PM_{2.5} NAAQS. The PM_{2.5} sampler is an adaptation of the PM₁₀ lo-vol sampler that initially removes, by impaction, particles larger than PM₁₀. Downstream lies a second impactor (Well Impactor Ninety-Six [WINS]) that reduces the cut point to $2.5\ \mu\text{m}$.

The dimensions and materials of sampler components that come in contact with the sampled air stream (the first stage inlet, the downtube, the second stage separator [WINS], the upper filter holder, the filter cassette, and the filter support screen) are specified by design (40 CFR part 50, Appendix L, July 18, 1997). The design of the other components of the FRM sampler is left to manufacturers, as long as resulting samplers meet all the prescribed performance specifications.

Performance specifications include active monitoring of a number of operational characteristics of the samplers, including sampler volumetric flow, temperature, and pressure. The performance criteria specify strict requirements for controls that must be observed for sampler operations. These include sampling efficiency, accuracy, precision, sampling medium, flow controller, laboratory, calibration, and measurement procedures. The details of the performance criteria are given in Appendix L of 40 CFR part 50 (see Appendix 5 part D to this document).

The current network of PM_{2.5} samplers in California (more than 80) was funded almost entirely by the U.S. EPA following the adoption of the federal PM_{2.5} standard. The U.S. EPA

continues to provide operating funds for the network. The samplers' operation is governed by federal regulation.

The network of PM_{2.5} samplers has been operating in California since 1999. Additional speciation samplers will eventually supplement the FRM samplers and provide information about the composition of the particulate matter in the sample. Staff recommends adopting both the FRM sampler and the performance and operational requirements of the methods for the proposed State PM_{2.5} standard. Staff is not proposing to adopt the U.S. EPA's FEM criteria for PM_{2.5}.

5.3 Available PM Sampling Methods

There are two fundamental methods commonly used to measure atmospheric PM₁₀ and PM_{2.5} that are potentially useable in California. The first is a laboratory-based, gravimetric, or filter method, in which particles segregated by size are collected on a pre-weighed filter medium and weighed after sampling to determine PM mass. PM concentration is calculated by dividing the mass increase of the filter by the 24-hour total volume of air (at ambient conditions) that passed through the filter.

The second fundamental technique employs in-situ field samplers that are based on different operational principles, but that all operate continuously and produce real-time, hourly average concentrations. There are pros and cons to either type of sampler. Over the years, the staff has heard reports of the need for both types of samplers. Consequently, staff is proposing to incorporate the leaders in both types of samplers as part of this regulation as California Approved Samplers for PM.

New technology samplers may be added in future years, and others perhaps deleted, from the list of approved sampler as the situation warrants. The samplers proposed in this action have been demonstrated to have wide applicability, and have good agreement with standard methods. The intent of this rulemaking is to incorporate recent advances in sampler technology, align the state with federal samplers where possible, and incorporate samplers that can be used widely in California in areas with persistent high PM levels. The proposal does not support approving different samplers for every air basin or approving samplers that respond differently based on season of the year unless absolutely necessary.

The staff carefully considered the limitations of a wide variety of samplers in making the method proposals. Filter based methods can result in loss of PM during or after sampling, or formation of PM on the filter medium during sampling. Loss of semi-volatile chemical species such as atmospheric ammonium nitrate and organics may occur during and after sampling as particles move from the particle to the gas phase. The amount of particulate matter lost is dependent on the concentration and composition of the semivolatile components, and the handling and retention time on the sampler at the conclusion of the sample run. Loss of volatile chemical species can underestimate PM mass. PTFE (polytetrafluoroethylene or Teflon[®]) filters can easily lose semi-volatile materials (a so-called negative artifact) (Eatough et al., 1993; Gundel et al., 1995). Therefore, regular sampling procedures now include steps to minimize these losses, including rapid removal of filters from the sampler, prompt storage in Petri dishes, transport in cool environments, expedited transport of filters from the field to the weigh rooms, and prompt extractions once the filters are weighed (Achtelik and Omand, 1998).

Adsorption of gases (such as SO₂) with subsequent chemical reactions with other gases on the filter surface, can, at sufficient concentrations, lead to gas-to-particle conversion, and can create positive artifacts on the filter. These can be reduced with the use of alkalinity-controlled filters and possibly the use of low-volume samplers.

Formation particles from gaseous species can lead to overestimation of PM mass (i.e., a positive artifact). Quartz filters can adsorb some gas-phase organics producing positive artifacts (Gundel et al., 1995; Turpin et al., 1994).

Operation of conventional filter-based samplers with laboratory gravimetric analysis is extremely time-consuming and labor intensive to produce a single mass measurement compared to real time, continuous samplers. Moreover, data are available only on a 24-hour average basis from conventional filter-based techniques. This limits using the data to investigate sub-24-hour health effects. The time lag inherent in data availability in conventional filter-based methods also precludes their use to provide the general public with timely warnings about episodic air pollution hazards. Filter-based systems can also have problems with particle loss during handling and transport, particularly when mass loading on the filter is high. These “sloughing” effects have been minimized by having strict operational protocols.

5.3.1 General Description of Gravimetric Methods

5.3.1.1 High-Volume Size Selective Inlet Sampler

The size selective inlet (SSI) sampler is described in Method P and is recognized by the U.S.EPA as an FRM. California identified the SSI in May 1986 as the PM₁₀ sampler to be used for the State AAQS. The U.S. EPA identified it in 1987 as an FRM (U.S. EPA/ORD, 2000).

The high-volume (hi-vol) SSI sampler used in the State and federal PM₁₀ networks consists basically of a PM₁₀ inlet, an impactor, a flow control system recorder, and a pump. The automatic flow control system consists of either a mass flow controller or a volumetric flow controller, which controls the flow to 40 ft³/min (at standard temperature and pressure). The flow rate through the impactor is used with the elapsed time to determine size of particle collected and the volume of air sampled. According to one manufacturer, its inlet has a cut-point of 9.7 μm in winds up to 22 miles per hour (36 kilometers per hour) (Thermo Andersen, Inc.).

PM₁₀ hi-vol samples are collected on an 8x10 inch (20x25 cm) quartz filter that offers high collection efficiencies and is resistant to absorbing artifacts related to the collection of sulfates and nitrates. However, the quartz filter can under some circumstances adsorb organic vapor more readily than a PTFE filter leading to an overestimation of PM mass (Turpin et al., 1994). Volatile constituent losses during sampling and transport are known to exist; however, prompt sample removal can minimize these losses.

There are three versions of the SSI samplers currently designated as FRMs. The unit widely used in California, the SA-1200 (Sierra-Anderson 1200), is a single-stage fractionator with hinged design to facilitate oiling and cleaning of the impaction shim.

The SSI sampler provides a direct measurement of PM₁₀ mass concentration. The large filter size provides two benefits. First, it increases the precision and accuracy of mass measurement, and second, it provides sufficient PM that can be analyzed for many of the primary constituents of interest.

5.3.1.2 Low-Volume Sampler

5.3.1.2.1 PM₁₀

Low-volume (lo-vol) PM₁₀ FRM samplers collect PM of a specific size range on a filter at a flow rate considerably less than for the hi-vol samplers. A lo-vol sampler consists of a PM₁₀ inlet, an impactor, a pump, a flow rate controller, and a timer. Fundamentally, the operational

principles of the lo-vol and the hi-vol (SSI) samplers are the same. The differences occur with features such as the inlet size, flow rate, and filter size. These differences are discussed below. The flow rate in both cases is a critical feature of the instrument's ability to segregate particle sizes. Lo-vol samplers were not available at the time Method P was promulgated.

Federally approved lo-vol samplers (FRM) are equipped with either a flat or tilted PM10 inlet, as specified in Appendix L of 40 CFR Part 50 (Figures L-2 through L-19). They use small PTFE-coated fiber filters. The filters are chemically stable, and suitable for a wide temperature range. The sampler may have a manual or an automatic filter-changing mechanism. It must be able to measure 24-hour PM10 mass concentrations of at least 300 $\mu\text{g}/\text{m}^3$, while maintaining the operating flow rate within the specified limits.

FRM lo-vol samplers operate at a flow rate of 16.67 lpm. They use gravimetric means to determine ambient PM mass concentrations. The PTFE filters can be analyzed for elements, but are incompatible for analysis of some elements such as carbon, and do not provide a large enough sample to analyze all chemical constituents. The FRM lo-vol samplers have the same labor-intensive limitations of the hi-vol samplers which, in air monitoring networks, allows for only intermittent, 24-hour sampling.

5.3.1.2.2 PM2.5

PM2.5 FRM samplers are updated versions of the PM10 lo-vol FRM samplers. Sampler operation is controlled by a microprocessor. Downstream of the PM10 inlet is a Well Impactor Ninety Six (WINS) impactor, a filter medium, a timer, and a flow controller.

The WINS is a particle separator, where suspended PM2.5 is separated from the PM10. The WINS impactor is a single jet impactor, which impacts into a "well" holding a 37 mm glass fiber substrate impregnated with 1 mL of tetramethyltetraphenyltrisiloxane (silicone oil) single-compound diffusion oil. The WINS impactor inertially separates fine particles of an aerodynamic diameter of 2.5 μm or less from PM10. Larger particles are captured in the oil-impregnated substrate in the wells of the impactor, and the PM2.5 and smaller particles are collected on a 47-mm filter.

The filter is made of PTFE, and has a particle collection efficiency of greater than 99.7 percent. Prior to its use, the filter is equilibrated for 24 hours at a temperature range of 20 to 23 C and at a relative humidity in the range of 20 to 40 percent, and preweighed in a laboratory. The well filter needs to be cleaned regularly or the resulting deposited material can begin to affect the cut point of the inlet.

The sampler flow rate is 16.67 lpm (1.000 m^3/hr), measured by volumetric flow rate at the temperature and pressure of the sample air entering the inlet.

5.3.1.2.3 Dichotomous Sampler

The dichotomous sampler (dichot) is another low-volume sampler (draws air at 16.67 lpm). Ninety percent of the air (15.00 lpm) flows through the fine particulate filter, and the remaining 10 percent (1.67 lpm) flows through the coarse particulate filter.

The dichotomous sampler uses a virtual impactor (region of stagnant air) to segregate the air sample into two fractions. The virtual impactor particle separator accelerates the air sample through a nozzle and then deflects the air at a right angle. Most particles smaller than 2.5 micrometers (fine fraction) will follow the higher air flow path and collect on a fine particulate filter. Particles between 2.5 and 10 micrometers (coarse fraction) have sufficient inertia to impact into the chamber below the nozzle and are collected on a coarse particulate filter. Ten

percent of the sample air flows through the coarse particulate filter and because of this, approximately 1/10 of the fine particulate are collected on the coarse particulate filter.

The coarse and fine particulate filters are 37 mm in diameter and are mounted in plastic rings. The filters are weighed to calculate mass concentrations and, where appropriate, analyzed to determine the concentration of selected chemical elements.

PM_{2.5} measurements made using the dichot with its virtual separation technique do not meet U.S. EPA requirements for PM_{2.5} sampling in terms of the impactor type, filter size, and flow rate. The dichot utilizes a PM₁₀ inlet similar to that in a lo-vol sampler, but the flow rate is only 10 percent of the total flow rate, hence introducing a potential source of difference from the lo-vol PM₁₀ sampler. Therefore, the use of this method for PM_{2.5} produces data that are not usable for compliance designation with the NAAQS for PM_{2.5}. It is a reference sampler, however, for PM₁₀.

5.3.2 General Description of Continuous Methods

Continuous methods produce hourly average PM concentration measurements in real time on a daily basis. In contrast to the intermittent sampling frequency of filter-based methods, continuous monitoring of atmospheric PM concentration has many advantages over periodic sampling; principally, the ability to assess air quality on those days missed by periodic samplers and finer time resolution. Arnold et al., (1992) collected daily 24-hour PM₁₀ samples with an automated monitor and noted that 80 percent of the highest 10 daily concentrations in 1989 and 1990 were not encountered by the commonly used every-sixth-day sampling schedule.

Continuous methods provide data that can be accessed remotely in real time, and fill many needs for information that are very impractical, if not impossible, for typical filter-based methods. These include timely warnings about episodic air pollution hazards, enhanced public health research, air quality indexing, investigating diurnal variation and short term peak exposure, model evaluation, complaint investigation, data analyses, and specifying source impacts.

Several brands of continuous measurement technologies are commercially available. These include the tapered element oscillating microbalance (TEOM) including the SES, FDMS and differential configurations, beta attenuation monitors (BAM), and continuous ambient mass monitors (CAMM).

The CAMM is based on a measure of increasing pressure drop across a membrane filter with increasing particle loading on the filter. The analyzer consists of a diffusion dryer to remove particle-bound water and a filter tape to collect PM. Babich et al. (2000), using a Fluoropore membrane filter, measured PM using the CAMM in seven U.S. cities. Results of comparison to the Harvard Impactor (HI) yielded a good correlation ($r = 0.95$) and the average of CAMM-to-HI of 1.07. When the same sampler was tested by the ARB in 1998/1999 at the Bakersfield monitoring station during the winter months, it yielded a slope of 0.74 and correlation of 0.98 (Chung et al. (2001)). Although well correlated, the sampler showed a bias of 25% compared to the FRM.

The BAM and the TEOM are the two most commonly used, commercially available, continuous PM analyzers in California. Both have been used to measure ambient PM₁₀ and PM_{2.5} mass concentrations. These two technologies are designated FEMs for PM₁₀. Because of their widespread use, a discussion of each is provided below.

5.3.2.1 Beta Attenuation Monitor

Several researchers (Jaklevic et al., 1981 and Kim et al., 1999) have used the measurement principle of absorption of beta radiation by PM on a filter as an indicator of particulate matter mass to provide real-time measurement of atmospheric PM. A Beta Attenuation Monitor (BAM) uses a lo-vol size selective inlet, a filter tape, a beta attenuation source and detector, a lo-vol flow controller, and a timer. The sampler contains a source of beta radiation (^{14}C or ^{85}Kr) and a detector to measure the beta absorption of PM accumulated on a filter. The filter material is a roll or cassette, which advances automatically on a time sequence. When particles are placed between the beta source and the detector, the beta rays are attenuated or absorbed by particles in their path. The difference in attenuation before and after the segment of the tape used to collect PM is attributed to the PM deposited on the filter. The reduction in beta ray intensity passing through the collected PM is assumed to be a function of the mass of material between the source and the detector. The degree of beta radiation attenuation is converted to PM concentration.

5.3.2.1.1 PM_{2.5} Results

Instrument inter-comparison studies of BAM PM_{2.5} units (a Met One model 1020) were conducted at Bakersfield (1998 – 1999) (Chung et al., 2001) and Fresno (1999 – 2000) (Appendix 5 part G). The results at Fresno were good (regression coefficient [R^2] of 0.97, slope of 1.07, intercept of 7.06). At Bakersfield (1998-1999), the PM_{2.5} BAM study compared one BAM equipped with a standard PM_{2.5} WINS inlet and one with sharp cut cyclone with the PM_{2.5} FRM. The comparison showed very good agreement ($R^2 = 0.99$ each, slopes of 0.91 and 0.97, and intercepts of 0.8 and 3.25, respectively). A minimum of 20 data pairs were gathered at each location (Chung et al., 2001). These studies were surveyed and considered in designing the 2001/2002 California Approved Sampler Study in Bakersfield, CA. The sampler comparison study is summarized in Appendix 5 part H. It included collocated Thermo Andersen BAMs (model FH 64 C14, here-after named And-BAM) and Met One BAMs (model 1020, here-after named Met-BAM) were configured to measure PM₁₀ and PM_{2.5}, and were operated in parallel with PM₁₀ (SSI and Partisol) and PM_{2.5} (RAAS) FRMs. Using the results of the collocated samplers, precision was determined. The accuracy was evaluated using the lo-vol FRM as the reference. Two of each of the continuous PM_{2.5} samplers were fitted with sharp-cut cyclones to isolate the PM_{2.5} fraction from PM₁₀.

The accuracy of the PM_{2.5} sampler data was determined by comparing 24-hr average data with the RAAS FRM (Table 4, Appendix 5 part H). There was excellent agreement between the continuous methods and the FRM. Regression analysis of the And-BAM and Met-BAM against the RAAS produced slopes of 1.03 and 1.03, respectively, correlations of 0.98 and 1.0 respectively, and intercepts of -1.32 and -1.58 respectively. A minimum of 102 data pairs was used in the analysis.

5.3.2.1.2 PM₁₀ Results

Data comparing the SSI to the Met One BAM PM₁₀ in Bakersfield in 1998-99 yielded limited but encouraging results ($R^2 = 0.99$ with slope of 1.01 and intercept of $1.90 \mu\text{g}/\text{m}^3$ for eight data pairs (Chung et al., 2001). A study in Fresno in 2000, however, showed a weaker relationship ($R^2 = 0.76$ with slope of 1.11 and intercept of $23.24 \mu\text{g}/\text{m}^3$ for 10 data pairs).

California Approved Sampler Study: In the ARB's 2001/2002 sampler comparison study in Bakersfield, (Appendix 5 part H) the And-BAM and Met-BAM PM₁₀'s compared favorably to the Partisol PM₁₀ yielding slopes of 1.04 and 1.13 respectively, correlation values of 0.99 and 1.0 respectively, and intercepts of -2.50 and -1.65 respectively. Thirty data pairs or more were used for comparison.

The results of comparison of continuous samplers with each other and with PM_{2.5} and PM₁₀ FRMs were compared with U.S. EPA PM₁₀ class II test specifications (slope 1 ± 0.1 , intercept $\pm 5 \mu\text{g}/\text{m}^3$, correlation ≥ 0.97 , and precision of 7%, Table 5, Appendix 5 part H). The rationale for selecting this test is provided in Appendix 5 part H.

Accuracy and precision values of these continuous samplers for both size cuts meet or exceed the proposed test specifications. Consequently, staff recommend that both the Thermo Andersen BAM (FH 64 C14 model), and the Met One BAM (1020 model) be approved for use to determine compliance with the State AAQS for PM_{2.5} and PM₁₀.

5.3.2.1.3 Tapered Element Oscillating Microbalance

The Tapered Element Oscillating Microbalance (TEOM) is a low-volume sampler (16.67 lpm) that uses a mass sensor to measure airborne particle mass in real time. A TEOM consists of a size-selective inlet, flow splitter, sample filter, microbalance, flow controller timer, and software that makes the operation of the instrument fully automatic. In practice, the TEOM collects PM on a filter located on the top of a hollow, oscillating tapered tube. A small portion of the incoming air flow is drawn through the filter and through the tube. The oscillation frequency of the tapered inlet tube is inversely proportional to the mass of the sample that is deposited on the collection filter. The frequency decreases as mass accumulates on the filter, providing a direct measure of inertial mass. The typical measurement is collected over a period of ten minutes. The sample chamber is maintained above ambient temperatures (30-50C) to minimize the effect of temperature changes and thermal expansion of the tapered element that may affect the oscillation frequency, and to reduce particle-bound water (Patashnick et al., 1991).

Several studies (Allen et al. 1997, Chung et al. 2001, Cook et al. 1995) have shown that the concentration of PM₁₀ or PM_{2.5} mass using the TEOM are often lower than PM measurements produced by other methods. Analysis of the constituents typically found in such cases indicates that this is caused by loss in the heated sample chamber of semi-volatile PM, such as ammonium nitrate and/or organic compounds. While most of the volatile components are found in the fine PM fraction (PM_{2.5}), discrepancies between PM₁₀ TEOM and reference samplers have also been observed.

Cook et al. (1995) studied the performance of the PM_{2.5} TEOM with a candidate FRM PM_{2.5} sampler at the Bakersfield monitoring station. The TEOM was operated at two temperatures, 30C and 50C, to determine the effect of temperature on measurement of PM mass. At both temperatures, the TEOM measured lower PM_{2.5} mass than the dichot or a single-stage lo-vol gravimetric sampler. PM concentrations from the TEOM at 50C were much lower (negative bias) compared to those at 30C, confirming the effect of temperature at that location on semi-volatile organics and nitrates from the filter.

In another study in Bakersfield, a PM₁₀ SSI (an FRM) and TEOM sampler operated in parallel from November 1998 to February 1999 (Appendix 5 part G). This is a period when PM concentrations, and in particular volatile components, are high. The samplers correlated well, but again, the TEOM showed a significant negative bias ($R^2 = 0.95$ with slope of 0.37). At the Fresno Supersite, for the 1999 - 2000 sampling period, similar samplers correlated as well, and less bias relative to the FRM was seen ($R^2 = 0.95$ and slope of 0.83).

When PM_{2.5} was evaluated at the Fresno Supersite, the TEOM showed poor correlation and a very large negative bias with respect to the PM_{2.5} ($R^2 = 0.31$ with a slope of 0.42). At both sites, the TEOM underestimated PM mass concentration where semi-volatile components of PM are a significant component in both PM fractions.

In general, EPA-approved TEOMs have not performed well in the two areas of the State with the most persistent PM problem, the San Joaquin Valley Air Basin and the South Coast Air Basin. The TEOM's disadvantage is that the temperature necessary for the proper operation of the microbalance volatilizes a substantial component of the PM as part of the measurement process. This is more pronounced for measurement of fine PM fraction where volatile components make up a large part of the PM. The instrument manufacturer acknowledges this situation, and has developed several enhancements in recent years that address this problem.

A Sampler Equilibration System (SES) conditions the incoming sample air to lower humidity and temperature, to reduce losses of volatile species for the TEOM (Meyer et al., 2000). The SES utilizes a Nafion dryer which fits between the flow splitter that follows the size-selective inlet and the sensor unit. This unit was evaluated by the U.S. EPA as part of the Environmental Technology Verification program. The results were encouraging; however, the negative bias still existed.

Patashnick et al. (2001) subsequently developed a differential TEOM, which is a matched pair of TEOM sensors that operate at ambient temperature. The intent of the design is to measure continuous PM mass including volatile components. Downstream flow from a common size selective inlet is passed through a dryer. At the dryer exit, the flow is split with each branch passing through an electrostatic precipitator (ESP), each of which alternately turns off and on, out of phase with the other. The flow through each ESP is directed to a separate microbalance. The difference in the effective mass measured by the two microbalances is the sum of PM masses due to non-volatile and volatile component, from which filter artifacts and effective mass due to instrument sensitivity due to temperature changes is subtracted. However, this instrument is very expensive and is not applicable for routine field use.

In 2001, Rupprecht & Patashnick developed the commercial version of the differential system, the filter dynamics measurement system (FDMS). The FDMS uses the TEOM-SES system, a dryer, a switch, a purge filter conditioning unit, and a microbalance configured in a way to measure both volatile and non-volatile PM mass.

The sampling process consists of alternate sampling and purge cycles of 5-minutes each. During the first five minutes a PM is collected on the microbalance filter and mass is determined. The next five minutes, the collected PM is purged by air from the purge filter control unit from which PM is removed. Any decrease in filter mass observed during the purging cycle is attributed to the loss of volatile PM. The mass lost is added back to the mass measured during the first cycle (before purging) thus compensating for any loss during sampling. The reported mass concentration approximates the sum of nonvolatile and volatile PM.

California Approved Sampler Study: In the latest Bakersfield sampler study (ARB, 2001 – 2002) (Appendix 5 part H), comparison of the Partisol PM10 and the FDMS produced a slope (1.05), correlation (0.97), and an intercept (1.08) that agree with the proposed test specifications (Table 5, Appendix 5 part H). Thirty data pairs were used in the comparison.

Comparison of PM2.5 FDMS with the RAAS PM2.5 produced a slope (1.03), correlation (0.99), and an intercept (2.92) that are within the acceptable ranges described in the test specifications. At least 100 data pairs were used for the comparison.

Because of its performance, the staff recommends that the FDMS be approved for use to determine compliance with the State AAQS for PM10 and PM2.5.

5.4 Recommendations

The staff recommends the following monitoring methods:

- PM10 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM10 as the method for California.
- PM2.5 Monitoring Method – Adopt the Federal Reference Method (FRM) for PM2.5 as the method for California.
- Continuous PM Samplers – Adopt those continuous PM samplers which have been found to be suitable for determining compliance with the state PM10 and PM2.5 AAQS, and designate them as California approved samplers (CAS).
- Sulfates Monitoring Method – Revise the sulfate monitoring method by deleting the current total suspended particle (TSP) sulfate method, ARB method MLD 033, and replacing it with the existing ARB method for PM10 sulfates, MLD 007.

A summary of measurement methods recommended by staff is provided below.

(a) Measurement of PM10 shall be accomplished by one of the two following techniques:

- (1) A sampler that meets the requirements of the U.S. EPA Federal Reference Method (FRM) sampler for PM10, as specified in 40 CFR Part 50, Appendix M (1997), and which employs an inertial impactor; or,
- (2) A sampler that has been demonstrated to the satisfaction of the Air Resources Board to produce measurements equivalent to the FRM.

At the time of Board consideration of this regulation, the following samplers are deemed to satisfy section (2) above, and staff is recommending their adoption by the Board: A continuous PM10 sampler as specified in Appendix 5 part H, Thermo Andersen BAM (model FH 62 C14), Met One BAM (model 1020), and Rupprecht & Patashnick FDMS (series 8500).

(b) Measurement of PM2.5 shall be accomplished by one of the following two techniques:

- (1) A sampler which meets the requirements of the U.S. EPA Federal Reference Method (FRM) sampler for PM2.5, as specified in the 40 CFR Part 50, Appendix L (1997); with either a WINS impactor or a U.S. EPA approved very sharp cut cyclone (Federal Register, 2002) to isolate PM2.5 from PM10, or
- (2) A sampler which has been demonstrated to the satisfaction of the Air Resources Board to produce measurements equivalent to the FRM.

At the time this regulation is considered by the Board, the following samplers are deemed to satisfy section (2) above, and staff is recommending their adoption by the Board: A continuous PM2.5 sampler as specified in Appendix 5 part H, with either a very sharp cut cyclone or a sharp cut cyclone: Thermo Andersen BAM (model FH 62 C14), Met One BAM (model 1020), and the Rupprecht & Patashnick FDMS (series 8500).

The rationale for these recommendations is given below

5.4.1 PM10

The Board needs to update the State PM10 method to reflect advancements and improvements in sampler technology. The FRM for PM10 is quite similar to Method P and includes requirements that are more up-to-date. The FRM sampler operation requirements

are currently used in the State and local air monitoring network. Incorporating the FRM into the AAQS will simply change legal requirements to reflect practice.

State methods have not been updated since the mid-1980's and need to recognize advances in both hi-vol and lo-vol measurement technology. Expanding the State method for PM monitoring to include all federal high-volume and low-volume samplers will allow the FRM samplers that perform well, but had not been approved for use in California, to be used for both State and federal regulatory activities. This will eliminate confusion of having two methods (State and federal) for the same parameter.

Allowing the use of the lo-vol PM10 method for the State PM10 standard offers the advantage of having one PM10 sampler produce data for both the State PM10 standard and as a possible element for a the potential federal PM coarse standard.

5.4.2 PM2.5

There are more than 80 PM2.5 FRM samplers currently in operation in California. Approval of the staff's proposal by the Board will incorporate these samplers into the State network and enhance their usefulness in the State. Adopting a continuous sampler technology that corresponds to a high degree with the FRM for PM2.5 has many programmatic and public health benefits to the State.

Staff proposes to maintain the provision in regulation for it to evaluate new measurement technologies and approve them pending a determination they are consistent with the applicable FRM.

5.4.3 Sulfates

The current sulfates standard uses MLD Method 033 for the sampling and analysis of sulfate by TSP. The ARB also has MLD Method 007 (latest version dated April 22, 2002) for measuring sulfates on PM10 filters, which uses PM10 sampling with sulfates analysis by ion chromatography. Staff recommends replacing the existing MLD Method 033 with MLD Method 007 as the proposed measurement method. This will provide the capability of using the PM10 sampling network for measuring sulfates, as well as allow for the minimization of any artifact-forming potential through the use of alkalinity-controlled filters.

5.5 Estimated Costs and Impacts

A substantial PM2.5 monitoring network, largely funded by the U.S. EPA, is now in place in California, and the U.S. EPA is in the process of implementing the last stages of the network build-up. A state-funded portion of the PM2.5 network also exists, primarily as continuous samplers. It was funded by the legislature in the late 1990's in response to Health & Safety Code section 39619.5, that requires the Board to conduct "monitoring of airborne fine particles smaller than 2.5 microns in diameter (PM 2.5)." The methods, samplers, and instruments proposed by staff include those used in, and so take full advantage of, these existing networks. Little extra expense is anticipated. However, approval of continuous samplers may result in requests for additional samplers, given their economies of operation.

The Board has had in place an extensive PM10 network for years. This proposal reaffirms the past samplers and incorporates the more recent federal samplers into the list of approved samplers for the State AAQS. The State's PM10 sampling method (Method P) has been the State ambient air monitoring method since 1985. The sampler of choice at that time was the hi-vol SSI. Implementing the proposed changes in Method P to explicitly acknowledge all FRM samplers would not incur any cost to either government entities or private businesses, because it would allow the operators of the PM samplers the option of retaining the current

sampling method. In fact, it would expand the number of acceptable samplers now in use to include heretofore unrecognized methods.

The recommended changes to Method P may result in cost saving to the extent that continuous PM10 monitoring methods are used in place of conventional filter-based methods. Continuous methods are less labor intensive than Method P and generate substantially more data. The staff cannot quantify any cost saving since it is unknown to what extent local agencies would choose to use to continuous samplers, instead of the conventional filter-based samplers used now.

Appendix 5 part I lists PM10 and PM2.5 monitoring sites and includes the various types of samplers that were being used at these sites in June 2001.

5.6 References

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6. Exposure to Particles

6.1 Area Designations

California has two ambient air quality standards for inhalable particulate matter (PM₁₀), one with a 24-hour averaging time and a level of 50 µg/m³, and an annual standard with a level of 30 µg/m³. Health & Safety Code (H&SC) section 39607(e) requires the Air Resources Board (ARB) to establish and periodically review criteria for designating areas as nonattainment, attainment or unclassifiable. The last review was completed in November 2000 (ARB 2000).

The Board designates areas based on recent ambient air quality data. The data must satisfy specific siting and quality assurance procedures established by the U. S. Environmental Protection Agency (U.S. EPA) and adopted by the ARB. An area is designated nonattainment if ambient PM₁₀ concentrations in that area violate either of the State standards at least once during the previous three calendar years.

The Board designates an area as attainment if air quality data show PM₁₀ concentrations have not violated the standards during the three previous years. Regions without adequate PM₁₀ monitoring data are designated unclassified.

Since highly irregular or infrequent events can lead to ambient PM₁₀ concentrations over the 24-hour State standard level, such exceedances are not considered violations. The area designation criteria define three types of highly irregular or infrequent events: extreme concentration, exceptional concentration, and unusual concentration.

An extreme concentration event is identified through a statistical procedure that calculates the PM₁₀ concentration that is expected to occur no more than once per year. This calculated PM₁₀ concentration is the Expected Peak Day Concentration (EPDC). The EPDC is calculated for each monitoring site using PM₁₀ concentration data collected during a three-year period. Unusual meteorology can cause an extreme concentration event. PM₁₀ concentrations measuring higher than the EPDC are identified as extreme concentrations and are not considered violations of the standard. Included in these criteria is a once per year expected rate of exceedances (on average).

An exceptional concentration event is an identifiable event that causes an exceedance of the State standard, but that is beyond reasonable regulatory control. Examples include wildfires, severe windstorms, and seismic activity.

An unusual concentration event is an anomalous exceedance of the State standard that cannot be identified as an extreme concentration or an exceptional event. Unusual concentration events apply only to areas designated attainment or unclassified.

As specified in the California Code of Regulations, title 17, section 70302, the geographical extent of an area designated for PM₁₀ usually is an entire air basin. However, the Board may designate smaller areas, based on a review of topography and meteorology, population density, location of emission sources, and existing political boundary lines.

As shown in Figure 6.1, virtually all of California violates the current State PM₁₀ air quality standards. Only Lake County is designated attainment for the State standards. In the Mountain Counties Air Basin, Amador County and portions of Mariposa and Tuolumne Counties are unclassified. The Yosemite National Park, located in Tuolumne and Mariposa Counties is designated nonattainment.

Figure 6.1. Area Designations for the State PM10 Ambient Air Quality Standards (Reference: Air Resources Board. Proposed area designations and maps. Staff report: Initial statement of reasons for proposed rulemaking, Sacramento, 2000).



Air districts with areas designated nonattainment for the State PM10 standards are not required by State law to develop plans for attaining the State PM10 standards. However, H&SC sections 40001 and 40913 require such districts to adopt and enforce rules and regulations to expeditiously attain the PM10 standards.

6.2 Monitoring Network

California has a PM10 monitoring network with over 130 monitors statewide (Figure 6.2). At each monitoring site, High Volume Size Selective Inlet samplers collect 24-hour average PM10 samples, usually once every six days. The network is described in further detail in the State and Local Air Monitoring Network Plan (ARB 2000a).

To assess the nature and extent of PM2.5 pollution in the State, ARB and local air districts began deploying PM2.5 samplers in 1998. Currently we have placed federally-approved PM2.5 mass monitoring equipment (Federal Reference Method, FRM monitors) at 81 sites across California (Figure 6.3). FRM monitors collect 24-hour average PM2.5 samples, usually once every three days. More information about the PM2.5 network is contained in ARB's 2000 California Particulate Matter Monitoring Network Description (ARB 2000b).

California's dichotomous (dichot) sampler network has been in operation since 1983. Until recently the network comprised 20 sites collecting 24-hour samples every sixth day (Figure 6.4). The dichot sampler, or virtual impactor, uses a low-volume PM10 inlet followed by a virtual impactor which splits the air stream in two, separating particles into two fractions: fine particles (PM2.5) and coarse particles (PM2.5-10). The sum of the fine and coarse fractions provides a measure of total PM10. With the implementation of the federally required PM2.5 network, a number of dichot monitoring sites were closed by early 2000. With the exception of the dichot site in Fresno, the complete phase out of the dichot network occurred in December 2000.

Figure 6.2. PM10 Mass Monitoring Sites



Figure 6.3. PM2.5 FRM Mass Monitoring Sites



Figure 6.4. Dichotomous Sampler Sites



6.3 Characterization of Ambient Air Quality

6.3.1 Overview

This section describes the characteristics of PM₁₀ and PM_{2.5} by each air basin in California, including: ambient concentrations; seasonal variations; identification of sources leading to the observed ambient particle concentrations; and the frequency distribution of the observed concentrations. To assess the spatial and temporal characteristics of PM₁₀ and PM_{2.5} concentrations, we analyzed the following ambient air quality data:

- PM₁₀ observations from Size Selective Inlet (SSI) monitors (from 1998 to 2000) (ARB 1998, ARB 2000a);
- PM_{2.5} information from the newly deployed Federal Reference Method (FRM) monitors, available only for two years (1999 and 2000) (ARB 2000b); and
- PM_{10-2.5} and PM_{2.5} data from dichotomous (dichot) samplers (from 1988 to 1999) (ARB 1998).

The data were extracted from the U.S. Environmental Protection Agency (U.S. EPA) Aerometric Information Retrieval System (AIRS) on November 15, 2001 (on May 18, 2001 for frequency distribution analysis).

For assessing the chemical composition of ambient PM₁₀ and PM_{2.5}, we reviewed information available from:

- The State's PM₁₀ and PM_{2.5} monitoring networks;
- Two-Week Samplers (TWS) used in the California Children's Health Study (Taylor et al. 1998);
- The Interagency Monitoring of Protected Visual Environments (IMPROVE) program; and
- From special studies conducted in Imperial Valley, Sacramento, San Francisco Bay Area, San Joaquin Valley (1995 Integrated Monitoring Study, IMS95), Santa Barbara County, and South Coast Air Basin (1995 PM₁₀ Enhancement Program, PTEP95).

6.3.1.1 PM₁₀ and PM_{2.5} Ambient Concentrations

Table 6.1 lists maximum 24-hour and annual average PM₁₀ concentrations in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) recorded in each air basin from 1998 through 2000 and PM_{2.5} concentrations from 1999 and 2000 – since federally approved PM_{2.5} monitors have been in operation in California. The revised State PM₁₀ and the new State PM_{2.5} standards are proposed to be based on an annual arithmetic mean. The average of quarters is the preferred method for determining the arithmetic mean. For PM₁₀ Table 6.1 includes two annual average statistics. The first is the annual geometric mean for the site with the highest value within the air basin. The annual geometric mean is used for the current State standard. The second statistic is the annual average of quarters with the highest annual average of quarters within the air basin, which is also the site with the highest annual geometric mean. We applied the data completeness criteria specified for the current State annual PM₁₀ standard for estimating both annual means. For PM_{2.5} the table lists the annual average of quarters for the site with the highest value. This is also the annual averaging used for the current federal standard. In addition, Table 6.1 shows the number of days with measured PM₁₀ concentrations over the current PM₁₀ State standard and the number of days with concentrations over the proposed State PM₁₀ standard. For PM_{2.5} the table lists the number of days with measured concentrations over the federal PM_{2.5} standard and the number of days with concentrations over the proposed State PM_{2.5} standard. No conclusions on attainment for the federal PM_{2.5} standards should be drawn from these data, since attainment designations will be based on three years of air quality data. No conclusions on attainment for the revised State PM₁₀ and new PM_{2.5} standards should be drawn from these data either, since attainment designations are part of a separate regulatory process. Detailed data by monitoring station for each air basin are presented in Appendices 6-A and 6-B. We used SSI data for PM₁₀ and FRM data for PM_{2.5} to generate these tables. Monitoring data are presently being evaluated for occurrences of exceptional events, consequently the data listed in Table 6.1 and Appendices 6-A and 6-B include data that in the future may be removed from AIRS.

Table 6.1. Maximum PM10 and PM2.5 Statistics per Air Basin

Air Basin	Year	PM10 ($\mu\text{g}/\text{m}^3$) ^{3,(1,2)}				PM2.5 ($\mu\text{g}/\text{m}^3$) ^{3,(1,2,3)}			
		Sampled Days over State Std.	Max. 24-hour Conc. (Std.=50)	Annual Average Concentrations ⁽⁴⁾		Sampled Days over Federal Std.	Sampled Days over New State Std.	Max. 24-hour Conc. (Federal Std.=65) (New State Std.=25)	Annual Avg. Concentration
				Max. Annual Geometric Mean ⁽⁵⁾ (Current Std.=30)	Max. Annual Arithmetic Average of Quarters ⁽⁷⁾ (Revised Std.=20)				Max. Annual Average of Quarters ^(6,7) (Federal Std.=15) (New State Std.=12)
Great Basin Valleys	1998	29	1116	20	51				
	1999	7	514	14	15		2	41	Incomplete data
	2000	28	3059	19	39	2	9	68	Incomplete data
Lake County	1998		35	Incomplete data	Incomplete data				
	1999		43	Incomplete data	Incomplete data			15	Incomplete data
	2000		22	10	11			9	Incomplete data
Lake Tahoe	1998	2	59	20	23				
	1999		41	17	20			21	8
	2000		50	18	20			23	8
Mojave Desert	1998	8	165	14	16				
	1999	12	109	28	32		2	48	12
	2000	11	90	19	23		4	39	12
Mountain Counties	1998	11	92	23	25				
	1999	13	125	23	25	4	13	92	11
	2000	10	98	16	18		10	48	9
North Central Coast	1998	5	76	26	28				
	1999	9	103	28	31		2	31	Incomplete data
	2000	4	74	24	26		1	26	Incomplete data
North Coast	1998		50	20	21				
	1999	11	100	21	25		4	37	9
	2000	2	51	20	22			24	9
Northeast Plateau	1998	4	66	Incomplete data	Incomplete data				
	1999	12	100	22	26		2	40	8
	2000	10	80	18	23		2	38	9

Table 6.1. Maximum PM10 and PM2.5 Statistics per Air Basin (continuation)

Air Basin	Year	PM10 ($\mu\text{g}/\text{m}^3$) ^(1,2)				PM2.5 ($\mu\text{g}/\text{m}^3$) ^(1,2,3)			
		Sampled Days over State Std.	Max. 24-hour Conc. (Std.=50)	Annual Average Concentrations ⁽⁴⁾		Sampled Days over Federal Std.	Sampled Days over New State Std.	Max. 24-hour Conc. (Federal Std.=65) (New State Std.=25)	Annual Avg. Concentration
				Max. Annual Geometric Mean ⁽⁵⁾ (Current Std.=30)	Max. Annual Arithmetic Average of Quarters ⁽⁷⁾ (Revised Std.=20)				Max. Annual Average of Quarters ^(6,7) (Federal Std.=15) (New State Std.=12)
Sacramento Valley	1998	17	130	23	29				
	1999	27	179	30	38	11	64	108	18
	2000	17	86	25	28	5	42	98	16
Salton Sea ⁽⁸⁾	1998	53	176	59	66				
	1999	63	227	66	78		15	53	15
	2000	92	268	73	85	1	16	84	17
San Diego County	1998	18	89	39	43				
	1999	24	121	48	52		70	64	18
	2000	25	139	32	34	2	55	66	16
San Francisco Bay Area	1998	5	92	23	25				
	1999	12	114	25	29	4	48	91	Incomplete data
	2000	7	76	24	27	1	47	67	14
San Joaquin Valley	1998	51	160	32	40				
	1999	62	183	50	60	42	109	136	28
	2000	64	145	45	53	32	106	160	23
South Central Coast	1998	18	110	24	25				
	1999	18	90	28	31		11	65	14
	2000	24	113	26	31		14	55	15
South Coast	1998	59	116	43	50				
	1999	55	183	65	72	12	108	121	31
	2000	83	139	55	59	20	189	120	28

Notes for Table 6.1.

- (1) Monitoring data are presently being evaluated for occurrences of exceptional events, consequently the table includes data that in the future may be identified as recorded during an exceptional event and be removed from consideration.
- (2) No conclusions on attainment for the revised State PM10 and new PM2.5 standards should be drawn from these data, since attainment designations are part of a separate regulatory process.
- (3) No conclusions on attainment for the federal PM2.5 standard should be drawn from these data, since attainment designations will be based on three years of data.
- (4) The same number of ambient PM10 observations is used for estimating each annual average for PM10; the only difference among the annual averages is the averaging method used.
- (5) For PM10 the table lists the monitoring site with the highest estimated annual geometric mean in the corresponding air basin. The same site also has the highest estimated annual arithmetic average of quarters.
- (6) For PM2.5 the table lists the monitoring site with the highest estimated annual average of quarters in the corresponding air basin.
- (7) The annual average of quarters for each monitor is estimated by first averaging the ambient 24-hour PM measurements to obtain quarterly means and then averaging the estimated quarterly means (as generally described in Appendix N to 40 CFR Part 50: National Ambient Air Quality Standards for Particulate Matter; Final Rule. July 18, 1997).
- (8) Salton Sea PM10 statistics exclude data from the Calexico-East Site, because data from this site do not represent widespread exposure.

As shown in Table 6.1, with the exception of Lake County, all air basins exceed the State 24-hour PM10 standard of 50 $\mu\text{g}/\text{m}^3$. The Great Basin Valleys Air Basin recorded the three highest 24-hour PM10 levels in the State, 3059 $\mu\text{g}/\text{m}^3$ in 2000, 1116 $\mu\text{g}/\text{m}^3$ in 1998, and 514 $\mu\text{g}/\text{m}^3$ in 1999. Four air basins exceeded the current annual PM10 State standard of 30 $\mu\text{g}/\text{m}^3$: Salton Sea, San Diego, San Joaquin Valley, and South Coast. The Salton Sea Air Basin had the highest PM10 annual geometric means - 73 $\mu\text{g}/\text{m}^3$ in 2000 and 66 $\mu\text{g}/\text{m}^3$ in 1999 - followed by the South Coast Air Basin - 65 $\mu\text{g}/\text{m}^3$ in 1999. In air basins exceeding both current State PM10 standards, the ratios of maximum 24-hour and annual concentrations compared to the respective standards suggest that the 24-hour State standard is controlling (Table 6.2). As shown in Table 6.1, with the exception of Lake County, all air basins exceeded the proposed annual PM10 State standard of 20 $\mu\text{g}/\text{m}^3$. Currently, eight air basins (Great Basin Valleys, Mountain Counties, Sacramento Valley, Salton Sea, San Diego County, San Francisco Bay Area, San Joaquin Valley, and South Coast) recorded 24-hour concentrations over the federal PM2.5 standard. Values over the 24-hour standard in Mountain Counties in 1999 may have been caused by extensive wildfires. With the exception of Great Basin Valleys, Mountain Counties and San Francisco Bay Area, the other five air basins also recorded maximum annual averages above the federal annual PM2.5 standard. In comparison, all air basins - with the exception of Lake County and Lake Tahoe - recorded 24-hour concentrations over the proposed State PM2.5 standard of 25 $\mu\text{g}/\text{m}^3$ and seven air basins (Sacramento Valley, Salton Sea, San Diego County, San Francisco Bay Area, San Joaquin Valley, South Central Coast and South Coast) also had maximum annual averages above the proposed State annual PM2.5 standard.

Table 6.2. Ratios of yearly maximum 24-hour PM10 and annual average concentrations compared to the respective State standards.

Air Basin	Year	Max. 24-hour/Std. (Std. = 50 $\mu\text{g}/\text{m}^3$)	Max. Annual Avg ⁽¹⁾ /Std. (Std. = 30 $\mu\text{g}/\text{m}^3$)
Salton Sea	1998	3.5	1.8
	1999	4.5	2.1
	2000	5.4	3.1
San Diego	1998	1.8	1.3
	1999	2.4	1.6
	2000	2.8	1.1
San Joaquin Valley	1998	3.2	1.1
	1999	3.7	1.7
	2000	2.9	1.5
South Coast	1998	2.3	1.6
	1999	3.7	2.2
	2000	2.8	1.8

(1) For the air quality monitoring site with the highest estimated annual geometric mean for PM10 in the corresponding air basin.

Background sites are intended to quantify regionally representative PM concentrations for sites located away from populated areas and other significant emission sources. Background concentrations are defined as concentrations that would be observed in the absence of anthropogenic emissions of PM and the aerosol particles formed from anthropogenic precursor emissions of VOC, NO_x and SO_x. However, it is very difficult to find true background sites. Depending on the season and meteorological conditions, even the monitoring sites located in pristine areas can be influenced by anthropogenic emissions and transport. This in turn may lead to higher annual average PM concentrations. Annual average PM concentrations from the IMPROVE network are presented in Table 6.3 (aggregated over a three year period, March 1996 to February 1999) (Malm et al. 2000).

Table 6.3. Annual Average PM10 and PM2.5 Concentrations at IMPROVE Sites

Site	Annual Average PM10 (ug/m ³)	Annual Average PM2.5 (ug/m ³)
Lassen Volcanic National Park	5.06	2.68
Pinnacles National Monument	10.97	4.55
Point Reyes National Seashore	12.42	4.01
Redwood National Park	7.45	2.44
San Geronio Wilderness Area	13.72	7.20
Sequoia National Park	18.64	8.86
Yosemite	8.52	4.33

As part of California's PM2.5 program, three locations have been selected to measure background PM2.5 concentrations: Point Reyes National Seashore in Northern California, and San Rafael Wilderness and San Nicholas Island in Southern California. These sites are located away from populated areas and other significant sources of particulate and particulate precursor emissions. The sites have been in operation since December 2000. Data from these sites are not yet available. However, data obtained from the IMPROVE program for Point Reyes from March 1996 through February 1999 indicate that the annual average concentrations were 4.01 µg/m³ for PM2.5 and 12.42 µg/m³ for PM10. PM10 and PM2.5 data collected at San Nicolas Island as part of PTEP95 program show a PM10 annual average of 18.7 µg/m³ and a PM2.5 annual average of 6.82 µg/m³ (Kim et al. 2000). In addition, as part of California Regional PM10/PM2.5 Study (CRPAQS), we will be evaluating data from several sites, including one site in a desert locality and one site in a forested area for determining regional background PM concentrations.

6.3.1.2 Historical Trends

We determined PM concentration trends using dichot PM2.5, PM10-2.5, and PM10 data collected from 1988 through 1999 at selected urban sites. The dichot sampler uses a low-volume PM10 inlet followed by a virtual impactor, which splits ambient air samples into fine (PM2.5) and coarse (PM10-2.5) particle fractions. The sum of these two fractions provides a measure of total PM10. We estimated annual arithmetic mean concentrations, by averaging quarterly (January through March, April through June, July through September, and October through December) arithmetic means. Data illustrated in Figure 6.5 indicate that, overall, the annual means of PM2.5 decreased until 1998, increasing in 1999 at most sites. Monthly rainfall

data obtained from National Weather Service stations indicate 1999 was a much drier year than 1997 and 1998, contributing to higher particulate matter concentrations in 1999. As shown in Figures 6.6 and 6.7, the coarse PM10-2.5 and the PM10 annual means exhibited similar trends, with a slightly less pronounced decrease in coarse fraction concentrations in the 1994 to 1999 period.

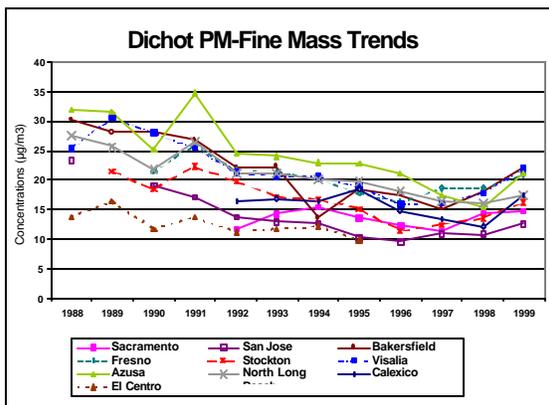


Figure 6.5. Annual trends in PM2.5 concentrations

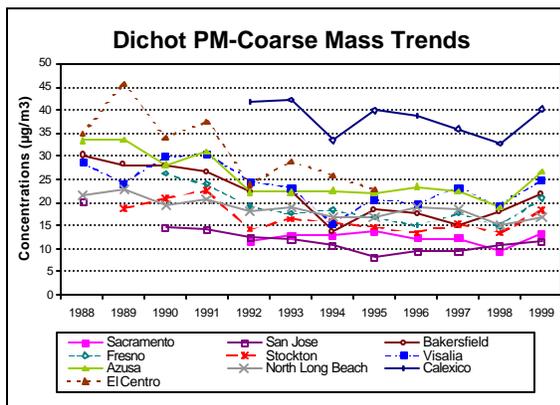


Figure 6.6. Annual trends in Coarse PM concentrations

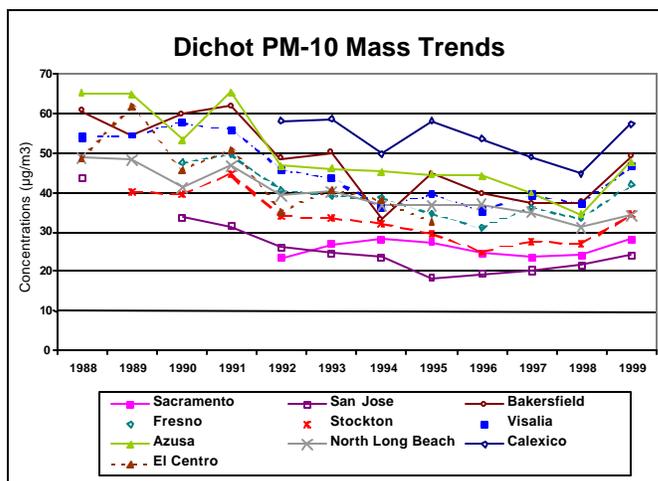


Figure 6.7. Annual trends in PM10 concentrations

6.3.1.3 Seasonality

Plots showing seasonal variation in ambient particulate matter concentrations were generated using FRM data for PM2.5 and SSI data for PM10. These seasonality plots are included in the subsections of this chapter describing particulate matter air quality in each air basin. The data represent the peak 24-hour PM concentration per month for each size fraction. In some cases PM2.5 is higher than PM10. This can occur for two reasons. First, the measurements are made on two different sampling systems and therefore have different levels of accuracy, precision,

and uncertainty. Second, in some cases peak PM10 and PM2.5 concentrations do not occur on the same day. The plots were generated to provide an understanding of the seasonality of peak concentrations, not to compare specific PM10/PM2.5 concentrations to each other.

In general, there are a number of air basins which exhibit strong seasonal patterns. Areas such as Sacramento, the San Joaquin Valley, and the San Francisco Bay Area record much higher PM2.5 and PM10 concentrations in the winter months (Figure 6.8). During this time of year, the PM2.5 size fraction drives the particulate matter concentrations.

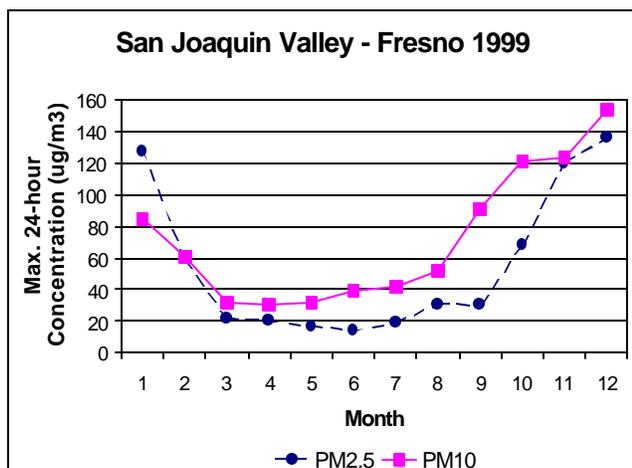


Figure 6.8. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations

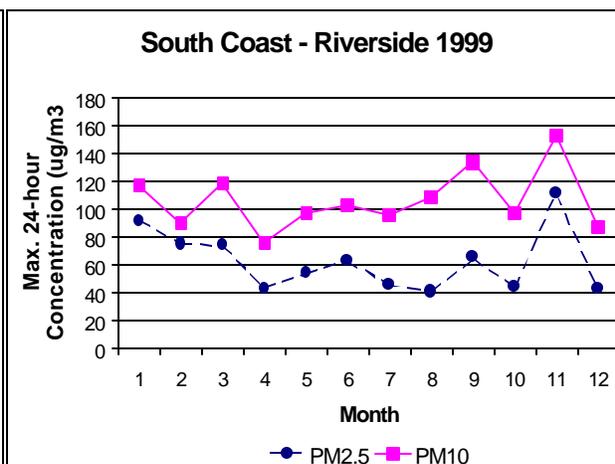


Figure 6.9. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations

Other areas such as the South Coast have a much more uniform distribution (Figure 6.9). In the South Coast, PM10 and PM2.5 concentrations remain high throughout the year.

In yet other areas there are specific episodic exceedances due to fugitive dust events (Great Basin Valleys, Salton Sea), or fires (Mountain Counties).

We used data collected with dichot samplers from 1998 to 2000 to estimate the ratios of PM2.5 to PM10 concentrations (e.g., Table 6.4). Figure 6.10 shows that in general, the average PM2.5 portion of PM10 was higher during the winter (November to February) than during the rest of the year (March to October). These seasonal differences were most pronounced in the San Joaquin Valley (75% in the winter and 38% during the rest of the year) and least prominent in the Mojave Desert (46% in winter and 39% during the rest of the year). No seasonal differences were apparent in the Great Basin Valleys Air Basin (see data for the Coso Junction monitoring site in Table 6.4)

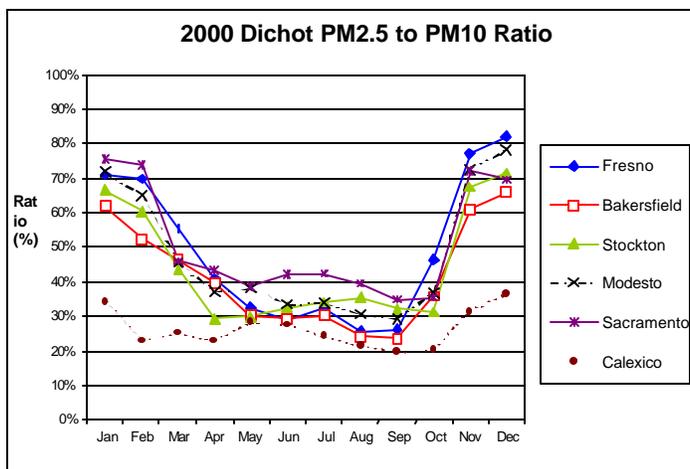


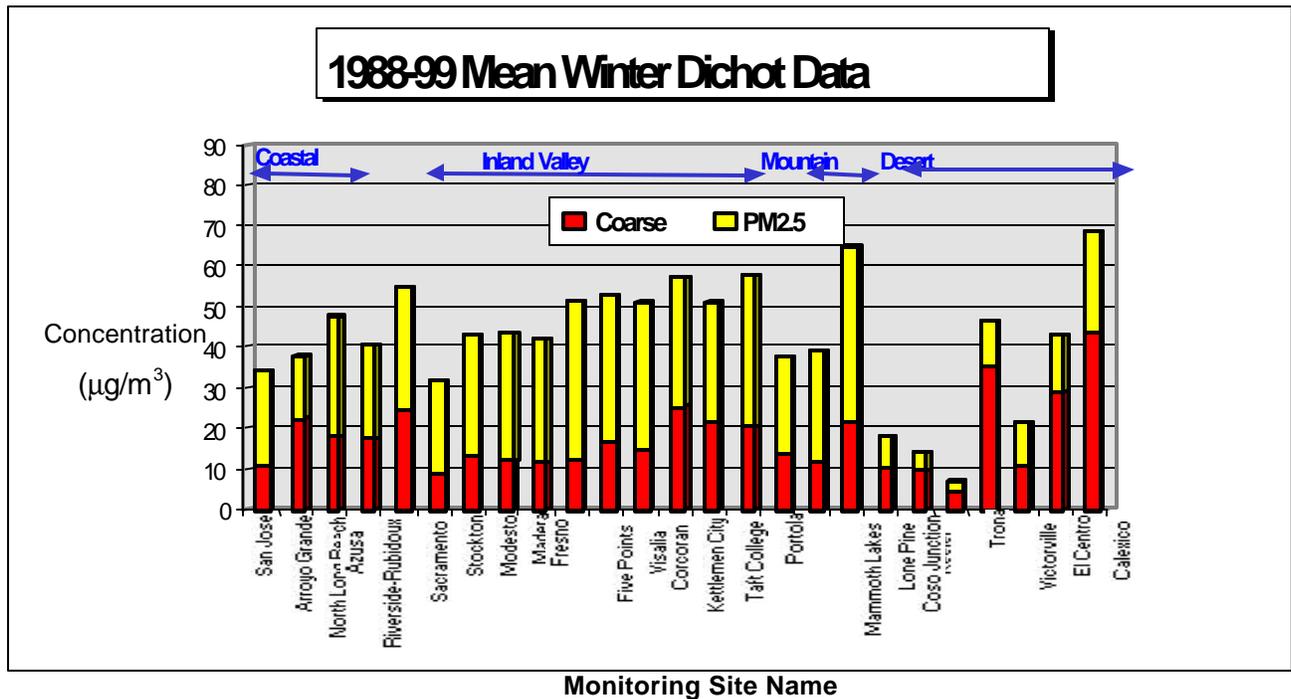
Figure 6.10. Monthly variation in the PM2.5 to PM10 ratio

Table 6.4. Ratios of monthly average PM2.5 to PM10 mass with a reported minimum and maximum at each location, 1999. Ratios were estimated using dichot data.

1999	Portola	Sacramento	San Jose	Modesto	Fresno	Bakersfield	Coso Jct	Victorville	Long Beach	Calexico
Jan	0.71	0.78	0.65	0.73	0.82	0.71	0.27	0.49	0.62	0.41
Feb	0.59	0.60	0.51	0.68	0.68	0.58	0.43	0.48	0.54	0.41
Mar	0.54	0.61	0.39	0.51	0.53	0.44	0.30	0.38	0.45	0.31
Apr	0.49	0.49	0.42	0.40	0.47	0.39	0.36	0.56	0.45	--
May	0.32	0.39	0.34	0.31	0.33	0.28	0.38	0.36	0.39	--
Jun	0.30	0.38	0.39	0.32	0.35	0.27	0.34	0.37	0.47	0.30
Jul	0.28	0.44	0.52	0.34	0.35	0.26	0.39	0.39	0.45	0.24
Aug	0.43	0.48	0.52	0.38	0.31	0.28	0.30	0.34	0.46	0.24
Sep	0.32	0.41	0.52	0.37	0.28	0.31	0.38	0.34	0.45	0.21
Oct	0.40	0.42	0.51	0.34	0.38	0.34	0.30	0.34	0.49	0.26
Nov	0.74	0.66	0.60	0.63	0.68	0.58	0.36	0.43	0.61	0.26
Dec	0.71	0.45	0.59	0.72	0.67	0.60	0.32	0.45	0.58	0.32
Max Ratio	0.91	0.86	0.80	0.85	0.88	0.82	0.73	0.75	0.96	0.59
Min Ratio	0.19	0.13	0.30	0.11	0.19	0.16	0.14	0.20	0.30	0.17

Seasonal variations in meteorological conditions and in the activity of emissions sources cause the size, composition, and concentration of particulate matter to vary by region and by season. Because air typically flows inland from the Pacific Ocean, the percentage of days exceeding the California 24-hour standard is generally lower along the coast than in inland areas. As the air parcel moves downwind across areas with significant anthropogenic activities, fresh emissions and gas-to particle conversion cause PM concentrations to increase with distance, for example, along the North Long Beach, Azusa, Riverside-Rubidoux corridor. PM2.5 concentrations are highest during the winter months (November to February). Cool temperatures, low inversion layers, and humid conditions favor the formation of secondary nitrate and sulfate particles, which are found predominantly in the fine fraction. Residential wood combustion also leads to higher PM2.5 concentrations during the winter. From 1988 to 1999, in the San Joaquin Valley, 97% of the four highest 24-hour PM2.5 concentrations and 68% of the four highest PM10 concentrations occurred during the winter. In the South Coast 53% of the four highest PM2.5 and 58% of the highest PM10 levels occurred in the winter season. Soil dust is the dominant contributor to PM10 in the summer. A desert environment generally has low PM concentrations, but on occasion high winds cause significant increases in dust.

Figure 6.11. Winter average PM10 and PM2.5 concentrations by region



6.3.1.4 Source Apportionment

Chemical Mass Balance (CMB) models are used to establish which sources and how much of their emissions contribute to ambient particulate matter concentrations and composition. CMB models use chemical composition data from ambient PM samples and from emission sources. These data are often collected during special source attribution studies. The quality of source apportionment results depends on the adequacy of the chemical markers used for each potential source and of the ambient chemical composition data used in the analysis, as well as the inclusion of appropriate sources. The source attribution data presented in this report was derived from a variety of studies with differing degrees of chemical speciation. In general, however, the source categories can be interpreted in the following manner. The road and other dust, wood smoke, cooking, vehicle exhaust, and construction categories represent sources which directly emit particles. Road and other dust represents the combination of mechanically disturbed soil (paved and unpaved roads, agricultural activities) and wind-blown dust. Wood smoke generally represents residential wood combustion, but may also include combustion from other biomass burning such as agricultural or prescribed burning and cooking. The vehicle exhaust category represents direct motor vehicle exhaust particles from both gasoline and diesel vehicles. Construction reflects construction and demolition activities. Ammonium nitrate and ammonium sulfate represent secondary species (i.e., they form in the atmosphere from the emissions of nitrogen oxides (NO_x), sulfur oxides (SO_x), and ammonia). Combustion sources such as motor vehicles and stationary sources contribute to the NO_x that forms ammonium nitrate. Mobile sources such as diesel vehicles, locomotives, and ships and stationary combustion sources emit the SO_x that forms ammonium sulfate. Ammonia sources include animal feedlots, fertilizers, and motor vehicles. The other carbon sources category reflects organic sources not included in the source attribution models, such as natural gas combustion, as well as secondary organic carbon formation. The unidentified category represents the mass that cannot be accounted for by the identified source categories. It can include particle-bound water, as well as other unidentified sources. Figure 6.12 illustrates the results of the PM2.5

source apportionment analysis conducted for Fresno using ambient air samples collected January 1st through 4th, of 1996.

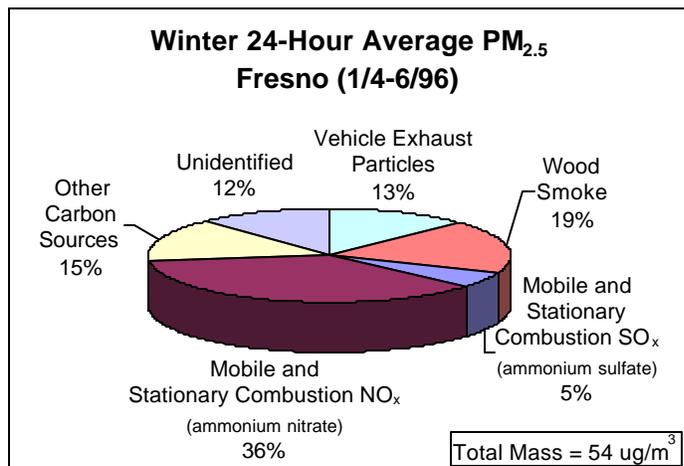


Figure 6.12. Source categories contributing to PM_{2.5} in Fresno during the winter.

For the area represented by the Children’s Health Study and by the IMPROVE network, specific source apportionment analysis has not been conducted. Instead, the primary chemical components of ambient PM_{2.5} are shown. As discussed above, nitrate and sulfate are secondary species. Soil, elemental carbon, as well as much of the organic carbon are primary species.

New data that is becoming available will allow for better, and more consistent source apportionment. For example, the PM_{2.5} speciation samplers measure the species needed for source apportionment analysis on the same sampler. Previously, ions and carbon were measured on the SSI, and elements on the dichotomous samplers, requiring data from different samplers to be combined for a complete picture. Data from special studies such as the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) and the 1997 Southern California Ozone Study (SCOS97) will also provide more detailed speciation data for source apportionment analysis.

As mentioned earlier, the size, concentration, and chemical composition of PM vary by region and by season. A number of areas exhibit strong seasonal patterns. Other areas have a much more uniform distribution – PM concentrations remain high throughout the year.

In the San Joaquin Valley, the San Francisco Bay Area, and the Sacramento area, there is a strong seasonal variation in PM, with higher PM₁₀ and PM_{2.5} concentrations in the fall and winter months. The higher concentrations are due to increased activity for some emissions sources and meteorological conditions that are conducive to the build-up of PM. During the winter, the PM_{2.5} size fraction drives the PM concentrations, and the major contributor to high levels of ambient PM_{2.5} is the secondary formation of PM caused by the reaction of NO_x and ammonia form ammonium nitrate. Emissions from wood smoke – mostly from fireplaces and wood stoves – vehicle exhaust particles, and other carbon sources also contribute significantly to PM_{2.5} levels. The San Joaquin Valley also records high PM₁₀ levels during the fall. During this season, the coarse fraction (PM_{10-2.5}) – mostly road and agricultural dust - drives the PM concentrations.

In the South Coast region, PM₁₀ and PM_{2.5} concentrations remain high throughout the year. The more uniform activity patterns of emission sources, as well as less variable weather patterns, leads to this more uniform concentration pattern. On an annual basis, dust from roads and construction is the major contributor to ambient PM₁₀. NO_x emitted from mobile and

stationary combustion sources, combined with ammonia, contributes significantly. Vehicle exhaust particles and other carbon sources also contribute.

In other areas, high PM can be more episodic than seasonal. For example, in Owens Lake in the Great Basin Valleys Air Basin, episodic fugitive dust events lead to very high PM₁₀ levels, with soil dust as the major contributor to ambient PM₁₀. In Imperial Valley in the Salton Sea Air Basin, fugitive dust and dust from roads and farming operations lead to high PM₁₀ levels.

Background sites often exhibit very different profiles. In national parks like Redwoods, Lake Tahoe, and Pinnacles, organic carbon is the major component of annual average fine particulate matter (Sisler 1996). Figures 6.13 and 6.14 show the PM_{2.5} chemical composition at two of the PM_{2.5} program background sites. Data for Point Reyes are from analysis of ambient air collected in 1995 as part of the IMPROVE program. Composition data for San Nicholas Island were collected as part of the PTEP95 study. The data show sea salt, sulfate, and organic carbon are the largest contributors to PM_{2.5} at both sites. Organic carbon particles in background sites originate from natural combustion processes such as wild fires and organic aerosols formed from VOC emissions from vegetation. In addition, natural emissions of gaseous sulfur compounds contribute to the background sulfate component.

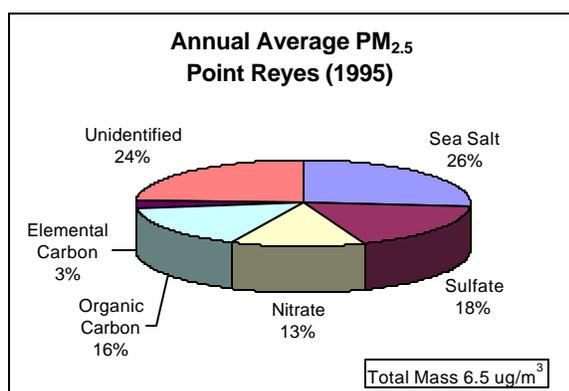


Figure 6.13. Chemical composition of ambient PM_{2.5} in the Point Reyes National Seashore

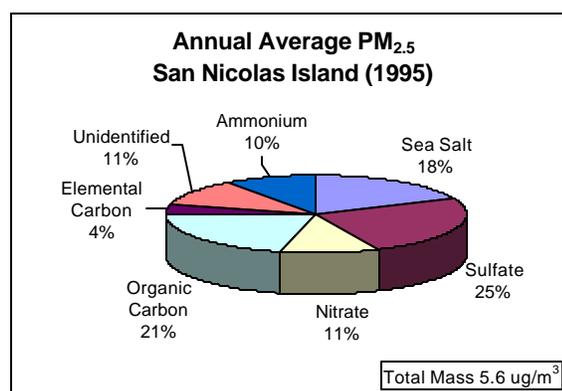


Figure 6.14. Chemical composition of ambient PM_{2.5} in San Nicolas Island

6.3.1.5 Frequency of Measured PM₁₀ and PM_{2.5} Concentrations

We generated histograms that represent the frequency distribution of observed particulate matter concentrations at all sites within an air basin. Separate histograms were plotted for 1998-2000 for PM₁₀ (Appendices 6-C1 to 6-C3) and 1999-2000 for PM_{2.5} observations (Appendices 6-D1 and 6-D2). As with previous analyses, the PM₁₀ data is derived from the SSI monitor and the PM_{2.5} data from the FRM monitor. These data were obtained from AIRS on May 18, 2001. Figures 6.15 and 6.16 show the PM_{2.5} histograms generated for the North Coast Air Basin and the South Coast Air Basin, respectively. Each bar represents the number of observations within the specified range. For example, for PM_{2.5} the first bar is the number of observations between 0 and 5 $\mu\text{g}/\text{m}^3$, the second between 5 and 10 $\mu\text{g}/\text{m}^3$ and so on. The histograms provide information on the frequency of high concentrations within each air basin, as well as the most frequent, or predominant concentration levels, and can provide insight into the impact of setting the standards at varying levels.

In many of the air basins, 80% of the PM10 observations are below 30 to 35 $\mu\text{g}/\text{m}^3$. However, other air basins, such as the San Joaquin Valley and the South Coast, have significant numbers of observations that are much higher. In these areas, the 80% cumulative frequency is not reached until about 70 $\mu\text{g}/\text{m}^3$. For PM2.5, in many of the air basins, most of the observations are below 10 to 20 $\mu\text{g}/\text{m}^3$ (in the North Coast Air Basin example shown on Figure 6.15, all observations are below 30 $\mu\text{g}/\text{m}^3$). However, as with PM10, areas such as the San Joaquin Valley and the South Coast (Figure 6.16), exhibit a distribution such that the 80% cumulative frequency is reached at 35 to 40 $\mu\text{g}/\text{m}^3$.

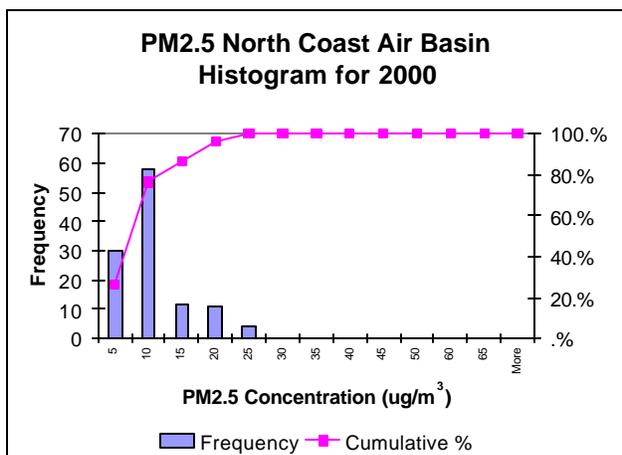


Figure 6.15. Frequency distribution of ambient PM2.5 levels in the North Coast Air Basin (measurements from all monitors in the air basin).

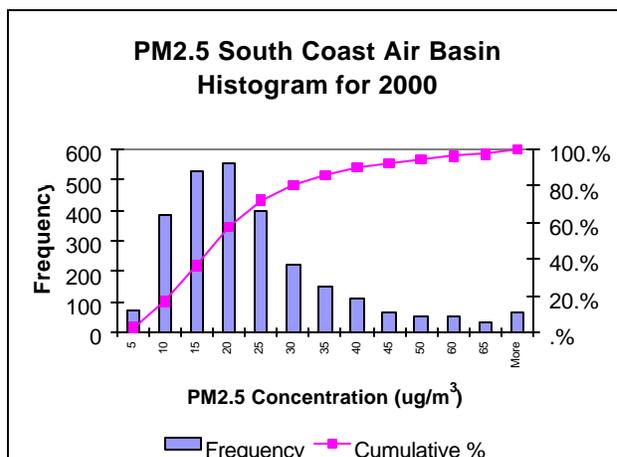


Figure 6.16. Frequency distribution of ambient PM2.5 levels in the South Coast Air Basin (measurements from all monitors in the air basin).

6.3.1.6 Diurnal Variation in PM10 levels

We used PM10 data collected with a Tapered Element Oscillating Monitor (TEOM) at two rural agricultural locations in the Sacramento Valley and filter-based samples collected at one urban and one rural site in the San Joaquin Valley to analyze hourly variations in PM10 levels. TEOM samplers collect PM10 samples continuously, while filter-based samples were collected every three hours. PM10 levels can vary significantly within a day and continuous monitoring data are most useful to study these variations. On a rice straw burning day, in the Sacramento Valley, PM10 concentrations reached 4 to 5 times the level of the State 24-hour standard for several hours, although the 24-hour average PM10 level was barely above the current State standard. In the San Joaquin Valley, PM10 levels varied significantly in urban Fresno during the course of a winter day, with the highest concentrations occurring at nighttime, while PM10 concentrations did not vary much throughout the day in rural SW Chowchilla. Chemical composition data indicate diurnal variations in ammonium nitrate were the primary cause of the PM10 variations in SW Chowchilla. The rise in PM10 concentrations in Fresno corresponded mostly to significant nighttime peaks in vegetative burning, mobile sources, and excess organic carbon.

6.3.1.7 Particle Size Distribution

Data on particle size distribution is limited. During the IMS95 winter study in San Joaquin Valley, air samples using a Micro-Orifice Uniform Deposit Impactor (MOUDI) sampler were collected at Bakersfield (Chow et al. 1997). The MOUDI partitions ambient PM samples into nine size cuts between 0.054 and 15 μm . We used these data to study the size distribution of PM10

components. Soil components were concentrated mainly in the larger size fractions ($>3.16 \mu\text{m}$), the coarse component of PM10. The size of nitrate particles peaked between 1 and $1.78 \mu\text{m}$, while organic carbon particles appeared in both larger (peak between 0.37 and $1 \mu\text{m}$) and smaller ($<0.054 \mu\text{m}$) size fractions.

6.3.2 Characterization of Ambient Particulate Matter by Air Basin

This section describes the characteristics of ambient particulate matter for each of the fifteen air basins in the State. The information presented includes: maximum 24-hour and annual average PM10 and PM2.5 concentrations, seasonal variation of particulate matter levels; frequency of measured PM10 and PM2.5 concentrations, and ratios of PM2.5 to PM10 levels. Where available, source attribution information is also included. For areas where no source attribution analyses are available, the primary chemical composition of ambient PM10 or PM2.5 is illustrated. Based on the 2000 annual average PM10 emission inventory, we identify the main sources of directly emitted PM10.

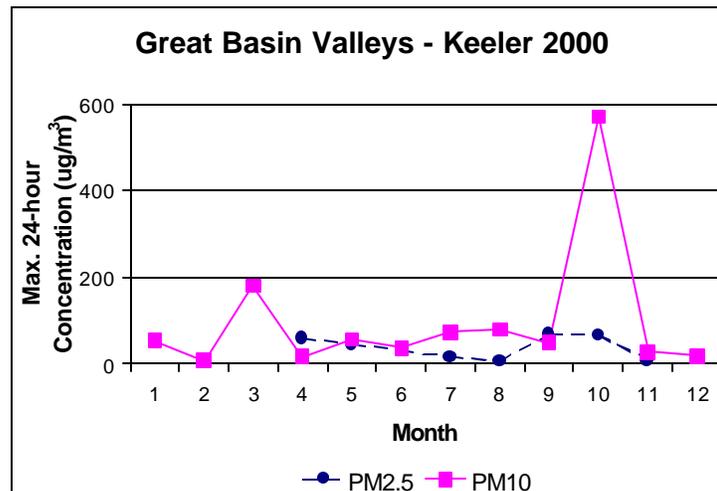


On an annual basis, particulate levels are low in the Great Basin Valleys Air Basin ($PM_{10} = 14$ to $20 \mu\text{g}/\text{m}^3$). Eighty percent of the 24-hour PM_{10} observations were below 25 to $30 \mu\text{g}/\text{m}^3$ and 80% of the 24-hour $PM_{2.5}$ observations were under 10 to $15 \mu\text{g}/\text{m}^3$. However, on a short term, episodic basis, Great Basin Valleys may record some of the highest monitored levels in the State. During windy conditions, dust from the Owens and Mono dry lakebeds produce extremely high concentrations of particulate in the air, reaching $3059 \mu\text{g}/\text{m}^3$ in Mono in 2000 and $1116 \mu\text{g}/\text{m}^3$ in Owens in 1998. Particulate levels exceeded the 24-hour State PM_{10} standard 64

times in the 1998-2000 period and two observations over the federal $PM_{2.5}$ standard were recorded in the 1999-2000 period. The Great Basin Valleys Air Basin did not exceed the PM_{10} annual standard.

Figure 6.17 illustrates the monthly variation of the maximum daily PM_{10} and $PM_{2.5}$ concentrations at Keeler in 2000. Keeler is located near the Owens dry lakebed. High PM_{10} concentrations can occur at any time of the year, though more frequently in the spring and fall. $PM_{2.5}$ concentrations are relatively uniform most of the year.

Figure 6.17. Monthly variation in maximum 24-hour PM_{10} and $PM_{2.5}$ concentrations at Keeler



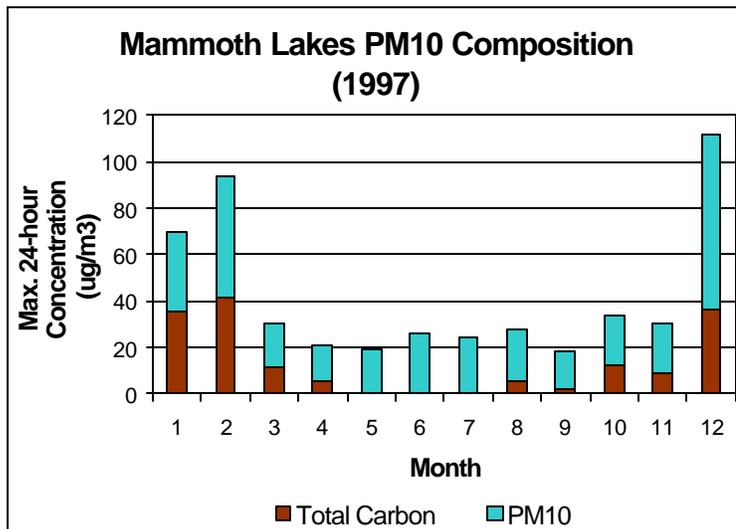
*The monitors used to measure PM_{10} and $PM_{2.5}$ are different and occasionally recorded concentrations of $PM_{2.5}$ which are greater than PM_{10} .

Data obtained from the Keeler and Coso Junction dichotomous samplers in 1999 indicate the $PM_{2.5}$ component of PM_{10} ranges from 14% to 89%, with an annual average of 33%.

Based on the 2000 annual PM10 emission inventory, the major sources of directly emitted particulate matter in the Great Basin Valleys Air Basin are unpaved road dust, windblown dust, residential wood burning, and wildfires.

In the town of Mammoth Lakes, high PM10 concentrations usually occur during the winter months (December – February). Figure 6.18 shows the monthly variation of the maximum daily PM10 concentrations in 1997. The chart also illustrates how much of the measured PM10 is total carbon. During the winter, total carbon comprises 30% to 50% of the measured PM10. Sources of carbon include residential wood combustion and motor vehicles.

Figure 6.18. Monthly variation in maximum 24-hour PM10 and total carbon levels at Mammoth.



Lake County Air Basin

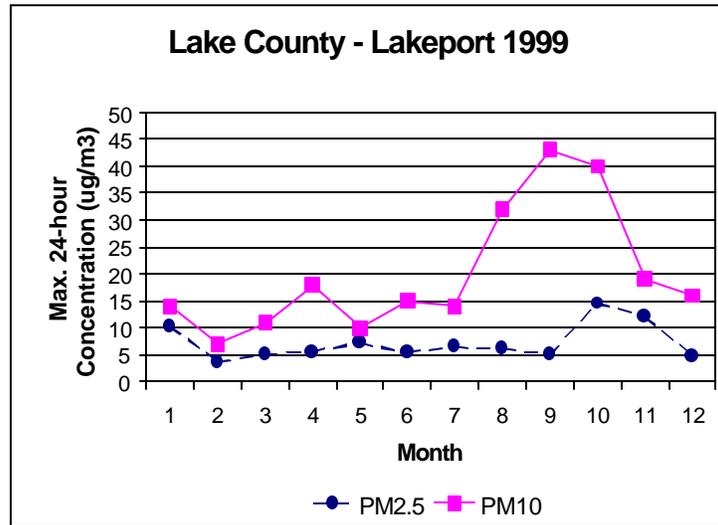


On average, Lake County has among the lowest particulate levels in the State. Maximum 24-hour PM10 ranges from 22 to 35 $\mu\text{g}/\text{m}^3$ and maximum 24-hour PM2.5 from 9 to 15 $\mu\text{g}/\text{m}^3$, with no exceedances of either standard.

Figure 6.19 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations at Lakeport in 1999. PM10 levels are highest from August through October and are low the rest of the year. PM2.5 concentrations peak in October and November.

Based on estimated 2000 annual average PM10 emission inventory data, the principal sources of directly emitted particulate matter in Lake County are unpaved road dust and residential wood burning. Occasionally, Lake County also has significant levels of particulates from wildfires.

Figure 6.19. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Lakeport



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

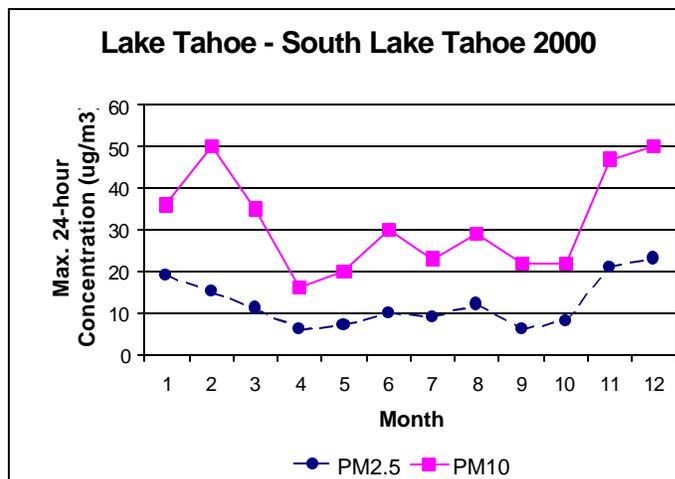
Lake Tahoe Air Basin



In the Lake Tahoe Air Basin, particulate levels exceeded the 24-hour State PM₁₀ standard two times in the 1998-2000 period, but fine particulate levels were well below the federal PM_{2.5} standards. The State annual PM₁₀ standard was also not exceeded. In 1998, 80% of the PM₁₀ observations were below 45 to 50 $\mu\text{g}/\text{m}^3$. In the last two years, 80% of the PM_{2.5} observations were below 10 to 15 $\mu\text{g}/\text{m}^3$.

Figure 6.20 illustrates the monthly variation of the maximum daily PM₁₀ and PM_{2.5} concentrations in South Lake Tahoe in 2000. PM₁₀ as well as PM_{2.5} levels are highest during the late fall and winter (November through February), and are lowest in the in spring and summer.

Figure 6.20. Monthly variation in maximum 24-hour PM₁₀ and PM_{2.5} concentrations at South Lake Tahoe



*The monitors used to measure PM₁₀ and PM_{2.5} are different and occasionally recorded concentrations of PM_{2.5} which are greater than PM₁₀.

Based on the 2000 annual PM₁₀ emission inventory, the major sources of directly emitted particulate matter are unpaved road dust and residential wood burning.

Mojave Desert Air Basin



In the Mojave Desert Air Basin, particulate levels exceeded the 24-hour State PM10 standard 31 times in the 1998-2000 period, but fine particulate levels were below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. Eighty percent of the PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 observations were below 20 to 25 $\mu\text{g}/\text{m}^3$.

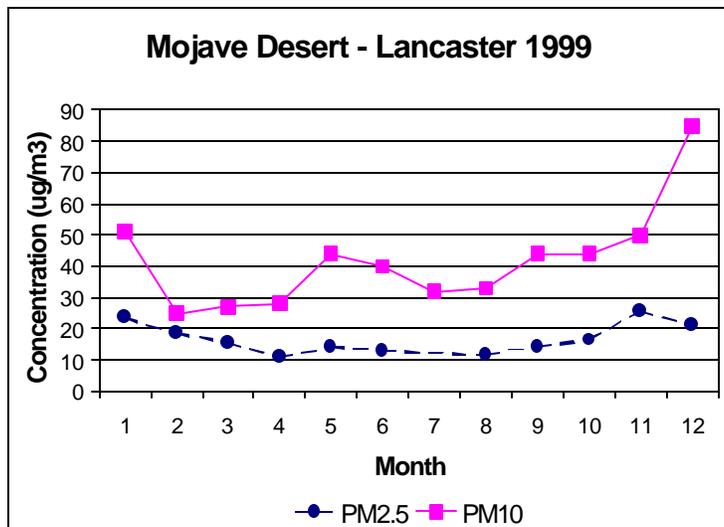
Figure 6.21 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Lancaster in 1999. PM10 as well as PM2.5 levels are highest during the winter months - December and January. During the rest of the year, PM2.5 levels are quite low, while PM10 levels fluctuate with no distinct pattern.

Data from the dichotomous sampler at Victorville in 1999 indicate the PM2.5 component of PM10 ranges from 19% to 75%. The average PM2.5 fraction of PM10 is 46% from November to February and 39% from March to October.

Ambient air quality data from 1997 through 1999 show low levels of secondary nitrate and sulfate particulate in the Mojave Desert, indicating that most of the particulate matter is primary in origin.

Based on the 2000 annual PM10 emission inventory, the major contributors to primary particulates in the Mojave Desert Air Basin are unpaved road dust, windblown dust, paved road dust, and construction related dust. A few point source categories, such as mineral processing facilities, also contribute significant emissions.

Figure 6.21. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Lancaster



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

**Mountain Counties
Air Basin**



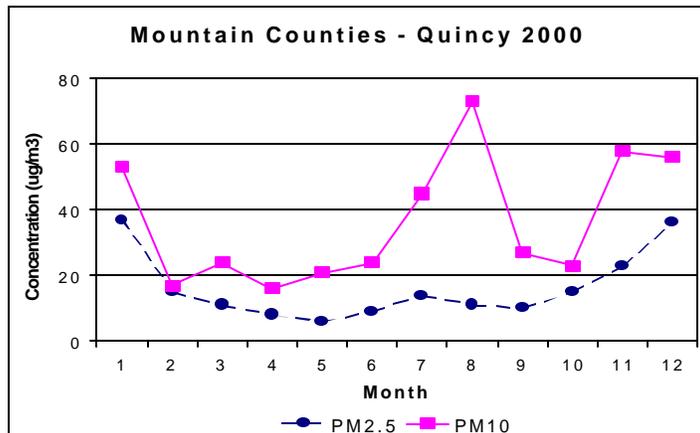
In the Mountain Counties Air Basin, particulate levels exceeded the 24-hour State PM10 standard 34 times in the 1998-2000 period and four observations over the federal 24-hour PM2.5 standard were recorded in 1999. Fine particulate exceedances in 1999 were most probably due to wild fires which occurred in the late summer and early fall. Neither the State PM10 nor the federal PM2.5 annual standards were exceeded. In the Mountain Counties 80% of the PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 readings were below 10 to 15 $\mu\text{g}/\text{m}^3$.

Figure 6.22 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Quincy in 2000. Highest ambient concentrations of PM10 occur during the summer and winter months, while fine particulate matter levels are highest in the late fall and early winter months of November through January.

Figure 6.22. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Quincy

Data obtained from the Portola dichotomous sampler in 1999 show that the PM2.5 portion of PM10 ranged from 19% to 91%. The average PM2.5 fraction of PM10 was 72% from November through January and 41% during the rest of the year.

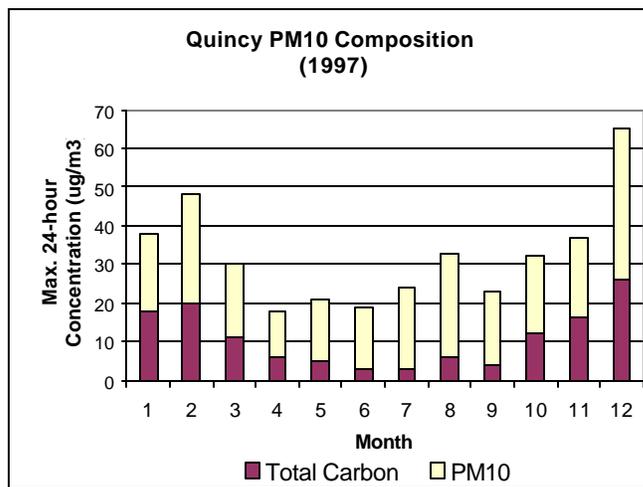
Based on the 2000 annual PM10 emission inventory, directly emitted particulate sources are unpaved road dust, wood burning stoves and fireplaces, and open burning.



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

As shown on Figure 6.23 , substantial levels of organic carbon are observed in the late fall and winter months, most likely due to residential burning and motor vehicles. There may also be episodic particulate emission impacts when forest management burning takes place.

Figure 6.23. Monthly variation in maximum 24-hour PM10 and total carbon concentrations at Quincy



North Central Coast Air Basin

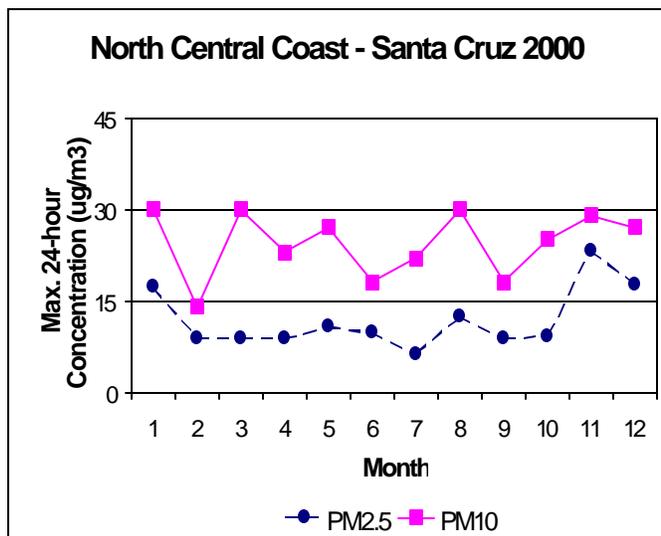


In the North Central Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 18 times in the 1998-2000 period, but fine particulate levels were below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. In the North Central Coast, 80% of the PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 measurements were below 10 to 15 $\mu\text{g}/\text{m}^3$.

Figure 6.24. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Santa Cruz

Figure 6.24 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Santa Cruz in 2000. Fine particulate levels are highest from November through January and are very low the rest of the year. PM10 levels fluctuate throughout the year, with no distinct seasonal pattern.

Based on the 2000 annual PM10 emission inventory, the major sources of directly emitted particulates in the North Central Coast Air Basin are unpaved roads, windblown dust, dust from farming operations, paved road dust, and residential wood burning.



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

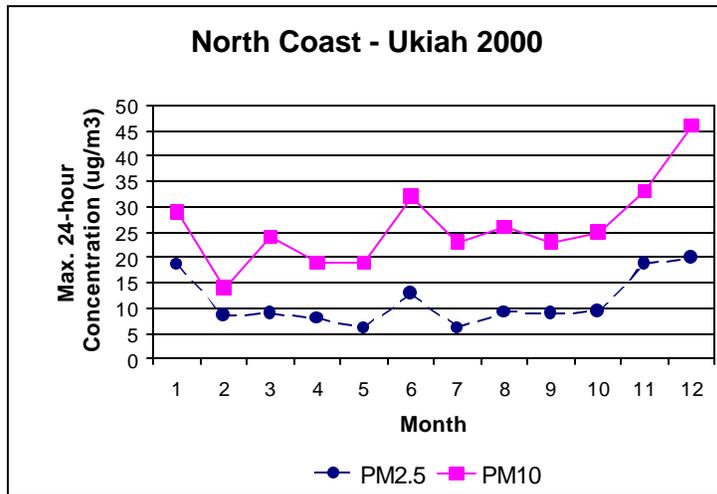
North Coast Air Basin



In the North Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 13 times in the 1998-2000 period, but fine particulate levels were below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. In the North Coast Air Basin, 80% of the PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 measurements fell below 10 to 15 $\mu\text{g}/\text{m}^3$.

Figure 6.25 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Ukiah in 2000. PM10 as well as PM2.5 levels are highest during the months of November through January, with a smaller peak in June.

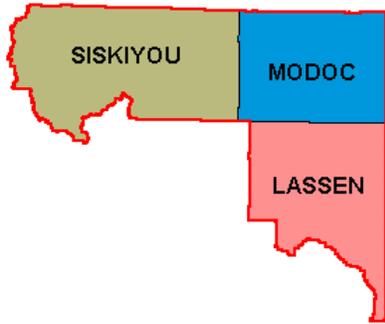
Figure 6.25. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Ukiah



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Based on the 2000 annual PM10 emission inventory, the principal source of directly emitted particulate matter is unpaved road dust. Other significant sources are residential wood burning and waste burning, which could include forest management burning.

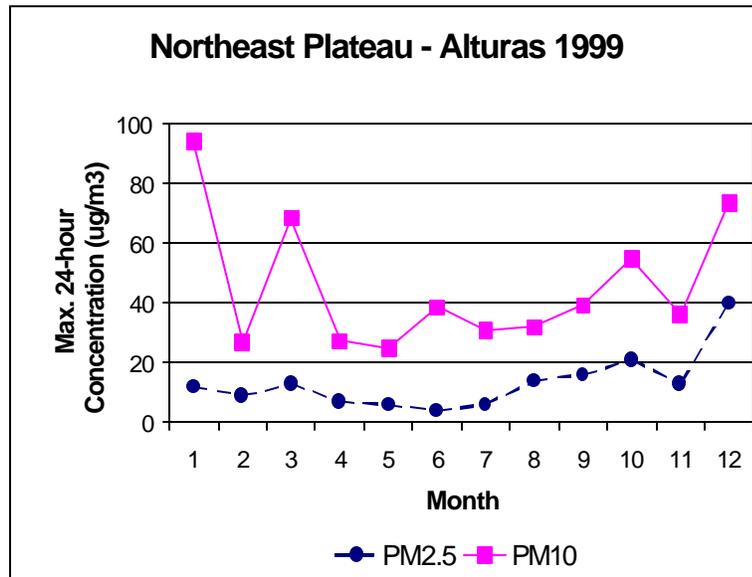
Northeast Plateau Air Basin



In the Northeast Plateau Air Basin, particulate levels exceeded the 24-hour State PM10 standard 26 times in the 1998-2000 period, but fine particulate levels were below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. In this air basin, 80% of the PM10 measures were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 observations were below 15 to 20 $\mu\text{g}/\text{m}^3$.

Figure 6.26 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Alturas in 2000. PM10 levels are highest during the winter months of December through March with lower concentrations during the spring and summer. PM2.5 levels are highest in December.

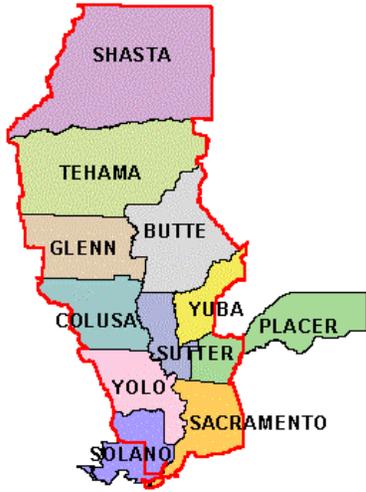
Figure 6.26. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Alturas



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

The 2000 annual PM10 emission inventory shows that unpaved road dust is the predominant source of directly emitted particulates. The Northeast Plateau Air Basin may also have occasional high emissions from wildfires and forest management burning.

Sacramento Valley Air Basin



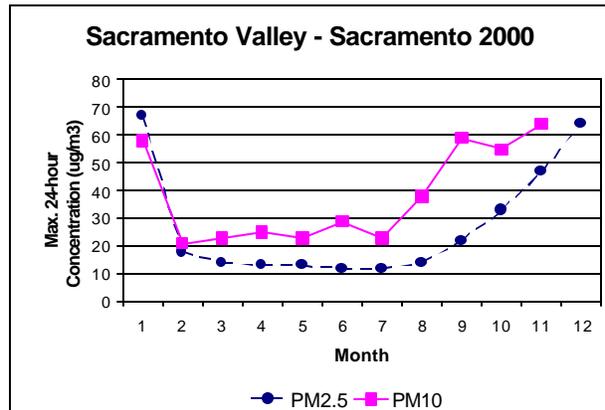
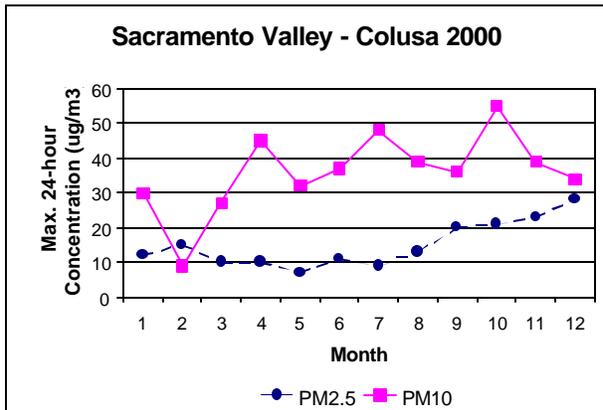
In the Sacramento Valley Air Basin, particulate levels exceeded the 24-hour State PM10 standard 61 times in the 1998-2000 period and PM2.5 concentrations over the federal PM2.5 standard were recorded 16 times in the 1999-2000 period. Particulate levels also exceeded both the State PM10 and federal PM2.5 annual standards. In the Sacramento Valley Air Basin, 80% of the PM10 observations are below 45 to 50 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 measurements are below 20 to 25 $\mu\text{g}/\text{m}^3$.

Figures 6.27 and 6.28 illustrate the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Colusa, a rural community in the central portion of the Valley, and the city of Sacramento, in the southern portion of the Valley for 2000, respectively. In Colusa, PM10 levels oscillate throughout the year with no distinct seasonal pattern. PM2.5 levels are highest in the fall and winter. In contrast, in Sacramento, both PM10 and PM2.5 levels are low during the spring and summer, with PM10 reaching peak values in the fall and early winter and PM2.5 reaching highest values in the winter. Data obtained from the Sacramento dichotomous sampler show that in 1999 and 2000 the PM2.5 portion of PM10 ranged from 13% to 86%. The two-year average PM2.5 portion of PM10 from November through February was 68% dropping to 43% from March through October.

Sacramento, both PM10 and PM2.5 levels are low during the spring and summer, with PM10 reaching peak values in the fall and early winter and PM2.5 reaching highest values in the winter. Data obtained from the Sacramento dichotomous sampler show that in 1999 and 2000 the PM2.5 portion of PM10 ranged from 13% to 86%. The two-year average PM2.5 portion of PM10 from November through February was 68% dropping to 43% from March through October.

Figure 6.27. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Colusa

Figure 6.28. Monthly variation in maximum 24-hour PM10 and PM2.5 concentrations at Sacramento



*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Based on the 2000 annual PM10 emissions inventory, the major sources of directly emitted particulates in the Sacramento Valley include soil from farming, construction dust, paved road dust, smoke from residential wood combustion, and exhaust from mobile sources such as cars and trucks.

Figures 6.29 and 6.30 illustrate source contributions to ambient PM₁₀ and PM_{2.5} during the winter in Sacramento. The data are from the analysis of ambient air samples collected from November through January, during six years - 1991 through 1996 (Motallebi 1999, Motallebi 2001). The constituents shown can vary based on a variety of factors such as meteorology and which particulate sources are most active.

Figure 6.29. Source contribution to PM₁₀ during the winter

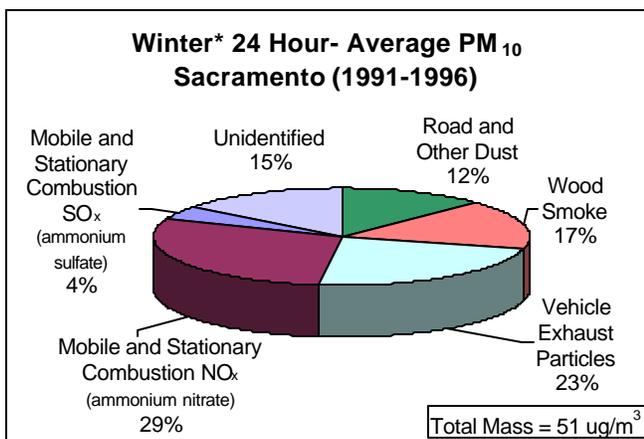
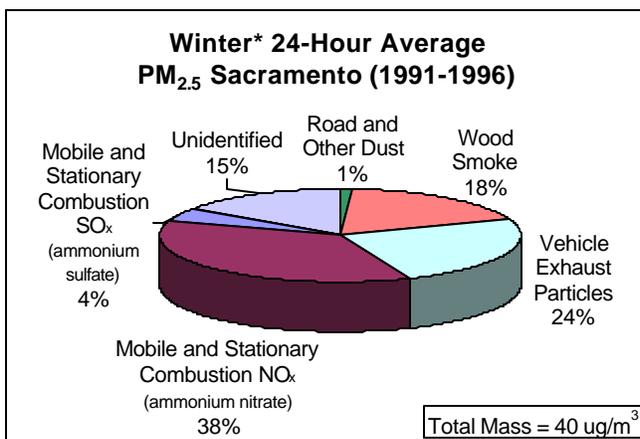


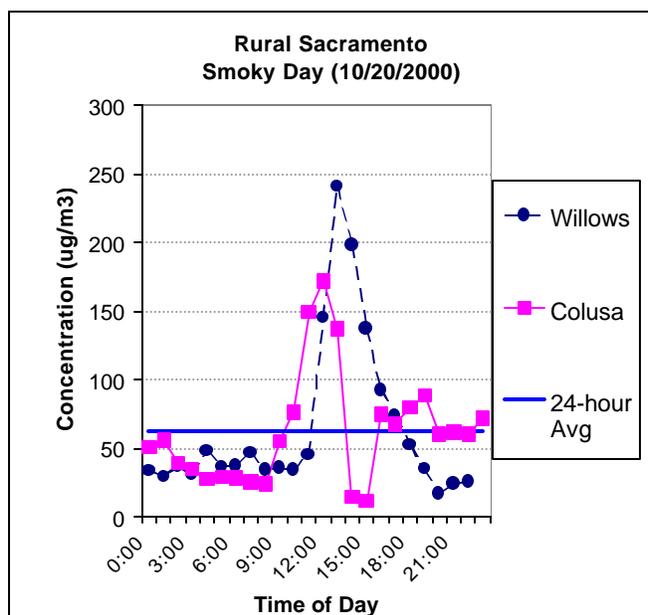
Figure 6.30. Source contribution to PM_{2.5} during the winter



*Average of days with PM₁₀ > 40 µg/m³.

NO_x emissions from mobile and stationary combustion sources, combined with ammonium, contribute the most to ambient PM levels. Vehicle exhaust particle emissions and wood smoke from residential wood combustion also contribute significantly. While road and other dust is a significant component of ambient PM₁₀, its contribution to PM_{2.5} is minor.

Figure 6.31. Hourly PM₁₀ levels on a smoky day in rural Sacramento



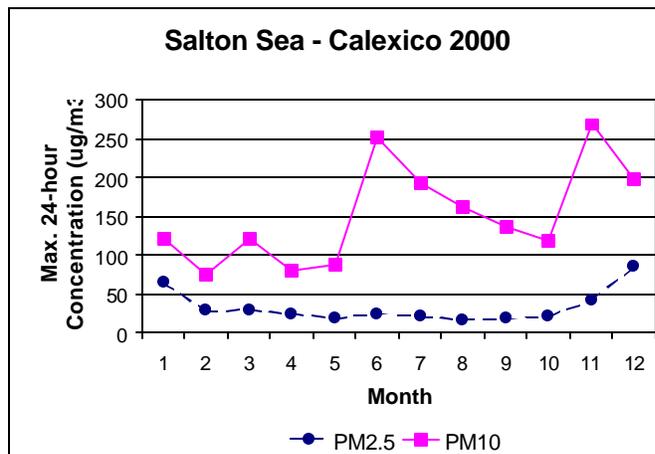
The northern Sacramento Valley can be impacted by seasonal agricultural burning, mostly during the fall. Figure 6.31 illustrates the hourly variation in PM₁₀ levels on a rice straw burning day in Willows and Colusa in 2000. PM₁₀ levels reached 4 to 5 times the level of the State 24-hour PM₁₀ standard for two hours in Willows and an average of 3 times the level of the standard for three hours in Colusa.



In the Salton Sea Air Basin particulate levels exceeded the 24-hour State PM10 standard 208 times in the 1998-2000 period, but only one observation over the 24-hour federal PM2.5 standard was recorded in 2000. Particulate levels also exceeded both the State PM10 and federal PM2.5 annual standards. Eighty percent of the PM10 observations were below 100 to 120 $\mu\text{g}/\text{m}^3$, while 80% of the PM2.5 measurements fell below 20 to 25 $\mu\text{g}/\text{m}^3$.

Figure 6.32 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Calexico in 2000. PM10 levels peak in the summer and fall. Fine particulates show a small increase in the fall and winter.

Figure 6.32. Monthly variation in maximum 24-hour PM10 and PM2.5 in Calexico



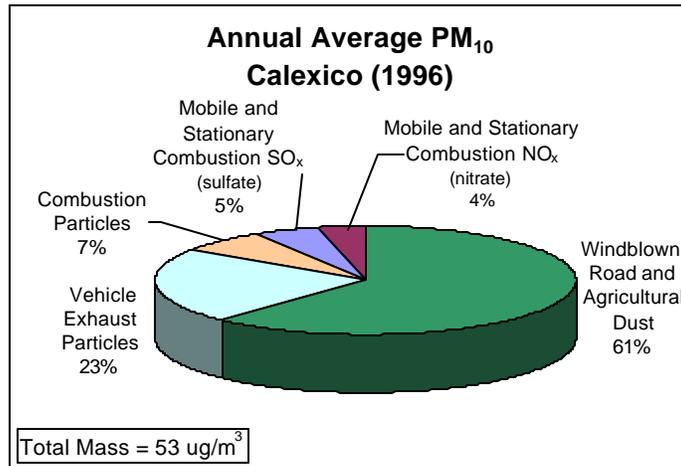
*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 greater than PM10.

Data obtained from the Calexico dichotomous sampler in 2000 indicate the PM2.5 component of PM10 ranges from 13% to 49%. The average PM2.5 fraction of PM10 from November to January is 34% and from February to October is 24%.

Based on the 2000 annual PM10 emission inventory, the major contributor of directly emitted particulates in the Salton Sea is windblown dust. Unpaved road dust and farming related dust also contribute.

Data for Figures 6.33 and 6.34 are from the source apportionment analysis of ambient samples collected during 1996 in Calexico. The source profiles developed by Chow and Watson (1997) were used in the analysis (Woodhouse, 2001).

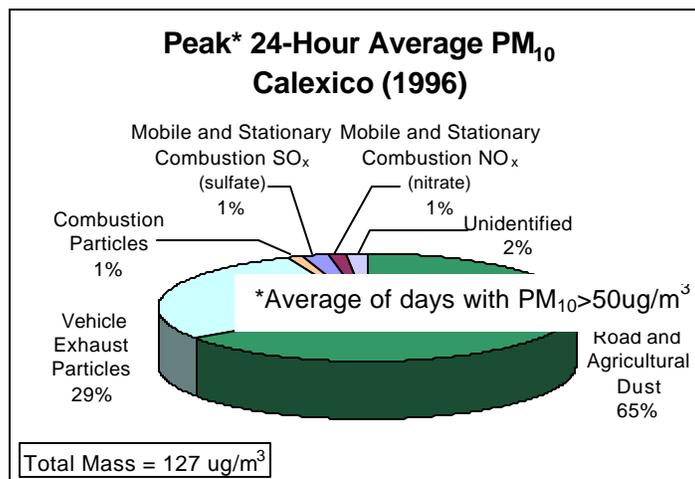
Figure 6.33. Sources contributing to annual average PM₁₀ levels in Calexico



In both cases, dust – windblown, road and agricultural – is the major contributor to PM₁₀. Vehicle exhaust particle emissions also contribute significantly. Combustion emissions from industrial processes and agricultural burns contribute noticeably to PM₁₀ on an annual basis, but are a minor contributor to the peak 24-hour average PM₁₀ levels.

The observed results could partially be due to transported pollutants from the neighboring city of Mexicali, which has high traffic. Secondary sulfate and nitrate formed from reactions in the atmosphere of nitrogen oxides and sulfur oxides from motor vehicle exhaust and other combustion processes also are small contributors to particulate matter levels in the air basin.

Figure 6.34. Sources contributing to peak 24-hour PM₁₀ levels in Calexico



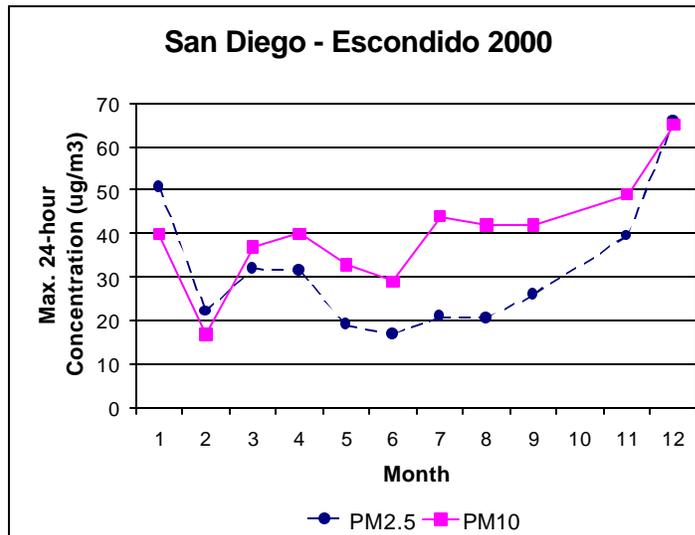
San Diego Air Basin



In the San Diego Air Basin, particulate levels are high year-round, exceeding both the annual State PM10 and federal PM2.5 standards over the 1998-2000 period. Ambient particulate levels also exceeded the State 24-hour PM10 standard 67 times in these three years and two PM2.5 observations over the federal PM2.5 standard were recorded in the 1999-2000 period. In San Diego County, 80% of the PM10 measurements were below 40 to 50 $\mu\text{g}/\text{m}^3$ and 80% of the PM2.5 observations were below 20 to 25 $\mu\text{g}/\text{m}^3$.

Figure 6.35 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Escondido in 2000. PM10 concentrations exhibit no distinct seasonal pattern, while PM2.5 concentrations are highest during the fall and winter.

Figure 6.35. Monthly variation of maximum 24-hour PM10 and PM2.5 levels in Escondido

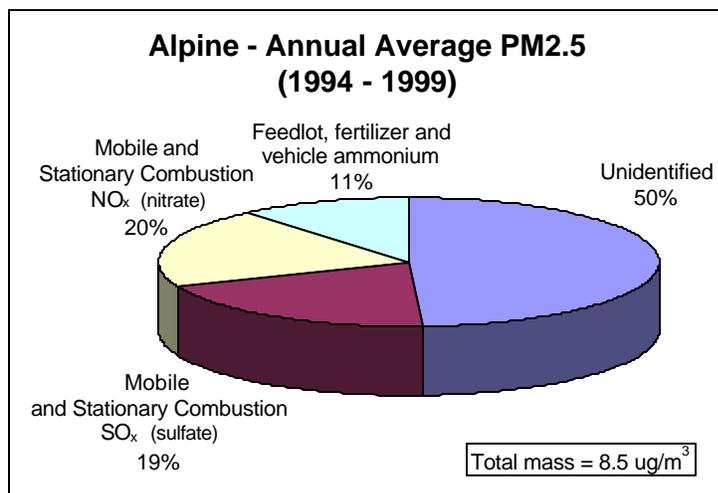


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Based on the 2000 annual PM10 emission inventory, the major contributors to directly emitted particulates in the San Diego Air Basin are construction dust, paved road dust, and unpaved road dust. Other sources are fireplaces and woodstoves, mobile sources, and mineral processes.

Data for Figure 6.36 are from the chemical analysis of ambient data collected in Alpine from 1994 through 1999 as part of the Southern California Children's Health Study. The data show substantial contributions from secondary nitrate and sulfate formed from reactions in the atmosphere of nitrogen oxides and sulfate oxides from motor vehicle exhaust and other combustion processes. The unidentified category represents emissions from dust sources and from total carbon. Carbon sources include wood smoke, other combustion sources, and motor vehicles (Salmon et al. 2001).

Figure 6.36. Sources contributing to annual average PM2.5 levels in Alpine



San Francisco Bay Area Air Basin

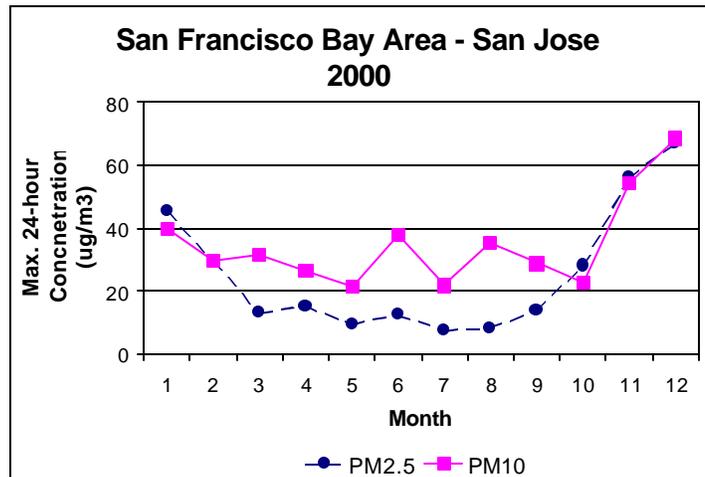


In the San Francisco Bay Area Air Basin, particulate levels exceeded the 24-hour State PM10 standard 24 times in the 1998-2000 period and five PM2.5 observations over the 24-hour federal PM2.5 standard were recorded in the 1999-2000 period. Eighty percent of the 24-hour PM10 observations were below 25 to 30 $\mu\text{g}/\text{m}^3$ and 80% of the 24-hour PM2.5 measurements were below 20 to 25 $\mu\text{g}/\text{m}^3$.

Figure 6.37 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in San Jose in 2000. Highest concentrations of both PM10 and PM2.5 occur during the winter months of November through January. PM2.5 drives PM10 concentrations during the winter, while smaller summer peaks are driven by PM10.

Figure 6.37. Monthly variation of maximum 24-hour PM10 and PM2.5 levels in San Jose

Data obtained from the San Jose dichotomous sampler in 1999 indicate the PM2.5 portion of PM10 ranges from 30% to 80%. The average PM2.5 portion of PM10 from November to January is 61%, dropping to 46% from February to October.



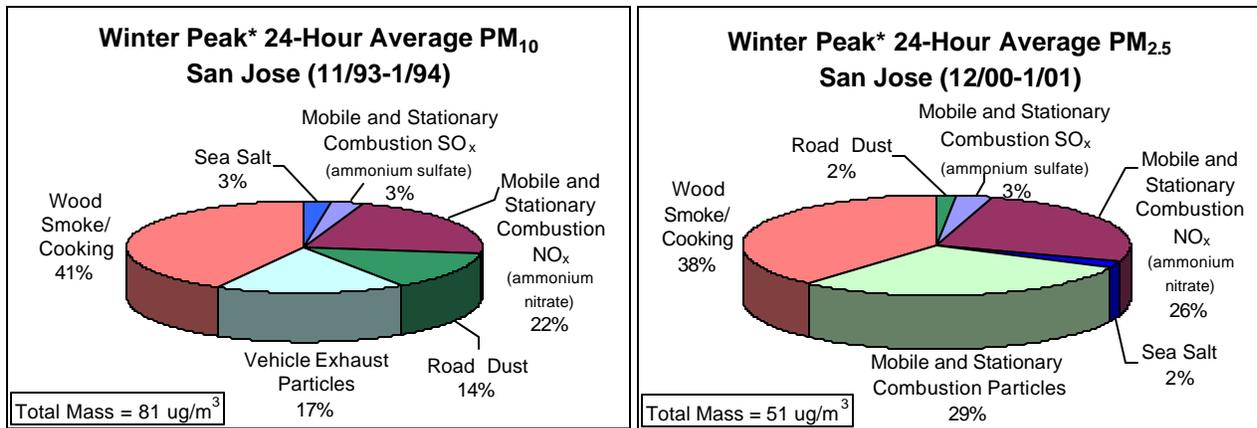
*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Based on the 2000 annual PM10 emission inventory of directly emitted particulate matter, major sources include smoke from residential wood combustion, dust from construction operations, and the dust created by vehicles traveling on paved roads. There are also significant emissions from unpaved road dust in some counties and motor vehicle exhaust from cars and trucks.

Figures 6.38 and 6.39 illustrate the sources of PM during the winter in the San Francisco Bay Area. The data are from the source apportionment analysis conducted by the Bay Area Air Quality Management District using samples collected during two special studies (Fairley, 1996, 2001).

Figure 6.38. Sources contributing to winter peak 24-hour levels of PM₁₀ in San Jose

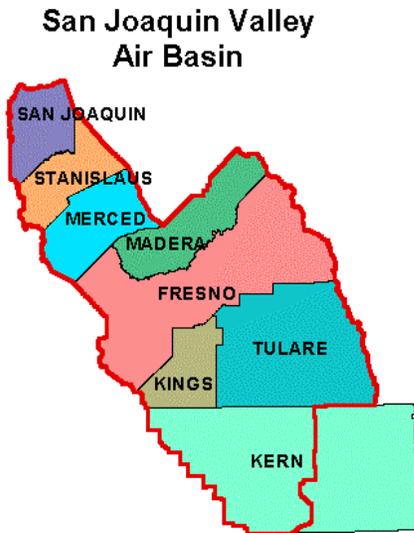
Figure 6.39. Sources contributing to winter peak 24-hour levels of PM_{2.5} in San Jose



*Average of days with PM₁₀ > 50 ug/m³.

*Average of days with PM_{2.5} > 40 ug/m³.

During the winter in San Jose, high PM concentrations are associated with high levels of wood smoke - primarily from residential wood combustion, and cooking. NO_x emitted from mobile and stationary combustion sources, in combination with ammonia, contributes about one-fourth of the PM levels. Particle emissions from mobile and stationary combustion sources are also a major contributor to PM_{2.5}. Road dust is a significant contributor to PM₁₀, but not PM_{2.5}.



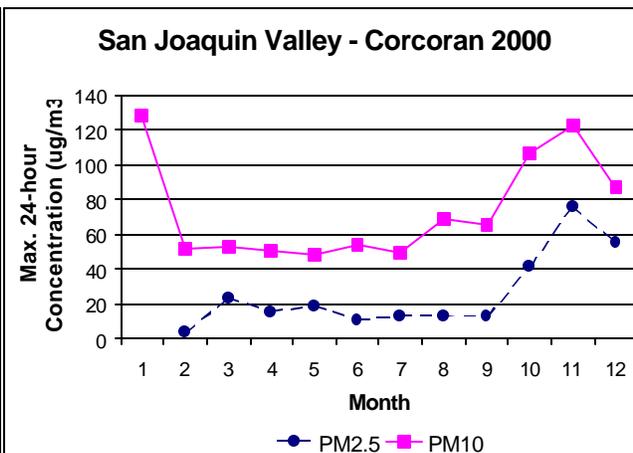
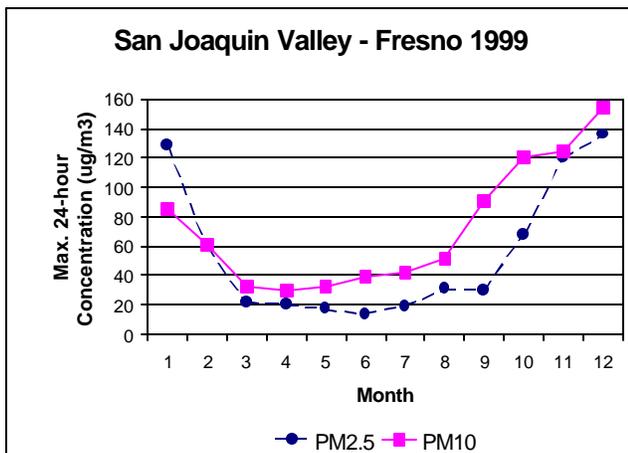
In 1999 and 2000, the San Joaquin Valley Air Basin recorded the highest PM_{2.5} levels in the State – more than twice the federal standard - and 74 PM_{2.5} observations over the federal standard were recorded. Particulate levels exceeded the 24-hour State PM₁₀ standard 177 times in the 1998-2000 period. Particulate concentrations also exceeded both the State PM₁₀ and federal PM_{2.5} annual standards. In the San Joaquin Valley Air Basin, 80% of the PM₁₀ observations were below 60 to 65 $\mu\text{g}/\text{m}^3$ and 80% of the PM_{2.5} measurements were below 35 to 40 $\mu\text{g}/\text{m}^3$.

Figures 6.40 and 6.41 illustrate the monthly variation of the maximum daily PM₁₀ and PM_{2.5} concentrations in Corcoran in 2000 and in Fresno in 1999. In Corcoran, PM₁₀ levels are highest in October and November, with PM_{2.5} peaking in November. In Fresno, PM₁₀ and

PM_{2.5} are highest from October through January. PM_{2.5} drives PM₁₀ concentrations during the wintertime in Fresno. The PM_{2.5} fraction of PM₁₀ is smaller in Corcoran with fall peaks driven by PM₁₀. Data obtained from the Fresno dichotomous sampler from 1998 through 1999 indicate

Figure 6.40. Monthly variation of maximum 24-hour PM₁₀ and PM_{2.5} levels in Fresno

Figure 6.41. Monthly variation of maximum 24-hour PM₁₀ and PM_{2.5} levels in Corcoran



*The monitors used to measure PM₁₀ and PM_{2.5} are different and occasionally recorded concentrations of PM_{2.5} which are greater than PM₁₀.

the PM_{2.5} component of PM₁₀ ranges from 19% to 88%. The November through February average PM_{2.5} fraction is 75% of PM₁₀ and the March through October average is 38%. Data obtained from the Corcoran dichotomous sampler from 1998 and 1999 show that the PM_{2.5} component ranges from 12% to 90%. The November through February average PM_{2.5} portion of PM₁₀ is 62% and the March through October average is 28%.

Figure 6.42 shows the daily variations in PM_{2.5} levels in Fresno during the winter of 2000 to 2001. The data were obtained as part of the CRPAQS study. PM_{2.5} concentrations were over the federal 24-hour PM_{2.5} standard close to 40% of the time.

Based on the 2000 annual PM10 emission inventory, the major sources of directly emitted particulates in the San Joaquin Valley are agricultural and unpaved road dust, paved road dust, and windblown dust. Other sources include stationary industrial activities, residential wood combustion, and particulates emitted by mobile sources such as cars and trucks.

Figures 6.43 and 6.44 illustrate source contributions to ambient PM in the San Joaquin Valley during the fall and winter. These are the results from a detailed chemical analysis of samples collected during the 1995-Integrated Monitoring Study (Magliano et al. 1999).

Figure 6.42. Daily variations in winter PM2.5 levels in Fresno

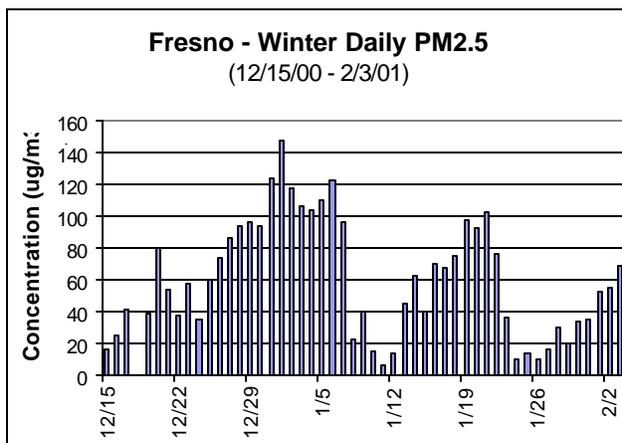


Figure 6.43. Sources contributing to PM10 levels in the fall in Corcoran

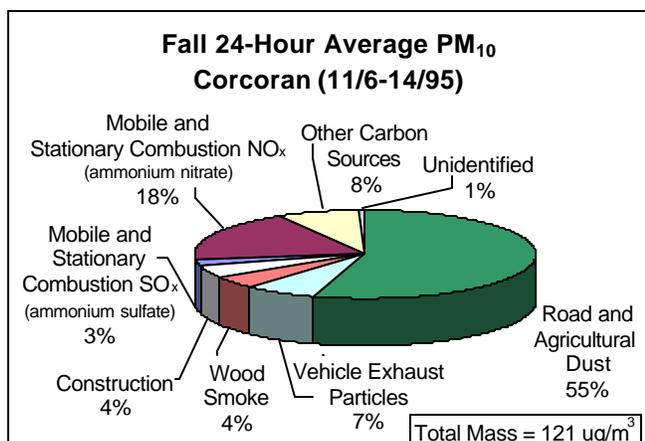
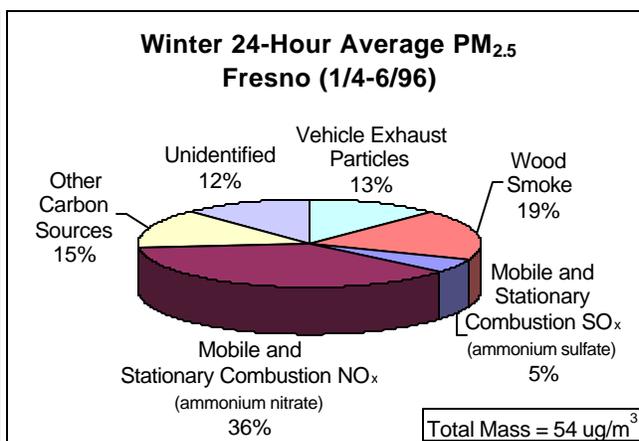


Figure 6.44. Sources contributing to PM2.5 levels in the winter in Fresno



In the fall at Corcoran, elevated concentrations of PM10 were associated with high levels of road and agricultural dust. NO_x emissions from mobile and stationary combustion sources, combined with ammonia, led to significant secondary ammonium nitrate contributions to PM10. During the winter, in Fresno, secondary ammonium nitrate was the major contributor to PM2.5 and PM10. Emissions from wood smoke, vehicle exhaust particles, and other carbon sources also contributed significantly to PM2.5 levels.

Figure 6.45 illustrates the source contributions to winter PM2.5 levels at two urban and two rural areas in the valley. The Bakersfield and Fresno sites were located in large urban areas; the Kern Wildlife Refuge site was located amidst natural vegetation, while the SW Chowchilla site was in a rural area, surrounded by agricultural fields. At the peak of a winter PM2.5 episode, PM2.5 concentrations at the two rural sites were about half of the PM2.5 levels at the two urban sites. Secondary ammonium nitrate was the largest contributor at all four sites. Vegetative burning and direct mobile source exhaust contributed 19% and 12% of the PM2.5 mass in the urban areas, but only an average of 8% and 9% at the rural sites. The excess organic carbon resulting from combustion sources other than vegetative burning and mobile sources as well as secondary organic carbon – was significant at the urban, but not at the rural sites.

Figure 6.45. Sources contributing to the PM2.5 levels at the peak of a winter episode in two urban and two rural areas

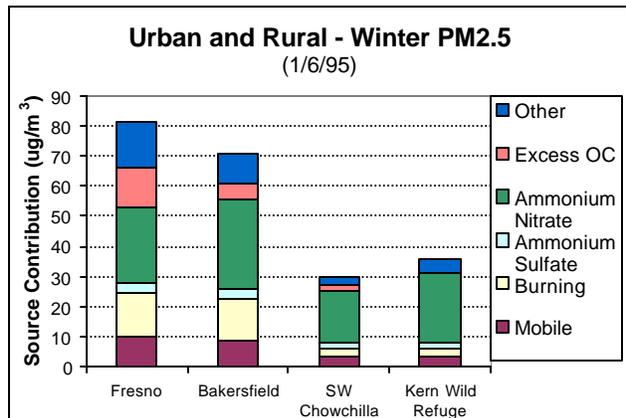


Figure 6.46. Comparison of hourly variations in winter PM2.5 levels at urban Fresno and rural SW Chowchilla

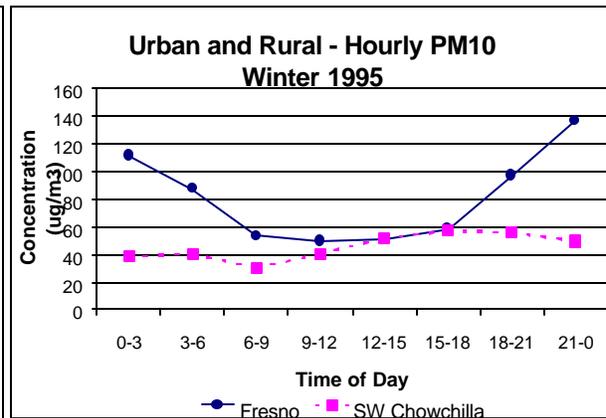
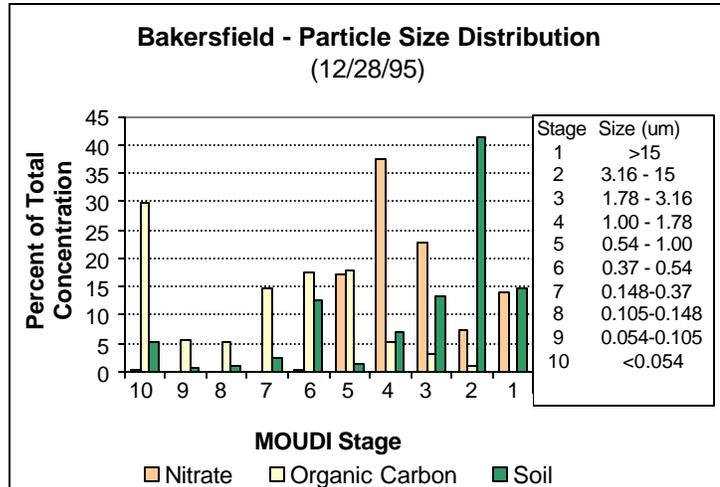


Figure 6.46 illustrates that in the winter in Fresno, PM10 levels varied significantly during the course of the day, with the highest concentrations occurring during the nighttime. In contrast, in rural SW Chowchilla PM10 levels did not vary much within a day. Chemical composition data indicate diurnal variations in ammonium nitrate were the primary cause of the PM10 variations in SW Chowchilla. The rise in PM10 concentration in Fresno corresponded mostly to significant nighttime peaks in vegetative burning, mobile sources, and excess organic carbon (Magliano et al. 1999).

Figure 6.47. Particle size distributions for nitrate, organic carbon and soil during a winter episode in Bakersfield



Data for Figure 6.47 are from air samples collected with a Micro-Orifice Uniform Deposit Impactor (MOUDI) sampler at Bakersfield during IMS95 (Chow et al. 1997). The size distribution of nitrate particles peaked between 1 and 1.78 μm . Organic carbon particles appeared in both smaller ($<0.054 \mu\text{m}$) and larger (peak between 0.37 and 1 μm) stages. The ultrafine carbon particles ($<0.08 \mu\text{m}$) result from direct emissions from combustion sources or from the condensation of gases cooled down soon after they are emitted. The soil components were concentrated mainly on the larger particle size fractions ($>3.16 \mu\text{m}$), the coarse fraction of PM10.

**South Central Coast
Air Basin**

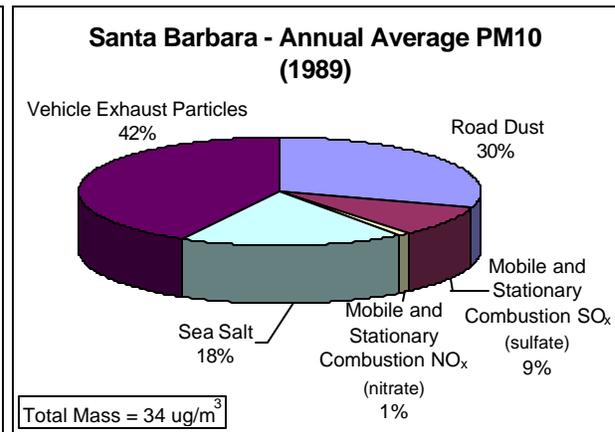
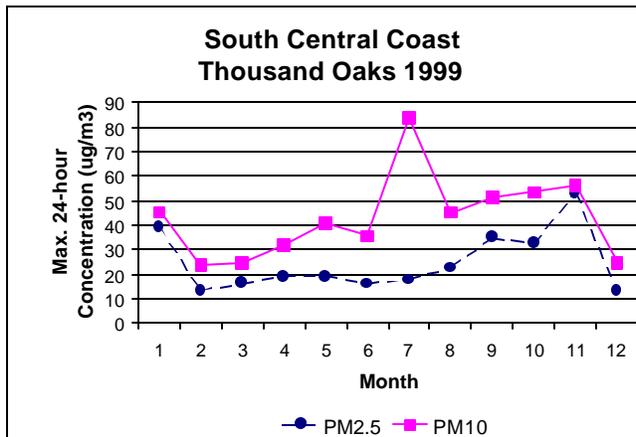


In the South Central Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 60 times in the 1998-2000 period. Neither of the federal PM2.5 standards or the State annual PM10 were exceeded in the last few years. Eighty percent of the 24-hour PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the 24-hour PM2.5 measurements were under 10 to 15 $\mu\text{g}/\text{m}^3$.

Figure 6.48 illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations at Thousand Oaks in 1999. PM10 concentrations tend to peak in the summer, while highest PM2.5 levels occur in November and January.

Figure 6.48. Monthly variation of maximum 24-hour PM10 and PM2.5 levels in Thousand Oaks

Figure 6.49. Sources contributing to annual average PM10 levels in Santa Barbara

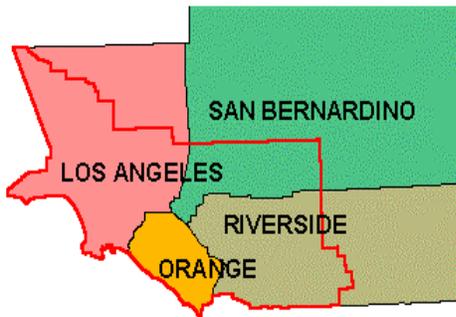


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Based on the 2000 annual PM10 emission inventory, the major contributors of directly emitted particles in the South Central Coast Air Basin are paved and unpaved road dust, dust from farming operations, and residential and waste burning. This region can also have significant seasonal wildfire emissions

Data for Figure 6.49 are from source apportionment analysis performed for the 1989 Santa Barbara County PM10 Study (Chow et al. 1996). The constituents shown can vary daily and from year to year depending on factors such as meteorology and which particulate sources are most active. On an annual basis, in the city of Santa Barbara, vehicle exhaust is the major contributor to PM10 levels. Sea salt and road dust also contribute significantly. Secondary ammonium nitrate and sulfate are relatively small contributors.

South Coast Air Basin



In the South Coast Air Basin, particulate levels exceeded the 24-hour State PM₁₀ standard 197 times in the 1998-2000 period, and 38 PM_{2.5} observations over the 24-hour federal PM_{2.5} standard were recorded in the 1999-2000 period. Particulate levels also exceeded both the State PM₁₀ and federal PM_{2.5} annual standards. The South Coast recorded some of the highest levels of PM_{2.5} in the State – almost twice the level of the standard. Eighty percent of the 24-hour PM₁₀ observations were below 65 to 80 $\mu\text{g}/\text{m}^3$ and 80% of the 24-hour PM_{2.5} measurements were below 35 to 40 $\mu\text{g}/\text{m}^3$.

Figure 6.50 illustrates the monthly variation of the maximum daily PM₁₀ and PM_{2.5} concentrations in Riverside in 1999. Both PM₁₀ and PM_{2.5} concentrations exhibit no distinct seasonal pattern, with high concentrations throughout the year.

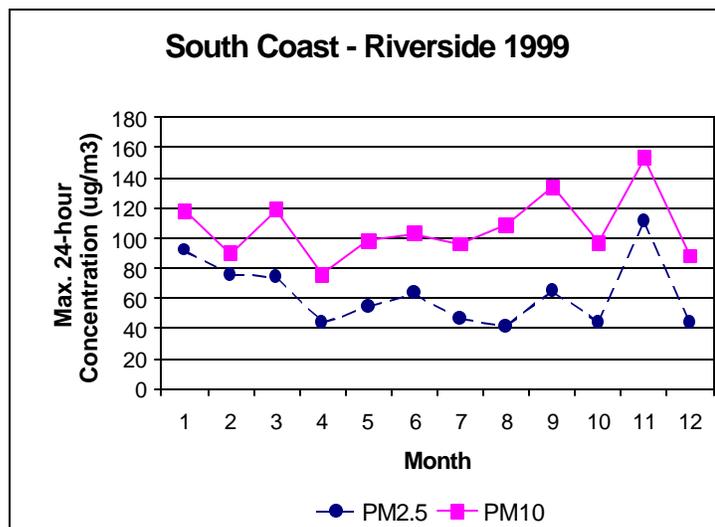
Data obtained from the Long Beach dichotomous sampler in 1999 indicate the PM_{2.5} portion of PM₁₀ ranges from 30% to 96%. The average PM_{2.5} portion of PM₁₀ from November to February is 59% dropping to 45% from February to October.

The 2000 annual PM₁₀ emission inventory shows that the major sources of directly emitted particulates in the South Coast Air Basin are paved road dust, unpaved road dust, construction related dust, and the general categories of motor vehicle emissions and industrial emissions.

Data for the illustrations below are from the source apportionment analysis that the South Coast Air Quality Management District (SCAQMD) performed for the 1997 Air Quality Management Plan. SCAQMD collected samples during a one-year special study from January 1995 to February 1996 as part of the PM₁₀ Technical Enhancement Program (SCAQMD, 1996).

Figure 6.51 shows that on an annual basis, in Central Los Angeles, dust from roads and construction is the major contributor to ambient PM₁₀. This is not the case for the episode on November 17, 1995 (Figure 6.52). In both cases, NO_x and SO_x emitted from mobile and stationary combustion sources, combined with ammonia, contribute significantly. Vehicle exhaust particles and emissions from other carbon sources also contribute to both annual and episodic ambient PM₁₀ levels.

Figure 6.50. Monthly variation of maximum 24-hour PM₁₀ and PM_{2.5} levels in Riverside



*The monitors used to measure PM₁₀ and PM_{2.5} are different and occasionally recorded concentrations of PM_{2.5} which are greater than PM₁₀.

On an annual basis, in Rubidoux, dust from roads and construction is the major contributor to ambient PM₁₀ (Figure 6.53). In contrast, as shown in Figure 6.54, dust was a minor contributor to the PM₁₀ episode on November 17, 1995. In both cases, NO_x emitted from mobile and stationary combustion sources, combined with ammonia, contributes significantly. Vehicle exhaust particles and emissions from other carbon sources also contribute to both annual and episodic ambient PM₁₀ levels.

Figure 6.51. Sources contributing to annual average PM₁₀ levels in Central Los Angeles

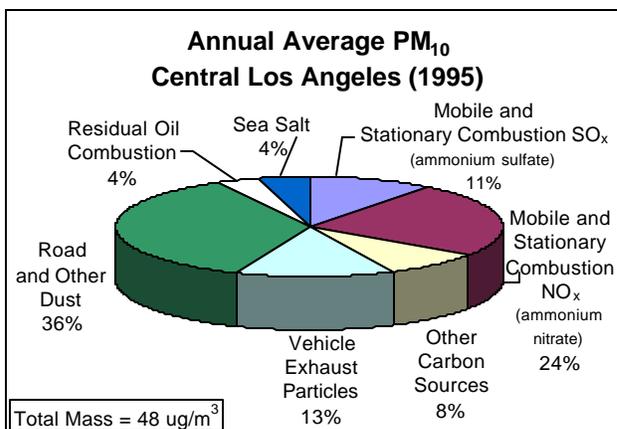


Figure 6.52. Sources contributing to PM₁₀ levels during a November episode in Central Los Angeles

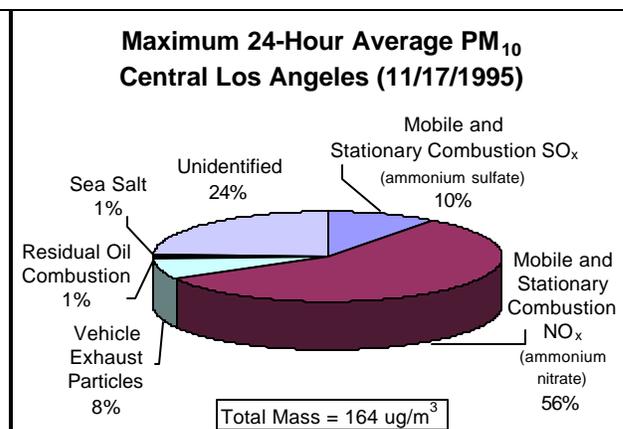


Figure 6.53. Sources contributing to annual average PM₁₀ levels in Rubidoux

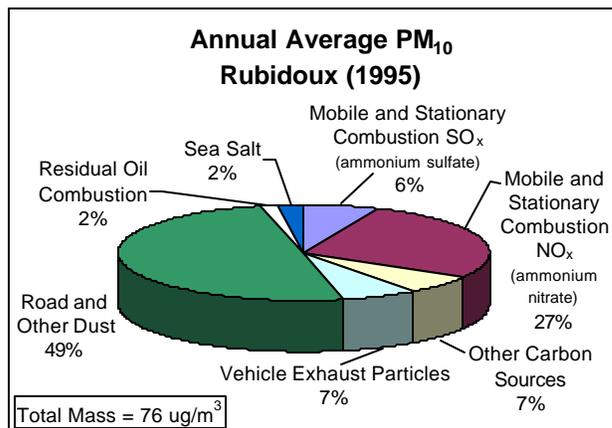
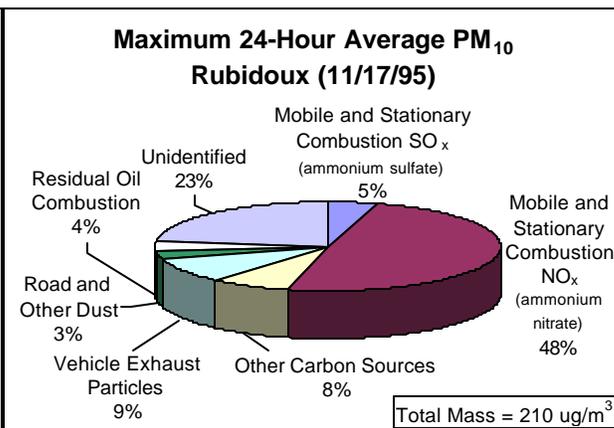


Figure 6.54. Sources contributing to a PM₁₀ levels during a November episode in Rubidoux



6.4 Ambient Air Quality Population Exposure

6.4.1 Introduction

This section addresses two main questions: 1) what percent of the population in each air basin is exposed to ambient concentrations over the levels of the current and revised State PM10 standards, the current federal PM2.5 standards and the new State PM2.5 standards. 2) what is the population weighted average PM10 and PM2.5 concentration in each air basin?

We recognize that PM can vary in a small spatial scale. Our exposure analysis is limited by the number of PM monitors in the State and their geographic distribution in relation with location to the population. In addition, research on which PM sizes (e.g., coarse, fine, ultrafine) and which compounds of PM are the most toxic is an on-going effort at laboratories in the U.S. and abroad. Studies on the spatial distribution of specific PM compounds and particle size number are ongoing at the Fresno and Los Angeles Supersites. Samples to study these variables in the San Joaquin Valley were collected as part of the 2000-2001 California Regional PM10/PM2.5 Study, and are now being analyzed. We realize that these points need to be considered in future PM standard reviews.

6.4.2 Ambient Air Quality Exposure Model Details and Assumptions

The basic procedure for determining exposure was first adopted by the ARB in 1993 to fulfill the requirements of section 39607(f) of the Health and Safety Code. Full details are provided in *Guidance for Using Air Quality-Related Indicators in Reporting Progress in Attaining the State Ambient Air Quality Standards* (ARB 1993). For this application, ambient PM concentrations and population counts were associated by census tract and merged to assemble a distribution of exposures to different concentrations of PM.

Concentrations of many air pollutants including particulate matter change significantly from one place to another. PM10 concentrations may be well under the State standard in one location but above the standard less than 10 kilometers away. Accordingly, population exposures tend to be more accurate when the population data used to estimate them are highly resolved geographically.

Population counts by census tract provide a convenient basis for determining population exposures to air pollutants. A typical census tract contains several thousand people. Densely populated areas have many census tracts, while sparsely populated regions have very few.

Air pollutant data from a network of air quality monitors are used to determine appropriate values at census tracts that lie between them. The concentration for a census tract is a weighted average of the concentrations at all monitors within a maximum allowed distance. For the present analyses of PM10 and PM2.5, the maximum distance was 50 kilometers (75 km in the Great Basin Valleys Air Basin). A small number of census tracts are more than 50 km from any PM monitor, so their populations were not included in the analyses. The population numbers will be affected slightly by different choices for the maximum distance.

The weight assigned to each monitor is the inverse square of its distance from the census tract. In this way, close monitors are more influential than distant monitors are. Geographical features, such as mountain ranges, were not used in the model

6.4.3 Data Used

Ambient PM air quality data were extracted from AIRS on May 18, 2001. Exposure calculations were performed for three metrics: for PM10: annual arithmetic mean (AAM), annual geometric mean (AGM), and peak 24-hour concentration, represented by the Expected Peak Day Concentration (EPDC). For PM2.5 we performed calculations for the annual arithmetic mean and the EPDC. PM10 data from 1998 through 2000 and PM2.5 data from 1999 through 2000 were obtained from all monitors in the State meeting quality assurance criteria for valid data. For each metric, different numbers of monitors were available which met the specified validity criteria. Therefore the population represented for each metric is slightly different. For PM10 the population used in the analysis represented 99 percent of the 1990 statewide total population, while for PM2.5 it ranged from 62% to 66%, due to smaller number of monitors available. For variations among air basins see Appendices 6-G1 to 6-G3 and 6-H1 to 6-H2.

As mentioned in section 6.1, the EPDC for a monitoring site is the peak 24-hour PM10 (or PM2.5) concentration expected to occur no more than once per year. The EPDC is a highly precise estimate of the 99.7th percentile (364/365th percentile) of the 24-hour PM10 (or PM2.5) concentrations measured at the monitoring site. Since the sampling frequency for PM10 concentrations is usually once every six days and for PM2.5 it varies by monitoring site (once every six days, once every three days or daily), the method used for calculating the EPDC automatically compensates for sampling frequencies that are less than daily. To calculate the EPDC, we use the highest twenty percent of all measurements during the last three years. An “exponential-tail” model is used for this purpose (Larsen and Nystrom, 1992; Breiman et al., 1978). The computer program to determine the EPDC is available to the public upon request (Contact: Larry Larsen, ARB).

1990 census data reported by census tract were used as the 2000 data were not yet available in the census tract format. The census data contains the shape, size, and centroid of each census tract, as well as the population count.

6.4.4 Discussion of the Ambient Air Quality Exposure Model Results

The detailed output of the exposure model for each of the three PM10 metrics is provided in Appendices 6-E1 to 6-E6 and for the PM2.5 metrics in Appendices 6-F1 to 6-F6. For each metric there is a statewide summary as well as a summary by air basin. For the PM2.5 AAM, the concentration data are shown in 2 $\mu\text{g}/\text{m}^3$ and in 5 $\mu\text{g}/\text{m}^3$ increments with the associated population exposed to concentrations within that range. For the PM2.5 EPDC and the three PM10 statistics, the concentration data are shown in 5 $\mu\text{g}/\text{m}^3$ increments. An additional column is provided to indicate the percent of the population that is above the relevant standards. Table 6.5 summarizes the results of the PM10 statewide assessment.

Table 6.5. Population in the State Exposed to PM10 Levels above the Current State Standards.

Area	Above Current PM10 Standards				Above Revised Annual PM10 Standard		Pop. Exposed to Revised Annual Std. – Pop. Exposed to Current Annual Std.	
	24-hour EPDC > 50 µg/m ³		Annual Geometric Mean > 30 µg/m ³		Annual Arithmetic Mean > 20 µg/m ³			
	Percent of Population Exposed	1990 Population Exposed ⁽¹⁾ (x100,000)	Percent of Population Exposed ⁽¹⁾	1990 Population Exposed ⁽¹⁾ (x100,000)	Percent of Population Exposed ⁽¹⁾	1990 Population Exposed ⁽¹⁾ (x100,000)	Percent of Population	1990 Population (x100,000)
Great Basin Valleys	100	0.29	0	0	22.5	0.03	22.5	.03
Lake County	0	0	0	0	0	0	0	00
Lake Tahoe	100	0.39	0	0	66.7	0.26	66.7	.26
Mojave Desert	100	3.29	7.9	0.23	51.5	1.35	43.6	1.12
Mountain Counties	100	3.27	0	0	70	2.17	70	2.17
North Central Coast	92.4	5.75	0	0	78.7	4.90	78.7	4.90
North Coast	84.8	1.72	0	0	24.7	0.69	24.7	0.69
Northeast Plateau	51.8	0.19	0	0	24.3	0.09	24.3	0.09
Sacramento Valley	100	20.12	2.3	0.47	93.4	18.78	91.1	18.31
Salton Sea	100	3.45,	91.8	3.21,	100	3.36	8.2	0.15
San Diego County	100	24.67	36.1	8.90	100	24.67	63.9	15.77
San Francisco Bay Area	100	58.77	0	0	68.3	40.14	68.3	40.14
San Joaquin Valley	100	25.60	68.9	18.28	100	25.60	31.1	7.32
South Central Coast	86.6	10.87	0	0	74	9.34	74	9.34
South Coast	100	128.62	90.6	116.48	100	128.61	9.4	12.13
Statewide	98.9	287.00	50.7	147.57	89.5	259.99	38.8	112.42

(1) This represents the percent of the 1990 population used in the exposure analysis. The total population used in the analysis varied by metric, since the number of monitors with data meeting specified validity criteria was different for each metric (Appendices VI-G1 to VI-G3).

Figures 6.55, 6.56 and 6.57 show the distribution of the statewide population exposed to different ambient PM10 concentration ranges.

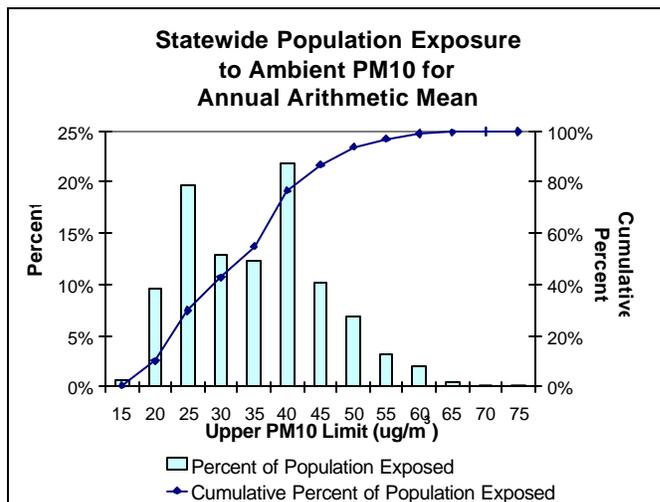


Figure 6.55. Estimated percentages of the statewide population exposed to various annual arithmetic mean levels of ambient (outdoor) PM10.

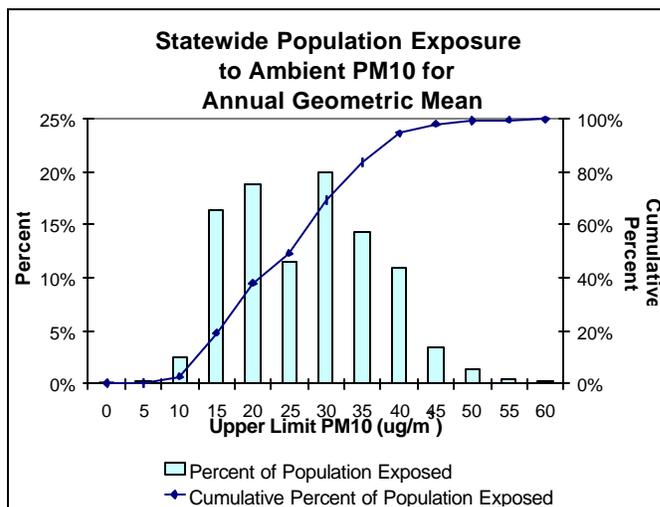


Figure 6.56. Estimated percentages of the statewide population exposed to various annual geometric mean levels of ambient (outdoor) PM10.

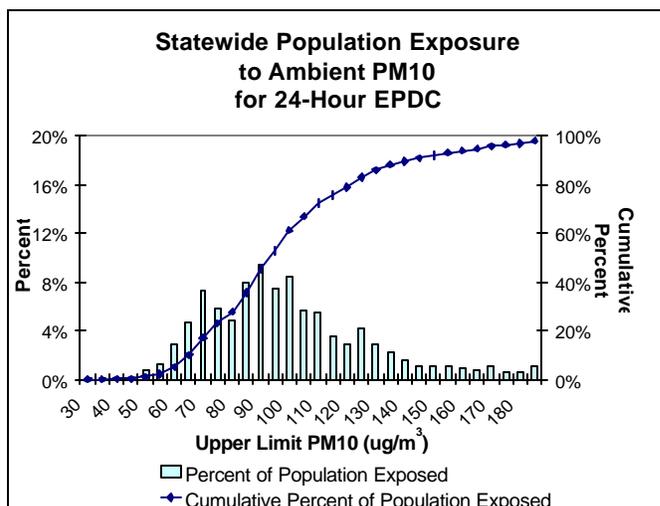


Figure 6.57. Estimated percentages of the statewide population exposed to various 24-hour average levels of ambient (outdoor) PM10.

The AAM statistics show that 57% of the statewide population is exposed to ambient PM10 concentrations over $30 \mu\text{g}/\text{m}^3$, while 33% is exposed between 20 and $30 \mu\text{g}/\text{m}^3$. The AGM statistics indicate 47% of the people in the State are exposed to annual ambient PM10 levels between 15 and $30 \mu\text{g}/\text{m}^3$. Based on the EPDCs, essentially the whole State has PM10 levels exceeding the 24-hour State PM10 standard.

The air basin statistics in Appendices 6-E1 to 6-E3 show that for the two forms of the PM10 annual average, the percent of the population exposed to concentrations of $30 \mu\text{g}/\text{m}^3$ or more is highest in the South Coast (over 90%), Salton Sea (over 90%), and San Joaquin Valley (over 68%). San Diego follows with over 36% of its population exposed to annual PM10 levels exceeding the State annual PM10 standard. Based on AAMs, less than 12% of the population in the Great Basin Valleys, Mojave Desert, North Central Coast, South Central Coast, and Sacramento Valley are exposed to concentrations equal to or above $30 \mu\text{g}/\text{m}^3$. But, based on the AGMs, less than 8% of the population living in the Mojave Desert and San Joaquin Valley are exposed to PM10 levels over $30 \mu\text{g}/\text{m}^3$, while no one in Great Basin Valleys, North and South Central Coast is exposed over these levels.

The 24-hour EPDC statistics show that essentially the entire State has PM10 levels exceeding the 24-hour State PM10 standard. Lake County is an exception, with its entire population exposed to concentrations below the current standard. Annual Geometric Mean values, show that about half of the State's population is exposed to annual average PM10 concentrations over the current annual PM10 State standard of $30 \mu\text{g}/\text{m}^3$. A much larger fraction (90%) of the State's population is exposed to annual average levels over the revised annual PM10 standard of $20 \mu\text{g}/\text{m}^3$, as shown by the Annual Arithmetic Mean statistics. A sizable portion of the population (36% to 92%) in four air basins (Salton Sea, San Diego, San Joaquin Valley, and South Coast), 2% of the population in Sacramento, and 8% of the population in Mojave Desert is exposed to annual average PM10 concentrations over the current State annual PM10 standard. In contrast, a significant fraction (23%-100%) of the total number of inhabitants in all air basins, with the exception of Lake County, are exposed to ambient PM10 levels over the revised annual State standard. The revised State annual PM10 standard would protect an additional 39% of the State population included in the study or 11 million persons over the current annual standard.

Table 6.6 summarizes the results of the PM2.5 assessment.

Table 6.6. Population in the State Exposed to Ambient PM2.5 Levels above the Current Federal and New State Standards.

Area	Above Current Federal PM2.5 Standards				Above New State PM2.5 Standards				Pop. Exp. to. New State Std – Pop. Exp. to. Federal Std			
	24-hour EPDC > 65 µg/m ³		Annual Mean > 15 µg/m ³		24-hour EPDC > 25 µg/m ³		Annual Mean > 12 µg/m ³		24-hour		Annual Mean	
	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)	Pop. Exp. ⁽¹⁾ (%)	1990 Pop. Exp. ⁽¹⁾ (x10 ⁵)
Great Basin Valleys	20.6	0.03	0	0	20.6	0.03	0	0	0	0	0	0
Lake County	0	0	0	0	0	0	0	0	0	0	0	0
Lake Tahoe	0	0	0	0	100	0.26	0	0	100	0.26	0	0
Mojave Desert	0	0	0	0	100	1.34	0	0	100	1.34	0	0
Mountain Counties	17.2	0.13	0	0	100	0.76	12.5	0.27	82.8	0.63	12.5	0.27
North Central Coast	0	0	0	0	69.5	2.75	0	0	69.5	2.75	0	0
North Coast	0	0	0	0	100	1.21	0	0	100	1.21	0	0
Northeast Plateau	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sacramento Valley	99.0	13.24	30.5	0.41	100	13.37	49.3	6.68	0.1	0.13	15.8	2.66
Salton Sea	7.4	0.17	21.4	0.50	100	2.31	51.3	1.20	92.6	2.14	29.9	0.70
San Diego County	0	0	63.4	10.43	100	16.44	100	16.46	100	16.44	36.6	6.03
San Francisco Bay Area	90.7	35.53	8.6	0.34	100	39.18	58.4	22.88	9.3	3.65	49.8	22.54
San Joaquin Valley	100	17.12	89.3	14.43	100	17.12	98.9	17.49	0	0	9.6	3.06
South Central Coast	0	0	0	0	100	7.18	59.2	4.96	100	7.18	0	0
South Coast	99.9	85.24	98.4	83.95	100	85.33	98.8	84.74	0.1	0.11	0.4	0.79
Statewide	80.7	151.30	60.6	113.67	96.5	180.93	82.5	154.60	15.8	29.63	21.8	40.93

(1) This represents the percent of the 1990 population used in the exposure analysis. The total population used in the analysis varied by metric, since the number of monitors with data meeting specified validity criteria was different for each metric (Appendices VI-H1 to VI-H2).

Figures 6.58 and 6.59 show the distribution of the statewide population exposed to different PM2.5 concentration ranges.

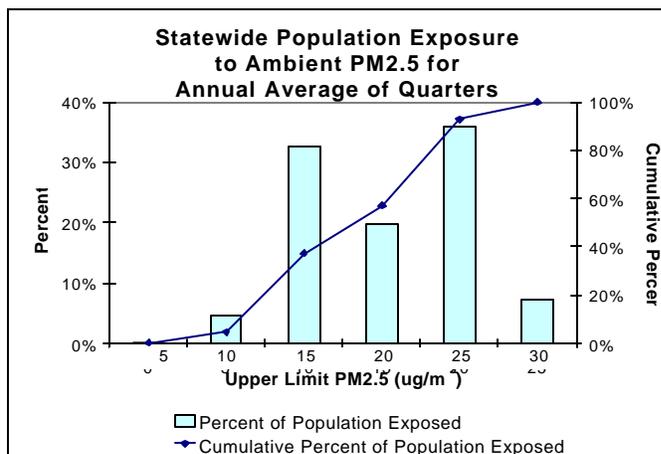


Figure 6.58. Estimated percentages of the statewide population exposed to various annual average of quarter mean levels of ambient (outdoor) PM2.5.

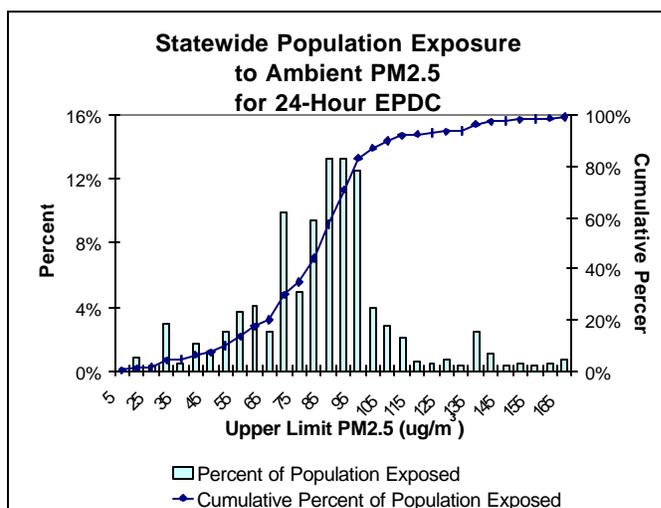


Figure 6.59. Estimated percentages of the statewide population exposed to various 24-hour average levels of ambient (outdoor) PM2.5.

The 24-hour EPDC statistics show that 80% of the Statewide population is exposed to PM2.5 levels above the current federal 24-hour PM2.5 standard of 65 $\mu\text{g}/\text{m}^3$, while 97% of the Statewide population is exposed to ambient PM2.5 concentrations over 25 $\mu\text{g}/\text{m}^3$, the level of the new State 24-hour PM2.5 standard. The fraction of the population in the seven air basins with 24-hour EPDCs over 65 $\mu\text{g}/\text{m}^3$ ranges from 7% in the Salton Sea to 100% in the South Coast. With the exception of Lake County and Northeast Plateau, all air basins have at least 20% of their population exposed to 24-hour concentrations over the new State 24-hour PM2.5 standard. The new State 24-hour standard would protect an additional 16% of the population in the State (close to 3 million persons) over the protection offered by the current federal standard.

Annual Mean statistics show that 61% of the statewide population corresponding to 11 million inhabitants (21%-98% in six air basins) is exposed to annual average PM2.5 concentrations over the current federal standard of 15 $\mu\text{g}/\text{m}^3$. In contrast, 83% of the State's population (15 million persons) is exposed to PM2.5 levels over the new State annual PM2.5 standard of 12 $\mu\text{g}/\text{m}^3$. In addition to the protection rendered by the current federal annual PM2.5 standard the new State annual standard would provide significant additional protection to people living in

the Mountain Counties, Salton Sea, San Francisco Bay Area, and the South Central Coast air basins.

From the data presented in Appendices 6-E1 to 6-E3 and 6-F1 to 6-F2, we estimated PM10 and PM2.5 annual and 24-hour population weighted concentrations for each air basin. We assumed that the population in a specific concentration bin is exposed to the midpoint concentration in that bin. Table 6.7 lists the results of the analysis for PM10.

The annual statistics show that in three air basins - South Coast, San Joaquin Valley, and Salton Sea - the basinwide population weighted annual geometric mean PM10 concentrations are above 30 $\mu\text{g}/\text{m}^3$. The Salton Sea has the highest PM10 annual averages in the State (58 $\mu\text{g}/\text{m}^3$). The South Coast (with an average of 37 $\mu\text{g}/\text{m}^3$) and the San Joaquin Valley (with 34.3 $\mu\text{g}/\text{m}^3$) follow. With the exception of Great Basin Valleys and Lake County, all air basins have population weighted annual arithmetic means over 20 $\mu\text{g}/\text{m}^3$.

The results of the 24-hour PM10 concentration analysis show that, with the exception of Lake County, the rest of the State has basinwide population weighted average EPDCs over 50 $\mu\text{g}/\text{m}^3$. The desert areas - Great Basin Valleys and Salton Sea - have the highest EPDCs, around 300 $\mu\text{g}/\text{m}^3$. The South Coast and San Joaquin Air Basins follow, with EPDCs above 100 $\mu\text{g}/\text{m}^3$. The rest of the air basins have EPDCs between 50 and 100 $\mu\text{g}/\text{m}^3$.

Table 6.7. Estimated Population Weighted Annual Means and 24-hour EPDC for PM10

Population Weighted Metrics for PM10			
Air Basin	Annual Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Annual Geometric Mean ($\mu\text{g}/\text{m}^3$)	Expected Peak Day Concentration ($\mu\text{g}/\text{m}^3$)
Great Basin Valleys	16.7	11.1	337.1
Lake County	10.8	9.2	40.8
Lake Tahoe	20.8	17.5	69.2
Mountain Counties	23.0	15.8	86.4
Mojave Desert	21.6	23.4	69.4
North Coast	17.5	15.9	59.6
North Central Coast	24.2	22.7	73.0
Northeast Plateau	13.0	9.7	61.2
South Coast	40.7	37.0	105.3
South Central Coast	23.0	21.4	62.4
San Diego	28.8	28.8	72.8
San Francisco Bay Area	21.7	19.4	79.4
San Joaquin Valley	39.5	34.3	158.8
Salton Sea	70.2	58.0	299.9
Sacramento Valley	24.5	21.0	100.6
Statewide	33.1	30.0	100.4

Table 6.8 lists the population weighted statistics calculated for PM2.5. The PM2.5 annual means show that three air basins – South Coast , San Diego and San Joaquin Valley - have basinwide population weighted averages above 15 $\mu\text{g}/\text{m}^3$, while three additional air basins – San Francisco Bay Area, Salton Sea and Sacramento Valley – have population weighted annual means over 12 $\mu\text{g}/\text{m}^3$.

Four air basins have population weighted average 24-hour EPDCs over 65 $\mu\text{g}/\text{m}^3$. The San Joaquin Valley has the highest EPDC (132 $\mu\text{g}/\text{m}^3$) of about twice the level of the standard, followed by the Sacramento Valley (93.1 $\mu\text{g}/\text{m}^3$), South Coast (87 $\mu\text{g}/\text{m}^3$), and San Francisco Bay Area (71 $\mu\text{g}/\text{m}^3$). Seven additional air basins have population weighted EPDCs over 25 $\mu\text{g}/\text{m}^3$.

Table 6.8. Estimated Population Weighted Annual Means and 24-hour EPDC for PM2.5

Population Weighted Metrics for PM2.5		
Air Basin	Annual Arithmetic Mean ($\mu\text{g}/\text{m}^3$)	Expected Peak Day Concentration ($\mu\text{g}/\text{m}^3$)
Great Basin Valleys	7.5	18
Lake County	2.5	17.5
Lake Tahoe	7.5	27.5
Mountain Counties	9.8	44.9
Mojave Desert	12.3	27.6
North Coast	7.5	35.6
North Central Coast	7.5	23.8
Northeast Plateau	NA	NA
South Coast	22.3	87
South Central Coast	11.8	43.1
San Diego	15.7	54.3
San Francisco Bay Area	12.9	71
San Joaquin Valley	20.3	132
Salton Sea	13.6	45.3
Sacramento Valley	12.8	93.1
Statewide	18.2	81.4

6.5 Characterization of Personal and Indoor Exposures

6.5.1 Personal PM Exposures

Peoples' actual exposures to PM, or their "personal exposures," have been shown in numerous studies to differ notably from outdoor PM concentrations measured at ambient monitoring stations, and often are much higher than outdoor PM levels. This is primarily due to people's close proximity to sources of PM throughout the day, especially PM sources inside of buildings, where people spend the large majority of their time. Personal PM exposures are estimated by

measuring pollutant concentrations in a person's breathing zone, the area near their nose and mouth, using portable instruments worn by the individuals. Because people often spend time in enclosed environments close to PM sources such as smoking, cooking, and cleaning activities, personal concentrations also are often higher than indoor PM concentrations measured at fixed locations in the indoor environment. The results of recent studies of personal and indoor concentrations of PM most relevant to understanding Californians' exposures are presented in Table 6.9. and discussed below.

The first major study to demonstrate personal PM concentrations above indoor and outdoor concentrations was the Particle Total Exposure Assessment Methodology (PTEAM) Study, conducted in 1990 in Riverside, California. Investigators measured PM₁₀ and PM_{2.5} for 12-hour daytime and nighttime periods in 178 homes during September to November. They found 12-hour daytime personal PM₁₀ concentrations to be about 50% higher than simultaneously measured daytime residential indoor or outdoor concentrations. Daytime personal concentrations averaged 150 µg/m³, while indoor and outdoor concentrations both averaged about 95 µg/m³ (Clayton et al. 1993, Ozkaynak et al. 1996a,b). Most importantly, 12-hour daytime personal PM₁₀ concentrations exceeded the California 24-hour ambient air quality standard of 50 µg/m³ for about 90 percent of the monitoring days and exceeded the federal PM₁₀ standard of 150 µg/m³ for 25 percent of the monitoring days. During nighttime, personal PM₁₀ concentrations decreased and were similar to concurrent indoor and outdoor concentrations (roughly 80 µg/m³), reflecting the importance of the proximity of people to PM sources during normal activities in determining personal exposure concentrations.

The PTEAM study used a probability sampling design, in which study subjects were carefully chosen to ensure that the sampled population represented the city of Riverside as a whole. These types of studies are large and expensive, and therefore not frequently performed. Three other probability studies of personal PM levels have been performed since PTEAM; in two, investigators found higher personal concentrations than corresponding outdoor concentrations, while outdoor concentrations were not measured in the third study. In Toronto, the investigators found average personal and outdoor PM_{2.5} concentrations of 28 µg/m³ and 15 µg/m³, respectively (Pellizzari et al. 1999). For PM₁₀, average personal and outdoor concentrations were 68 µg/m³ and 24 µg/m³, respectively. In Basel, Switzerland, average personal and residential outdoor PM_{2.5} concentrations were measured at 24 µg/m³ and 19 µg/m³, respectively; for nonsmokers, average personal and residential outdoor concentrations were both 18 µg/m³, showing the large impact smoking can have on personal PM_{2.5} exposures (Oglesby et al. 2000). In Mexico City, personal PM₁₀ concentrations, averaged 97 µg/m³, but no outdoor measurements were available for comparison (Santos-Burgoa et al. 1998).

Many smaller-scale particle exposure studies that have not used probability sampling design have been performed, in both the general population and in populations sensitive to PM such as the elderly or patients with chronic obstructive pulmonary disease (COPD). Recent U.S. studies of personal PM₁₀ and PM_{2.5} in which all or most of the study subjects were elderly and/or COPD patients include Evans et al. 2000, Linn et al. 1999, Rojas-Bracho et al. 2000, Sarnat et al. 2000, and Williams et al. 2000a,b,c. Like PTEAM, these smaller studies have also shown that personal exposures can be higher than simultaneously measured residential indoor and outdoor concentrations.

Table 6.9. Recent Personal-Ambient Air Particulate Matter Exposure Studies

Reference	Location and population	No. of subjects	Study period	Age range	PM Size ^a	N ^b	Concentration: arithmetic mean (SD); all in $\mu\text{g}/\text{m}^3$			Personal-ambient correlation ^d	
							Personal	Indoor	Ambient	Value	Type
<i>Probability-based studies</i>											
Clayton et al., 1993	Riverside, CA PTEAM	178	08-11/90	10-70	PM10-day	171	150 (84)	95 (61)	91 (48)	0.37 ^c	P
					PM10-night	168	77 (40)	63 (37)	77 (48)	0.54 ^c	P
Pellizzari et al., 1999	Toronto, Canada	732	11/95-10/96	>16	PM2.5	922	28	21	15	0.23	P
					PM10	141	68	30	24	NA ^f	
Oglesby et al., 2000	Switzerland EXPOLIS Subset with no ETS exposure	50	01/97-12/97	25-55	PM2.5	44	24 (17)	NA ^f	19 (12)	0.07	P
		20	01/97-12/97	25-55	PM2.5	20	18 (13)	NA ^f	18 (7)	0.21	P
<i>Not probability-based, California studies</i>											
Linn et al., 1999	Los Angeles; Elderly COPD	30	10/96-02/97	56-83	PM2.5	60	24 (15)	24 (15)	25 (15) ^c	0.26 ^e	P
					PM10	59	35 (15)	33 (16)	40 (18)	0.22	P
Evans et al., 2000	Fresno, CA; Elderly	5	02/99	>60	PM2.5	56	13	9.7	22	0.41	P
	Fresno, CA; Elderly	16	04/99-05/99	>60	PM2.5	190	11	8.0	8.6	0.84	P
<i>Not probability-based, recent United States studies</i>											
Rojas-Bracho et al., 2000	Boston, MA; COPD	18	01-09/96,	38-60	PM2.5	224	22 (14)	18 (14)	14 (11)	0.61 ^g	L
			01-02/97		PM10	225	37 (23)	32 (25)	22 (19)	0.35 ^g	L
Sarnat et al., 2000	Baltimore, MD; Elderly	15	06-08/97	62-82	PM2.5	37	27 (14)	NA ^f	25 (12)	0.76	L
			06-08/97		PM10	37	34 (12)	NA ^f	34 (13)	0.64	L
			02-03/99		PM2.5	36	19 (11)	NA ^f	5.6 (49)	0.25	L
			02-03/99		PM10	36	28 (17)	NA ^f	7.5 (73)	0.53	L
Williams et al., 2000a,b,c	Baltimore, MD; Elderly, healthy and COPD	21	07/98-08/98	72-93	PM2.5	23	13	9.4	22	0.80	L

a-Refer to publication for measurement averaging times; most are 24 hr, 'day' refers to 12 hr daytime, 'night' refers to 12 hr nighttime.

b-Listed sample size for personal samples; see reference publication for sample size information for indoor and ambient samples.

c-Outdoor residential measurements substituted as ambient concentration data from a nearby monitoring site were unavailable.

d-Values are Pearson correlation coefficients unless otherwise noted; types are Pooled (P) or median Longitudinal (L).

e-Values were calculated as the square root of R^2 from mixed model regression

f-NA indicates information was not available

g-Spearman rank correlations

However, these studies of sensitive populations have generally shown smaller personal-outdoor or personal-ambient station differences than those found in the PTEAM study, and stronger correlations with ambient levels. This appears to be in part due to the reduced activity levels of many of the study subjects who have pre-existing lung disease (for example, fewer cleaning and cooking activities), as well as the use of longitudinal study designs (multi-day monitoring) which are more likely to reflect personal to outdoor relationships. These studies have also generally found smaller differences between personal and ambient levels for PM_{2.5} as compared to PM₁₀, and that correlations between ambient and personal levels are generally higher for PM_{2.5} than for PM₁₀. Notable exceptions exist, however, such as the results from two recent studies of elderly subjects in Fresno, California and Baltimore, Maryland (Evans et al. 2000, Williams et al. 2000a,b,c) where personal levels were lower than ambient levels, on average. Also, another study of elderly subjects in Baltimore found a lower correlation between personal and ambient levels of PM_{2.5} than for PM₁₀ (Sarnat et al. 2000). These results are likely explained by the reduced activity level of the study participants; seasonal differences in ambient levels, ventilation practices, local variability, and the presence or use of fewer indoor PM sources; and multi-day monitoring.

There are few data available on personal PM_{2.5} concentrations in California, although non-smoking elderly subjects in Fresno (Howard-Reed, et al., 2000, Evans et al. 2000) and COPD patients in Los Angeles (Linn et al. 1999) have been studied. Because none of the PM_{2.5} studies have used a probability-based design, and although much information is currently being gathered about PM_{2.5} in California, the extent to which Californians' personal exposures to PM_{2.5} are elevated above ambient concentrations is largely unknown.

Because measured personal exposures to PM are often greater than estimates based on time-weighted averages of concurrent indoor and outdoor PM levels, researchers have identified a "personal cloud" of PM. It is thought that this "personal cloud" is due to an individual's activities (which can generate or resuspend particles), their proximity to other activities that generate PM emissions, and their visits to non-monitored environments with elevated PM levels. Examples of activities that generate PM likely to contribute to elevated personal PM include smoking, cooking, cleaning, travel, some types of work, and playing on a carpeted floor.

In several PM exposure studies, researchers have estimated the magnitude of the "personal cloud." Wallace (2000a) reviewed several recent studies, and found that the personal cloud for PM₁₀ for healthy persons, from children to the elderly, was often about 30 $\mu\text{g}/\text{m}^3$, but it ranged from 3-67 $\mu\text{g}/\text{m}^3$ among individuals. The personal cloud for PM_{2.5} was smaller, ranging from 6-27 $\mu\text{g}/\text{m}^3$. The personal cloud for COPD patients in two studies was considerably smaller than that for the general population: 6-11 $\mu\text{g}/\text{m}^3$ for PM₁₀, and about 6 $\mu\text{g}/\text{m}^3$ for PM_{2.5}; this reduction is probably attributable to the reduced level of personal activities of the study subjects, and the lack of significant indoor PM sources in their homes.

The sources and composition of the personal clouds were not identified in these studies. Personal activities that resuspend particles from clothes, furnishings, and other surfaces may be an important source, in addition to the activities listed above. Recent studies have identified other factors that could affect the personal cloud composition and size fractions, such as the use of cosmetics and antiperspirants (Conner, et al., 2001), and the proximity and type of combustion sources such as incense burning and cooking (McBride et al. 1999; Fortmann et al. 2001).

In summary, in spite of the many studies cited, the ability to accurately estimate PM exposure concentrations for general populations, especially PM_{2.5} exposures, is still limited by the small number of probability design studies, the large amount of individual variability, and the limited seasonal coverage of the probability studies that have been conducted (which did not include

the important seasonal variations in air exchange rates; U.S. EPA 2001). The PTEAM study remains the only major probability sampling PM exposure study conducted in the U.S. and still provides the most relevant California PM₁₀ exposure data, although it essentially covered just one season in one city. Representative PM_{2.5} data for all Californians are lacking.

6.5.2 Sources of Indoor PM

Indoor PM sources often increase particle concentrations inside a building above ambient concentrations, due to the trapping effect of the building shell. A key factor in the effectiveness of this trapping is the air exchange rate of the building, which tends to vary by season and is strongly affected by open windows and doors, mechanical ventilation, and building construction characteristics.

Outdoor air infiltration and indoor combustion sources such as smoking and cooking are typically the greatest sources of indoor PM (Wallace 1996; Ozkaynak et al. 1996*a,b*; Brauer et al. 2000; Abt et al. 2000; Fortmann et al. 2001). For example, through source apportionment the PTEAM investigators estimated that, on average, about 76% of the indoor PM_{2.5} mass and 66% of the indoor PM₁₀ mass originated outdoors. They also estimated that, on average, 5% of PM_{2.5} and 4% of PM₁₀ was attributed to tobacco smoking; 4% of PM_{2.5} and 5% of PM₁₀ was attributed to cooking; and 14% of PM_{2.5} and 26% of PM₁₀ were from unexplained sources (Ozkaynak et al. 1996*a*). Abt et al. (2000) and Long et al. (2000) found that the relative contribution of outdoor PM to indoor levels varied by particle size, with outdoor air generally contributing a majority of the smaller particles (less than 0.5 micrometers) measured indoors, while indoor sources contributed more to the larger (2-10 micrometers) size fraction. Thus, reductions in outdoor PM levels can have a major effect on the indoor concentrations.

For PTEAM homes with smokers, it was estimated that 30% of the PM_{2.5} mass and 24% of the PM₁₀ mass came from smoking. For homes in which cooking occurred during the monitoring period, 25% of the PM_{2.5} and PM₁₀ was estimated to come from the cooking activity (Ozkaynak 1996*b*). These results are consistent with those found in many previous indoor studies that have examined the impact of cigarette smoking on indoor PM levels, and led to subsequent studies of indoor cooking emissions that have confirmed the high impact that some cooking methods can have on indoor and personal PM levels (Abt et al. 2000; Wallace 2000*b*; Brauer et al. 2000; Fortmann et al. 2001). In a study of a variety of cooking activities using gas and electric stoves in a test home in northern California, kitchen PM₁₀ levels ranged to more than 1400 µg/m³ during frying, broiling, and baking activities (Fortmann et al., 2001). During use of the self-cleaning feature, oven cleaning resulted in kitchen PM₁₀ levels up to 3661 µg/m³, and indoor PM_{2.5} ranged to 2032 µg/m³, while concurrent outdoor levels ranged only to 20 µg/m³. The burning of wood, incense, and mosquito coils can also be important combustion sources of residential indoor PM, especially in the 2.5 µm size range and below (Brauer et al. 2000; Lofroth et al. 1991).

Physical generation or re-suspension of particles also can be an important PM source. Indoor surfaces such as carpets and draperies can attract and re-emit particles (Thatcher and Layton, 1995, Kamens et al. 1991). Particle concentrations from carpets can be high even in homes where good cleaning practices are used, and the particles can become re-entrained in the indoor air when people walk or play on the carpeted surface (Wallace 2000*a*; Roberts and Dickey 1995; Abt et al. 2000, Vette et al. 2001). Track-in of particles on shoes and by children and pets has also been shown to contribute significantly to indoor particle concentrations in residences (Roberts and Dickey 1995, Thatcher and Layton 1995). House dust particles have been found to include vapors, metals, and semi-volatile chemicals of intermediate vapor pressures, such as pesticides and polycyclic aromatic hydrocarbons (Rothenberg et al. 1989; Roberts and Dickey 1995; Lewis et al. 1999; U.S. EPA, 1999) that have their own toxic

properties. These contaminants are often adsorbed onto the surfaces of house dust particles, and are available for re-emission to the air and subsequent inhalation, and for dermal absorption and/or ingestion by children through floor contact and hand-to-mouth behavior (Lewis et al, 1994; Zartarian et al. 1998; Zartarian and Leckie, 1998). For toxics such as lead, floor dust levels can be a major determinant of exposure.

Biological contaminants such as fungi, bacteria, house dust mites, and pollen also can contribute to indoor particle concentrations, especially in buildings with moisture problems from flooding or roof leaks that have not been properly repaired. Many biological contaminants can trigger asthma attacks in sensitive individuals and cause other adverse health effects such as allergy symptoms, sinus and respiratory infections, headaches and irritant effects (NAS 1993; NAS 2000). Bioallergens, such as pollen, in outdoor air can also penetrate indoor spaces. Re-entrained road dust may be a particularly important source of bioallergens in both indoor and outdoor air (Miguel et al. 1998).

6.5.3 Relation of Personal PM Concentrations with Ambient Concentrations

Although much effort has been made to determine the relationship between outdoor and personal PM concentrations, no consistent predictive relationship has been found. Complicating factors include varying degrees of particle infiltration from outdoors, varying particle removal rates indoors, and the wide variety of peoples' activities and proximity to sources.

The complex relationships between personal exposures and outdoor concentrations are reflected in the variable correlations found between personal PM₁₀ concentrations and ambient concentrations. Correlations (*r*) of personal PM₁₀ concentrations with ambient concentrations in studies utilizing a cross-sectional study design (each individual monitored for one day), including PTEAM, have been low, ranging from 0 to about 0.3 (Dockery and Spengler 1981, Sexton et al. 1984*a,b*, Spengler et al. 1985, Liroy et al. 1990, Clayton et al. 1993, Ozkaynak et al. 1996*b*). In these studies, investigators have generally collected personal exposure samples over durations of 12 or 24 hours.

However, for longitudinal studies with seven or more repeated measurements, correlations for a given subject between personal and outdoor concentrations are greater than for a cross section of subjects with a single measurement period (Wallace 1996, Wallace 2000*a*). Additionally, recent studies for PM_{2.5} have found stronger correlations for personal PM_{2.5} concentrations with outdoor particle concentrations than were found for PM₁₀ in earlier PM₁₀ studies. Rojas-Bracho et al. (2000) found that the median longitudinal Spearman correlation coefficient (*r*) between personal and outdoor PM_{2.5} concentrations for each individual over multiple days was 0.61 in Boston. Median longitudinal Pearson correlations (*r*) were 0.25 and 0.76 for winter and summer, respectively, in Baltimore (Sarnat et al. 2000). Average Pearson correlation coefficients (*r*) between personal and outdoor PM_{2.5} concentrations were 0.41 and 0.84 for the winter and spring phases of study in Fresno, respectively (Evans et al. 2000), 0.26 during the fall and winter in Los Angeles (Linn et al. 1999), and 0.89 in Baltimore (Williams et al. 2000*a,b*). However, because most of these studies used elderly and/or ill subjects, the correlations may be greater than would be seen for healthy individuals. This appears to be due to the participants' reduced rates of activities and mobility relative to the general population (see Table 6.9 for a description of the demographic group observed in each study), the absence of major indoor PM sources, and increased operation of heating, cooling, and ventilation systems (which usually have air filtration) (Rodes et al. 2001; Williams et al. 2000*a*).

Strong correlations between personal and outdoor concentrations have also been observed in two European studies. In their longitudinal study of 13 children in the Netherlands, Janssen et al. (1999) found longitudinal correlation coefficients between personal and outdoor PM₁₀ of 0.75 for all children and 0.84 for children not exposed to environmental tobacco smoke.

Correlation coefficients for PM_{2.5} were 0.86 for all children and 0.92 when environmental tobacco smoke exposures were excluded. Personal concentrations averaged 28 µg/m³, while outdoor concentrations measured 17 µg/m³. In a study of elderly subjects with cardiovascular disease, the median Pearson correlation (r) for personal and outdoor PM_{2.5} was 0.79 in Amsterdam and 0.76 in Helsinki (Janssen et al. 2000).

In spite of the complex relationship between personal and outdoor PM concentrations, studies have shown outdoor PM to be a consistent and important contributor to overall PM exposure. Analysis of the results of personal exposure studies have estimated average outdoor contributions to personal PM mass exposures ranging from about 50% to 64% for PM₁₀ (Ozkaynak et al. 1996a, Mage 1998) and to 75% or more for PM_{2.5} (Koutrakis et al. 1992, Mage 1998). Mage (1999) also found that variations in personal exposures of persons with similar lifestyles and no exposure to tobacco smoke were driven by variations in ambient PM concentrations. The work of Mage et al. (1999) and Wilson et al. (2000) attempts to show that indoor and personal PM concentrations reflect the “superposition” of an ambient-derived indoor PM component, which tracks outdoor concentrations, and a more variable indoor-derived PM component, which does not. Sarnat et al. (2000) showed that personal-to-ambient concentration correlations improve greatly with increasing air exchange rates. Findings such as these help explain why mortality and morbidity effects seen in epidemiology studies have been linked to ambient PM concentrations despite the sometimes poor correlations between personal and outdoor concentrations for a given population on a given day, such as is reflected in cross-sectional studies.

6.5.4 Contributions of Outdoor Sources of PM to Indoor Concentrations

Outdoor particles enter buildings and contribute to indoor concentrations. The rate at which particles infiltrate into indoor environments and the ratio of indoor to outdoor concentrations are dependent on many factors, especially the air exchange rate of the building, the use of operable windows and doors, and the aerodynamic size of the particles. In addition, outdoor concentrations measured outside of or near the building where indoor measurements are taken can vary considerably in relation to corresponding ambient levels measured at stationary ambient monitoring stations, especially for PM₁₀ at higher concentrations (Ozkaynak et al. 1996b).

Indoor PM₁₀ concentrations in PTEAM were similar to nearby outdoor PM₁₀ concentrations during the daytime, but slightly lower during the nighttime (Clayton et al. 1993). Indoor PM_{2.5} concentrations were similar to outdoor concentrations during the daytime, and lower during the nighttime. However, through source apportionment techniques, the PTEAM investigators estimated that, of the total indoor mass of particles, outdoor particles contributed 66% of the PM₁₀ mass and 76% of the PM_{2.5} mass (Ozkaynak et al. 1996a,b).

Correlations (r²) between indoor PM_{2.5} and nearby outdoor PM_{2.5} were estimated in studies of elderly subjects to be 0.93 (winter) and 0.75 (spring) in Fresno (Evans et al. 2000), and 0.96 in Baltimore (Williams et al. 2000a). In a study of four Boston homes with air exchange rates below 1.0 hr⁻¹, Abt et al. (2000) estimated that only 20-43 percent of indoor particles from 2-10 µm were from outdoors, while 63-92 percent of indoor PM from 0.02-0.3 µm were from the outdoors.

The outdoor-derived fraction of indoor PM is determined by several factors (e.g., air exchange rate, particle penetration, and deposition) and, under steady-state conditions, can be calculated from the following equation, assuming no indoor sources are present:

$$C_{\text{out-in}} = C_{\text{out}} [P a / (a + k)]$$

where P is the particle penetration factor, a is the air exchange rate of the building, k is the particle deposition rate, $C_{\text{out-in}}$ is the concentration of particles of outdoor origin in indoor air (i.e., those that have infiltrated indoors), and C_{out} is the concentration of particles in outdoor air. Both P and k are in large part dependent on particle size, making the solution to this equation dependent on the particle size fraction considered, except when a is high. The steady state modeling approach is shown here for simplicity, but dynamic modeling is generally needed because pollutant source emissions and ventilation are episodic and not constant.

Air exchange rate is the rate at which the air in an indoor air space is exchanged with the same volume of outdoor air. In residential buildings, air exchange rates vary widely depending upon building construction, opening of windows and doors, wind-and fan-induced pressure changes, and seasonal changes. A number of investigators have reported air exchange rates for homes in California (Ozkaynak et al. 1996*a,b*, Sheldon et al. 1993, Wilson et al. 1993, Pellizzari et al. 1999, Wilson et al. 1986). Representative values for the mean and standard deviation of air exchange rates in residential buildings in California have been estimated at 1.2 and 1.0, respectively, with a log normal distribution (Air Resources Board, 1998*b*), and have been measured as high as 5 or more air changes per hour.

The penetration factor denotes, for a given volume of air that enters the building, the fraction of the outdoor contaminant mass that moves through the building shell to the indoor space without interception. For residential buildings, the main entry routes of outdoor air are open windows and doors, cracks in the building shell, and mechanical ventilation systems such as swamp coolers, whole house fans, and central systems with substantial duct leakage. Penetration factors are calculated based on measurements of other parameters, mainly indoor and outdoor particle mass concentrations and air exchange rates, and can vary depending on the size fraction of PM being considered. The values of the penetration factor for PM_{2.5} in residences have generally been estimated in the range of 0.5 to 1.0 (Long et al. 2001; Suh et al. 1994, Koutrakis et al. 1992, Dockery and Spengler 1981, Ozkaynak et al. 1996*b*), with California studies showing penetration factors for PM_{2.5} and PM₁₀ close to 1.0 (Ozkaynak et al. 1996*b*; Thatcher and Layton 1995). More recent field studies have found differences in penetration efficiencies among particles of different sizes, with larger sizes showing reduced penetration (Abt et al. 2000; Vette et al. 2001; Long et al. 2001), especially under conditions of low air exchange. Laboratory studies with simulated penetration and infiltration scenarios have generally supported and complemented the field results, although they are limited to leakage measurements (Mosley et al. 2001; Liu and Nazaroff 2001; Thornburg et al. 2001).

In public and commercial buildings, penetration depends on the size of the building, whether operable windows are present, and the presence or absence of a central HVAC system with filtration. A large, multi-story building with a central system and high efficiency filtration would generally have very low penetration and infiltration of particles of all sizes. At the other extreme, a small grocery or retail store with no central system and open windows and doors would be similar to many homes and have high penetration and infiltration due to the high air exchange rate with little interception of particles (Air Resources Board, 1998*b*).

In the process of entering an indoor environment, particle concentrations may be reduced by various mechanisms, including deposition, transformation, decay, decomposition, and adsorption. The cumulative effect of these processes is reflected in the particle deposition (removal) rate. Typically, particles of larger aerodynamic diameter have higher deposition rates. Values for the particle deposition rate for California homes, estimated as part of the PTEAM study, were 0.39 hr⁻¹ for PM_{2.5} and 0.65 hr⁻¹ for PM₁₀ (Ozkaynak et al. 1996*b*). Other investigators have found a wider range of deposition rates for particles of different aerodynamic size, with the lowest deposition rates shown by particles in the 0.1 to 1.0 micrometer range (Thatcher and Layton 1995; Long et al. 2001; and others). Additionally, the indoor furnishings

and material surfaces can affect deposition, with rough “fleecy” materials collecting particles more than smooth, slick surfaces.

In summary, the contribution of outdoor PM to indoor PM concentrations can be substantial but highly variable. The transport of outdoor PM into a building’s air volume and surfaces is very complex and varies greatly, depending on many factors through time for different particle size ranges. The indoor-outdoor relationships for PM also vary with outdoor PM concentrations, so that simple indoor-outdoor ratios do not reflect the true interrelationships. Using the PTEAM source apportionment results as an example from a large, population-based study in California, indoor PM can be expected to be comprised of about $\frac{1}{2}$ and $\frac{3}{4}$ outdoor PM₁₀ and PM_{2.5}, respectively. For elderly and ill persons in nursing homes, hospitals, or apartments, the outdoor PM contribution appears to be much less. The contribution of outdoor PM_{2.5} is generally greater than that for PM₁₀ due to increased penetration. During cold weather periods, the outdoor PM contribution appears to be less due to reduced air exchange rates. The contribution of outdoor PM to indoor PM in public, commercial and multi-family buildings would be expected to be somewhat less than that for single-family residences due to outdoor air filtration by mechanical ventilation systems; however, representative data are lacking in this area.

6.5.5 Indoor Concentrations in Public and Commercial Buildings

Because adults and children in California typically spend about 62% and 75% of their time in their residence, respectively (Jenkins et al. 1992, Phillips et al. 1991), residences are the most important locations for overall PM exposure for most people. However, significant time—about 25% on average—is also spent in other buildings, such as at work and school, so PM concentrations in these buildings are also important in estimating exposure to PM.

PM concentrations in public and commercial buildings appear to often be lower than ambient concentrations, but far fewer studies have been conducted for public buildings than residences. Reasons for lower indoor PM concentrations in public and commercial buildings include the use of particle filters in mechanical ventilation systems, inoperable windows, reduced exterior surface to volume ratios, and the lack of many indoor sources typically present in residences. However, as with residences, the presence of indoor sources in public and commercial buildings can produce indoor concentrations that exceed concurrent ambient concentrations, especially if smoking is allowed in the building. The largest public and commercial building PM study to date was conducted in the Pacific Northwest for 38 commercial buildings (Turk et al. 1987). Buildings where smoking was prohibited averaged $19 \mu\text{g}/\text{m}^3$ PM_{3.5} indoors, the same as the outdoor level, while buildings where smoking was permitted averaged $70 \mu\text{g}/\text{m}^3$, notably higher than the outdoor level. (PM_{3.5} was measured as respirable PM or “RSP”). Sheldon et al. (1988) measured PM in six buildings in the eastern U.S., and found indoor PM concentrations generally lower than outdoors where there was no smoking, but much higher indoor concentrations where smoking was allowed (14 to $56 \mu\text{g}/\text{m}^3$ versus 13 to $17 \mu\text{g}/\text{m}^3$ outdoors).

Elevated PM concentrations can occur in other enclosed environments such as inside motor vehicles, but few studies have been conducted to examine such exposures. The most comprehensive study to date has been that of Rodes et al. (1998) conducted in Sacramento and Los Angeles. Real-time fine particle count concentrations and black carbon concentrations inside vehicles increased up to ten times the average roadway concentrations when following certain diesel vehicles. However, average PM mass concentrations inside the vehicle were similar to outdoor concentrations measured at the nearest ambient monitor, while roadway PM concentrations were somewhat higher. Average in-vehicle PM₁₀ concentrations were about $27 \mu\text{g}/\text{m}^3$ for Sacramento runs and $61 \mu\text{g}/\text{m}^3$ for Los Angeles as compared to $29 \mu\text{g}/\text{m}^3$ and $73 \mu\text{g}/\text{m}^3$ at the nearest ambient stations, respectively. In-vehicle PM concentrations averaged 60 to 80% of those concentrations measured just outside the vehicle, which reflected the elevated

roadway concentrations. In summary, it appeared the impact of traffic on PM exposures inside vehicles was small with regard to total mass, although significant differences in traffic PM chemical composition and PM size distribution are probably present compared to ambient PM. Using carpool lanes appeared to reduce in-vehicle PM concentrations significantly, although carpool lanes were used in only two of the 29 two-hour runs.

6.5.6 PM Exposures in Sensitive Subgroups

Individuals with pre-existing respiratory disease, such as COPD and asthma, and pre-existing cardiovascular disease can be more susceptible to adverse effects from exposure to particulate pollutants. Until recently, personal exposures of such groups to particles had not been measured. Only a few small, recent studies have been conducted to examine the PM_{2.5} exposures of such groups. Elderly healthy persons and young children may also be more susceptible; the PM exposures of these subpopulations have been discussed earlier in this chapter.

Rojas-Bracho et al. (2000) and Linn et al. (1999) have reported on PM₁₀ and PM_{2.5} exposures for individuals with COPD. Rojas-Bracho et al. found that mean personal PM₁₀ and PM_{2.5} concentrations were 67% and 52% above outdoor PM₁₀ and PM_{2.5} concentrations, respectively, for 18 COPD patients in Boston. (PM₁₀ and PM_{2.5} concentrations were 22 and 14 $\mu\text{g}/\text{m}^3$ outdoors, 32 and 18 $\mu\text{g}/\text{m}^3$ indoors, and 37 and 22 $\mu\text{g}/\text{m}^3$ personal, respectively). Personal-to-ambient concentration median longitudinal correlations were moderate with better correlation observed for PM_{2.5} ($r=0.61$) than for PM₁₀ ($r=0.35$) or for PM_{2.5-10} ($r=0.35$). The authors attribute this to the higher deposition rate of PM_{2.5-10} compared to that for PM_{2.5}. The authors also found personal-to-outdoor concentration ratios to be high (i.e., greater than 3) when air exchange rates were low (less than one exchange per hour). Overall, this study found similar results to those of other studies for healthy adults except PM concentrations were lower.

Linn et al. monitored 15 COPD patients for PM_{2.5} exposures and 15 for PM₁₀ exposures in Los Angeles during the fall and winter. PM₁₀ and PM_{2.5} mean concentrations were 40 and 25 $\mu\text{g}/\text{m}^3$ for outdoors, 33 and 24 $\mu\text{g}/\text{m}^3$ for indoors, and 35 and 24 $\mu\text{g}/\text{m}^3$ for personal. The personal and indoor PM levels are similar to those discussed above for the Rojas-Bracho et al. study of COPD, although the outdoor PM levels in Los Angeles were higher. Unlike other studies, this study did not find personal concentrations to be significantly higher than indoors or outdoors. The authors suggest that the lack of increased personal PM in these subjects with severe COPD may be due to less personal activity, less time spent outside of the home, less personal particle generation, and failure to keep the personal monitor in their personal environment at all times. The pooled correlation of personal PM concentrations to ambient PM concentrations at a monitoring station (some of which were distant from the subject's home) were quite low ($r^2 < 0.1$). Daily indoor PM levels tracked PM levels outside the home more closely ($r^2 = 0.27$ for PM₁₀, $r^2 = 0.19$ for PM_{2.5}); presumably personal PM levels had similar correlations, because they correlated very closely with indoor PM levels.

Lillquist et al. (1998) reported indoor and outdoor PM₁₀ measurements in three Utah hospitals over one winter season. Significant variability in indoor PM levels was found both among room types and among hospitals, and the relationship between indoor PM₁₀ levels and outdoor levels was highly variable. The ICUs had significantly lower PM₁₀ levels than other types of rooms, after adjusting for hospital differences. Thus, the most critically ill individuals may experience some protection in hospitals from ambient PM; however, in general, hospitals do not offer regular protection from ambient PM.

Two studies nearing completion will add significantly to our understanding of Californians' exposures to PM in both sensitive subpopulations and healthy persons. Conducted by the Harvard School of Public Health, both studies are designed to longitudinally examine the

relationships between outdoor and indoor concentrations and personal exposures across different seasons. The first of the two studies is examining PM exposures of a group of 15 individuals with COPD in Los Angeles. This study will provide information on how 24-hour average PM₁₀ and PM_{2.5} mass, elemental carbon, particulate nitrate, and elemental concentrations vary by season, individual, and subject activity. The second study uses a similar design for a group of healthy persons, though it involves even more detailed characterizations of the PM levels and ventilation characteristics of the subject's homes, and focuses on determining the contribution of outdoor concentrations to personal exposures. The results from these two studies are expected to provide important new information on the relationships between outdoor and indoor concentrations as well as personal exposures for several components of PM, for both COPD patients and healthy persons in California.

6.5.7 Summary

Ambient PM is usually the major contributor to indoor and personal PM exposure, especially when few indoor sources are present. However, the relationships between indoor and ambient concentrations and personal and ambient PM concentrations are complex, and correlations between total PM mass concentrations in different microenvironments are sometimes low. People's use of, or proximity to, sources of PM, such as indoor cooking and cigarette smoke, typically results in higher personal exposure levels than indoor and ambient levels measured concurrently by stationary monitors. Indoor sources of PM such as cooking, tobacco smoke, and cleaning activities such as vacuuming often contribute to elevated indoor concentrations as well. Investigators have generally found somewhat greater correlations between personal and ambient PM concentrations for single individuals studied over several days as compared to single day analyses for more individuals, and for elderly or ill individuals with more limited activities and few indoor sources. Correlations also tend to be greater for PM_{2.5} than for PM₁₀, in part because of increased penetration and reduced deposition rates indoors for smaller particles. However, there remains much uncertainty in the current understanding of these relationships.

6.6 References

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