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**Review of the
California Ambient Air Quality Standards
For Particulate Matter and Sulfates**

Report to the Air Quality Advisory Committee

Public Review Draft

November 30, 2001

California Environmental Protection Agency

**Air Resources Board
and
Office of Environmental Health and Hazard Assessment**

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California Environmental Protection Agency

Winston Hickox, Secretary

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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	California Air Resources Board
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 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
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: $B_{\text{ext}} = - \ln ((I_0 - I_1)/I_0) / d$ 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
FEV ₁	forced expiratory volume in one second, a measure of lung function
Fine Particles	PM2.5, or particulate matter with a mean aerodynamic diameter of 2.5 microns or less
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
LRS	lower respiratory symptoms
Mie Scattering	light scattering by particles with diameters near the wavelength of the light (0.18 to 108). Mie scattering is the dominant cause of visible atmospheric haze.
MMEF	mid-maximal expiratory flow, a measure of lung function

Nephelometer	an instrument to measure light scattering in air.
nm	nanometer, or one billionth of a meter
NO ₂	nitrogen dioxide
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
PM10	particulate matter with an aerodynamic diameter of 10 microns or less
PM2.5	particulate matter with an aerodynamic diameter of 2.5 microns or less, also referred to as fine particles
PMNs	polymorphonuclear cells, a class of white blood cells involved in acute inflammatory response
Rayleigh Scattering	light scattering by atmospheric gases. Rayleigh scattering decreases as the fourth power of wavelength. In pure air, blue light ($\lambda = 400$ nm) is scattered 9 times more efficiently than red light ($\lambda = 700$ 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.
SBP	systolic blood pressure
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
SO ₂	sulfur dioxide
TB	tracheobronchial, referring to the conducting airways from the trachea through the bronchioles
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 micron (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
µg	microgram, or one millionth of a gram
µm	micron, or one millionth of a meter

1 Executive Summary

2 In December 2000, as a requirement of the Children's Environmental Health Protection Act
3 (Senate Bill 25, authored by Senator Martha Escutia, Stats. 1999, Ch. 731), the California Air
4 Resources Board (ARB or Board), approved a report (ARB and OEHHA, 2000), developed in
5 consultation with the Office of Environmental Health Hazard Assessment (OEHHA), that
6 contained a preliminary review of all of the existing health-based California ambient air quality
7 standards. There were two purposes for these reviews: (1) to determine whether, based on
8 public health, scientific literature, and exposure pattern data, the existing ambient air quality
9 standards adequately protected the health of the public, including infants and children, with an
10 adequate margin of safety [California Health & Safety Code section 39606(d)(1)]; and (2) to
11 prioritize for full review those standards determined not to adequately protect public health.

12 These reviews were not exhaustive, but rather were narrowly targeted to the two purposes
13 noted above. The critical reviews suggested that adverse health effects may occur in infants,
14 children, and other potentially susceptible subgroups exposed to pollutants at or near levels
15 corresponding to several existing California ambient air quality standards. The reviewers
16 recommended, and the Board concurred, that among the standards deemed possibly
17 inadequate, the standards for particulate matter less than 10 microns in aerodynamic diameter
18 (PM10) should be the first to undergo full review. Recent epidemiological literature on PM10
19 suggests the potential for health effects in infants and children, including mortality, reduced birth
20 weight, premature birth, asthma exacerbation, and acute respiratory infections. Epidemiological
21 studies suggest that increased mortality and hospital admissions among the elderly and those
22 with chronic heart and lung diseases may also be associated with exposure to PM10. Further,
23 since almost everyone in California is exposed to levels at or above the current State PM10
24 standard during some parts of the year, the statewide potential for significant health impacts
25 associated with PM exposure was determined to be large and wide-ranging. Finally, the
26 reviewers recommended, and the Board concurred, that the standard for sulfates should be
27 reviewed in conjunction with the PM10 standards since sulfates are a component of particulate
28 matter.

29 In this report, the staff of the ARB and OEHHA present the findings of their full review of the
30 public health, scientific literature, and exposure pattern data for PM and sulfates in California.

31 The scientific evidence suggests a need for standards to encompass fine particles (PM2.5,
32 particulate matter 2.5 microns or less in aerodynamic diameter) as well as PM10. PM2.5 and
33 PM10 are both associated with a wide range of serious adverse health outcomes, including
34 premature mortality, acute and chronic bronchitis, asthma attacks and emergency room visits,
35 upper respiratory symptoms, days of work loss, and days with some restrictions in activity.

36 California Ambient Air Quality Standards have four elements (California Health and Safety Code
37 Section 39014, and Title 17, California Code of Regulations, Article 2, Section 70101): (1)
38 definition of the air pollutant, (2) an averaging time, (3) a pollutant concentration, and (4) a
39 monitoring method to determine attainment of the standard. **Staff's recommendations for
40 each of these elements are summarized below:**

- 41 • PM10 Annual-average Standard – Lower the annual-average standard for PM10 from
42 30 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) to **20 mg/m^3** . Revise the averaging method to an
43 annual arithmetic mean.
- 44 • PM10 24-hour-average Standard – Retain the 24-hour-average standard for PM10 at
45 **50 mg/m^3** .

- 1 • PM2.5 Annual-average Standard – Establish a new annual-average standard for PM2.5 at
2 **12 mg/m³**. Establish the new PM2.5 standard as an annual arithmetic mean.
- 3 • PM2.5 24-hour-average Standard – Make no recommendation at this time.
- 4 • Sulfate 24-hour-average Standard – Retain the 24-hour-average standard for sulfates at
5 **25 mg/m³**.
- 6 • For all the particulate matter ambient air quality standards, the concentrations for the
7 standards noted above are established as “**not to be exceeded**”.

8 Although staff does not recommend establishing a PM2.5 24-hour-average standard at this
9 time, we recognize that PM2.5 exposures do have significant, short-term health impacts. PM2.5
10 exposures have been associated with acute mortality effects. Staff is also interested in health
11 impacts from PM2.5 and PM10 at less than 24-hour exposure periods (e.g., hourly average PM
12 standards). While there are compelling studies which associate long-term PM2.5 exposure to
13 increased mortality and morbidity effects, there are fewer studies of the effects from short-term
14 exposures. During the next cycle of review of the PM standards, a larger database of PM2.5
15 studies will be available to evaluate the basis for potential short-term PM2.5 effects and
16 standards. At that time, staff will again evaluate the potential for short-term PM2.5 standards.
17 Until then, the 24-hour average PM10 standard should provide protection from 24-hour-average
18 PM2.5 peaks and effects.

19 A quantitative risk assessment estimates that moving current levels of PM10 and PM2.5 in
20 California to attainment of the recommended standards would result in a reduction of 6,500
21 (3,200 – 9,800 for a 95 percent confidence interval) cases of premature mortality per year, or
22 about 3 percent of all mortality in the population above age 30. The corresponding mean annual
23 reductions in hospitalizations are 600 for chronic obstructive pulmonary disease (COPD), 900
24 for pneumonia, 1,500 for cardiovascular disease, and 500 for asthma cases. Among children
25 ages 7 to 14, attainment of the PM2.5 standard is estimated to result in about 209,000 (81,000 –
26 323,000 for a 95 percent confidence interval) less days of lower respiratory symptoms per year.
27 The sulfates standard is currently attained throughout California.

28 **The monitoring methods to determine attainment are summarized below.**

- 29 • PM10 Monitoring Method – Staff recommends that the State monitoring method for PM10
30 (Method P) be updated to remove some of its dated operational and design features, and
31 bring the State and federal reference samplers into alignment. This action will allow well-
32 tested, federally approved instruments to be used as part of the State’s PM program, and
33 takes advantage of the already extensive PM10 monitoring network.
- 34 • PM2.5 Monitoring Method – For the PM2.5 annual-average standard, the staff proposes to
35 adopt the Federal Reference Method (FRM) for PM2.5 as the method for California. The
36 instruments identified in the PM2.5 FRM have performed well, and are suitable for
37 determining compliance with the air quality standard. The U.S. Environmental Protection
38 Agency (EPA) has funded more than 80 PM2.5 samplers in California that have become the
39 backbone of the State’s network.
- 40 • Continuous PM Monitoring Methods – There is an increasing need for continuous PM
41 monitors, both Statewide and throughout the nation. These monitors require fewer staff to
42 operate, display PM concentrations in real-time for public warnings, monitor every day, and
43 better identify sources. In addition, their measurements allow for more refined estimates of
44 exposure in community health studies and they are capable of collecting the ambient data
45 needed to establish and determine compliance with possible future hourly average PM
46 standards. The biggest problem so far has been the ability of the continuous samplers to

1 produce results comparable to the reference samplers. Deployment has been slow in
2 California for PM10 because the continuous samplers on the market in the last ten years
3 generally performed poorly in many high PM areas of the State. Advances have been made,
4 and tests have been recently conducted in the State, that may make it possible to approve
5 continuous samplers. Staff is proposing to adopt either a sampler type, or principle of
6 operation for continuous samplers.

- 7 • Sulfate Monitoring Method – Staff recommends that the current total suspended particle
8 (TSP) sulfate method (which employs a high volume sampling with analysis by ion
9 chromatography), described in the ARB method MLD 033, be changed to an existing
10 method for PM10 sulfates, MLD 007. MLD 007 is based on high-volume SSI sampling and
11 ion chromatography. This change would allow California to take advantage of its existing
12 PM10 sulfates network.

13 In light of the adverse health effects observed at current ambient concentrations and the lack of
14 a demonstrated threshold, staff makes the following comments:

- 15 • In any air basin in California that currently attains the ambient air quality standards, for either
16 PM10 or PM2.5, the air quality should not be degraded from present levels.
- 17 • The ARB, in consultation with local air quality management districts, establishes a goal of
18 continued reductions in PM10 and PM2.5 concentrations over time.
- 19 • The standards be revisited within five years, in order to re-evaluate the evidence regarding
20 the health effects associated with particle size, chemistry, and concentration.

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

30 The staff recommendations in this Staff Report will be presented for review and comment at
31 public workshops on the following dates:

- 32 • December 3, 2001 (evening), Oakland
- 33 • December 7, 2001 (afternoon), Sacramento
- 34 • December 11, 2001 (evening), Bakersfield
- 35 • December 12, 2001 (evening), Mira Loma
- 36 • December 18, 2001 (afternoon), El Monte
- 37 • December 18, 2001 (evening), Huntington Park

38 Further details on the addresses and times of the workshops are available at the ARB website:
39 <http://www.arb.ca.gov/research/aaqs/std-rs/std-rs.htm> or by calling 916-445-0753.

40 A public meeting of the Air Quality Advisory Committee (AQAC), a University of California-
41 appointed external committee formed to peer review this Staff Report, will be held on January
42 23 and 24, 2002 in Berkeley, California. Further details are available at the ARB website:
43 <http://www.arb.ca.gov/research/aaqs/std-rs/std-rs.htm> or by calling 916-445-0753.

1 Written comments on this Staff Report and the recommended standards may be addressed to
2 Dr. David Mazzer at the Air Resources Board, Research Division, P.O. Box 2815, Sacramento,
3 CA 95612-2815 (dmazzer@arb.ca.gov, 916-445-9488, 916-322-4357 FAX) by December 31,
4 2001 for consideration by the Air Quality Advisory Committee at their meeting on January 23
5 and 24, 2002.

6 Following the meeting of the Air Quality Advisory Committee (AQAC), staff will revise this Staff
7 Report based on comments received from AQAC members and the public. The revised Staff
8 Report will then be made available for a 45-day public comment period in advance of a public
9 meeting of the Air Resources Board to consider the staff's final recommendations. The Board
10 meeting is tentatively scheduled for May 16, 2002.

11 **1.1 Reference**

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

2 Introduction

2.1 Setting California Ambient Air Quality Standards

California Health and Safety Code Section 39606 (a) (2) authorizes the Air Resources Board (Board) 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 intensities 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, they represent the minimum acceptable air quality. An AAQS adopted by the Board is implemented, achieved, and maintained by rules and regulations. These rules and regulations are primarily, though not exclusively, emission limitations established by the regional and local air pollution control and air quality management districts for stationary sources, and by the Board for vehicular sources (generally, Health and Safety Code Sections 39002, 40000, and 40001).

The California Clean Air Act 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 on the recommendation of the Office of Environmental Health Hazard Assessment (Office) [Health and Safety Code Section 39606 (a) (1)]. The premise of the process is to assure that sensitive population sub-groups are protected from exposures to levels of pollutants that may cause adverse health effects. In addition, the Office 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. The Office's assessment of these considerations is to follow current principles, practices, and methods used by public health professionals.

The law also requires that the scientific basis or the scientific portion of the method used to assess these considerations be peer reviewed [Health and Safety Code Section 39606 (c)]. The Office's peer review body for ambient air quality standards is the Air Quality Advisory Committee (AQAC). Under Health and Safety Code Section 57004 (d) (2), the committee prepares a written evaluation of the staff report describing the scientific basis of the proposed ambient air quality standard.

2.2 Schedule for Review of the California Ambient Air Quality Standards

The Children's Environmental Health Protection Act (Senate Bill 25, authored by Senator Martha Escutia, Stats. 1999, Ch. 731) required the Board, in consultation with the Office, 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 review, and if the review finds a standard 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 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 was PM10 including sulfates. Other standards with a high priority for review were ozone and nitrogen dioxide. Standards with a low priority for review were carbon monoxide, sulfur dioxide, hydrogen sulfide, and lead.

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

2.3.1 Particulate Matter, 24-hour and Annual Averages

The current California ambient air quality standards for particulate matter less than 10 micrometers in diameter (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. The recommendation of the Department of Health Services summarized the selection of these values in a staff report published in 1982 (ARB 1982). The Department of Health Services concluded that reviewed studies indicated an association of particulate pollution with 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 $60 \mu\text{g}/\text{m}^3$. 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 standard which was based on TSP 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

1 against cancer. Until more substantial evidence concerning cancer was available, the
2 Department of Health Services believed that the long-term standard should not be a relaxation
3 of the TSP standard. An annual geometric mean of $30 \mu\text{g}/\text{m}^3$ ($10 \mu\text{m}$ diameter) was
4 approximately the value of the former annual standard for TSP when corrected to PM10.

5 **2.3.2 Sulfates, 24-hour Average**

6 The current California ambient air quality standard for sulfates is $25 \mu\text{g}/\text{m}^3$ for a 24-hour average
7 not to be equaled or exceeded (ARB 1977). The rationale for the standard presented in the staff
8 report was the following. The experimental threshold concentration for demonstrating an
9 increase in respiratory rate in healthy adults (determined for the most part in brief exposures) is
10 approximately $350 \mu\text{g}/\text{m}^3$ for a 15-minute exposure to sulfuric acid aerosol. The subjects
11 selected for these studies were healthy and vigorous, while the humans most susceptible to
12 ambient air pollution effects are the diseased, the very young, and the aged. The factor of safety
13 commonly applied to the threshold levels in healthy subjects to protect sensitive groups in the
14 population is between 10 and 100. Application of these factors in this case would result in a safe
15 exposure range of about 3.5 to $35 \mu\text{g}/\text{m}^3$ for sulfate compounds. The occupational standard for
16 healthy workers exposed eight hours per day is $1 \text{mg}/\text{m}^3$. Extrapolation of this number to a 24-
17 hour day and using a factor of 10 to apply to the general population produces a value of
18 $33 \mu\text{g}/\text{m}^3$, which is in approximate agreement with the upper range of the exposure determined
19 above. On the basis on this analysis, the Department of Health Services concluded that an
20 appropriate sulfate standard, including a margin of safety, was $25 \mu\text{g}/\text{m}^3$ as a 24-hour average.

21 **2.4 Environmental and Economic Impacts**

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

31 **2.5 References**

- 32 Air Resources Board (1977). Review of the 24-Hour Sulfate Ambient Air Quality Standard. Staff
33 Report 77-20-3. Sacramento, CA.
- 34 Air Resources Board (1982). California Ambient Air Quality Standard for Particulate Matter
35 (PM10). Staff Report. Sacramento, CA.
- 36 Air Resources Board and Office of Environmental Health Hazard Assessment (2000). Adequacy
37 of California Ambient Air Quality Standards: Children's Environmental Health Protection Act.
38 Staff Report. Sacramento, CA. Available at <http://www.arb.ca.gov/ch/ceh/airstandards.htm>.

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, cause 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, one should note that 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).

1 **3.2 Physical Properties**

2 **3.2.1 Definition**

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

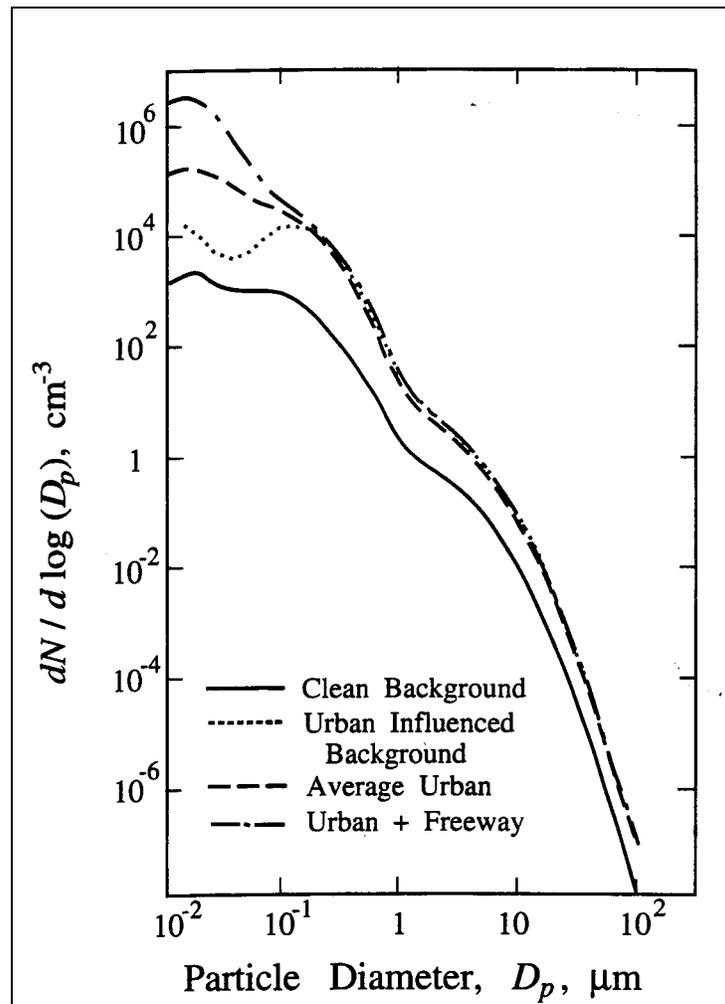
11 Atmospheric particles are usually referred to as having a radius or diameter, implying they are
12 spherical. However, many particles in the atmosphere have quite irregular shapes for which
13 geometrical radii and diameters are not meaningful. Hence, the size of such irregularly shaped
14 particles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

20 **3.2.2 Particle Size Distributions**

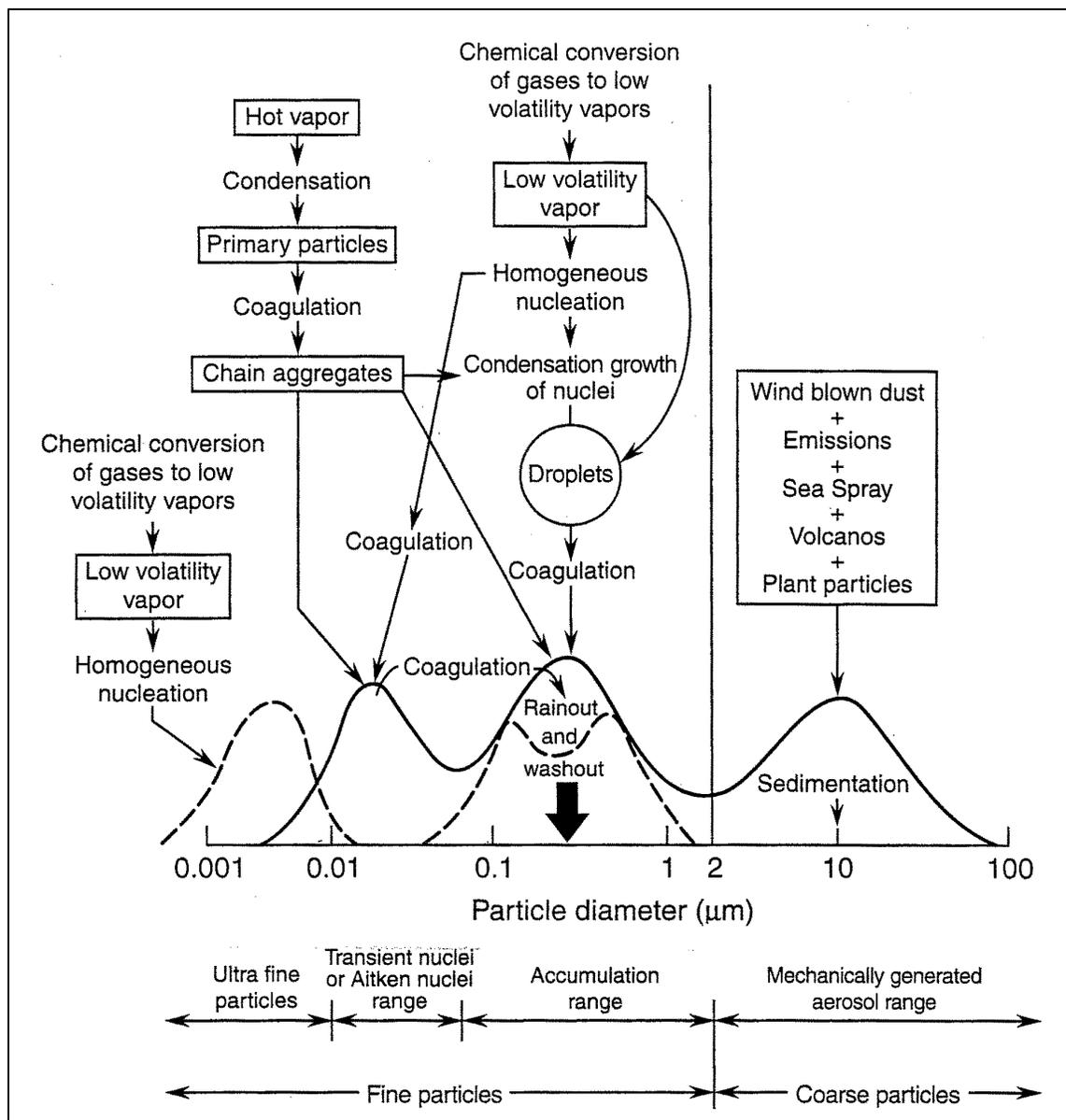
21 The atmosphere, whether in urban or remote areas, contains significant concentrations of
22 aerosol particles, sometimes as high as 10^7 to 10^8 particles/ cm^3 . The aerodynamic diameter of
23 these particles span over four orders of magnitude, from a few nanometers to around 100 μm .
24 Because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

27 Urban aerosols are mixtures of both primary and secondary particles. The number distribution is
28 dominated by particles smaller than 0.1 μm , while most of the surface area is in the 0.1 to 0.5
29 μm size range. The aerosol size distribution is quite variable in an urban area. Extremely high
30 concentrations of very fine particles (less than 0.1 μm) are found close to sources such as
31 highways, but their concentrations decrease rapidly with distance from their source. Figure 3.1
32 (Whitby and Sverdrup, 1980) describes the number of particles as a function of their diameter
33 for rural, urban–influenced rural, urban, and freeway-influenced urban aerosols. There are
34 roughly an order of magnitude more particles close to the freeway compared to the average
35 urban concentration.

36 An important feature of atmospheric aerosol size distribution is their multi-modal character.
37 Whitby and Sverdrup (1980) identified three modes: (1) nuclei, (2) accumulation, and (3) coarse.
38 As the technology for measuring small particles has improved, ultrafine particles (with diameters
39 less than 0.01 μm , i.e., $<10 \text{ nm}$) have also been increasingly studied. Particles in the
40 atmosphere are now frequently treated in terms of the four modes summarized in Figure 3.2
41 (Finlayson-Pitts and Pitts 1999). This figure shows the mechanisms such as condensation and
42 coagulation that transfer aerosol mass from one size range to another, it also shows the major
43 sources and removal processes for each one. The number distribution is dominated by particles
44 smaller than 0.1 μm , while most of the surface area is in the 0.1 to 0.5 size range. The mass
45 distribution has usually two distinct modes, one in the submicron regime (referred to as
46 accumulation mode) and the other in the coarse particle regime.



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



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

3 The nuclei mode, corresponding to particles below about 0.1 μm, may not be noticeable in
 4 volume or mass distributions. Nuclei mode particles are the result of nucleation of gas phase
 5 species to form condensed phase species with very low equilibrium vapor pressure. As an
 6 example, metallic ultrafine particles may be formed from metals in lubricating oil or fuel additives
 7 that are vaporized during combustion of gasoline or diesel fuels (Kittelson et al. 2000). Recent
 8 smog chamber studies and indoor experiments show that atmospheric oxidation of certain
 9 organic compounds found in the atmosphere can produce highly oxidized organic compounds
 10 with an equilibrium vapor pressure sufficiently low to result in nucleation (Kamens et al. 1999;
 11 Weschler and Shields 1999). Some scientists argue that ultrafine (nuclei-mode) particles pose
 12 potential health problems and that some health effects may be more closely associated with
 13 particle number or particle surface area than particle mass. Because nuclei-mode particles

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

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

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

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

28 While particles in the coarse particle mode are generally sufficiently large that they are removed
29 relatively rapidly by gravitational settling, there are large-scale mechanisms of transport that can
30 carry them long distances during some episodes. The results of several studies indicate the
31 transport of dust in larger particles from the Sahara Desert to the northwestern Mediterranean,
32 Atlantic Ocean, and the United States (Gatz and Prospero 1996; Moulin et al. 1997; and Li-
33 Jones and Prospero 1998). Similarly, dust transported from Asia has been reported on a regular
34 basis over the Pacific (Zhang et al. 1997). Asian dust has been observed during the Spring at
35 the Mauna Loa Observatory in Hawaii (Zieman et al. 1995; Holmes et al. 1997). At this location,
36 the elemental signature (in terms of silica to iron or titanium to iron ratios) in particles in the size
37 range 0.5 to 3.5 μm is very similar to those measured during dust storms in Beijing, consistent
38 with long-range transport of these particles.

39 The literature includes references to fine, coarse, suspended, respirable, inhalable, thoracic and
40 other adjectives to indicate a size segregation of PM. Uniform criteria are not always employed
41 in the application of these designations. Particles less than 2.5 μm in aerodynamic diameter are
42 generally referred to as "fine" and those greater than 2.5 μm diameters as "coarse". The
43 selection of PM₁₀ as an indicator was based on health considerations and was intended to
44 focus regulatory concern on those particles small enough to enter the thoracic region. Detailed
45 definitions of the various sizes and their relationships are given in standard aerosol textbooks
46 (e.g., Friedlander 1977, Reist 1984, 1993, Seinfeld and Pandis 1998, Hinds 1999, 1995, Willeke
47 and Baron 1993, and Fuchs 1964, 1989).

1 3.2.3 Particle Formation and Growth

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

10 Nucleation can occur both in the absence or presence of foreign material (pre-existing particles,
11 such as primary particles emitted by sources). Homogeneous nucleation is the nucleation of
12 vapor on embryos comprised of vapor molecules only, in the absence of foreign substances.
13 Heterogeneous nucleation is the nucleation on a foreign substance or surface, such as an ion or
14 a solid particle. In addition, nucleation processes can be homomolecular (involving a single
15 species) or heteromolecular (involving two or more species). Once the initial nucleation step has
16 occurred, the nuclei of the new phase tend to grow rapidly. Nucleation theory attempts to
17 describe the rate at which the first step in the phase transformation process occurs – the rate at
18 which the initial very small nuclei appear. For a review of nucleation in the atmosphere, the
19 reader is referred to literature on nucleation and atmospheric aerosols (Fukura and Wagner
20 1992; Kulmala and Wagner 1996; Seinfeld and Pandis 1998).

21 Condensation occurs when the vapor concentration of a species exceeds its equilibrium
22 concentration (expressed as its equilibrium vapor pressure). Condensable species can either
23 condense on the surface of existing particles or can form new particles. The relative importance
24 of nucleation versus condensation depends on the rate of formation of the condensable species
25 and on the surface or cross-sectional area of existing particles (McMurry and Friedlander 1979).
26 In ambient urban environments, the available particle surface area is sufficient to rapidly
27 scavenge the newly formed condensable species. Formation of new particles (nuclei mode) is
28 usually not important except near sources of condensable species. The results of several
29 studies report observations of the nuclei mode in traffic (Kittelson et al. 1988; Hildemann et al.
30 1991; Abdul-Khalek et al. 1998). New particle formation also can be observed in cleaner,
31 remote regions. Bursts of new particle formation in the atmosphere under clean conditions
32 usually occur when aerosol surface area concentrations are low (Covert et al. 1992). High
33 concentrations of nuclei mode particles have been observed in regions with low particle mass
34 concentrations, indicating that new particle formation is inversely related to the available aerosol
35 surface area (Clarke 1992). For more detailed discussions of the quantitative treatment of
36 condensation processes in the atmosphere, the reader is referred to articles by Pandis et al.
37 1995, and Kerminen and Wexler 1995.

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

1 rate of this process is a strong function of the particle concentration as well as the particle size
2 (Pandis et al. 1995).

3 **3.2.4 Removal Processes**

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

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

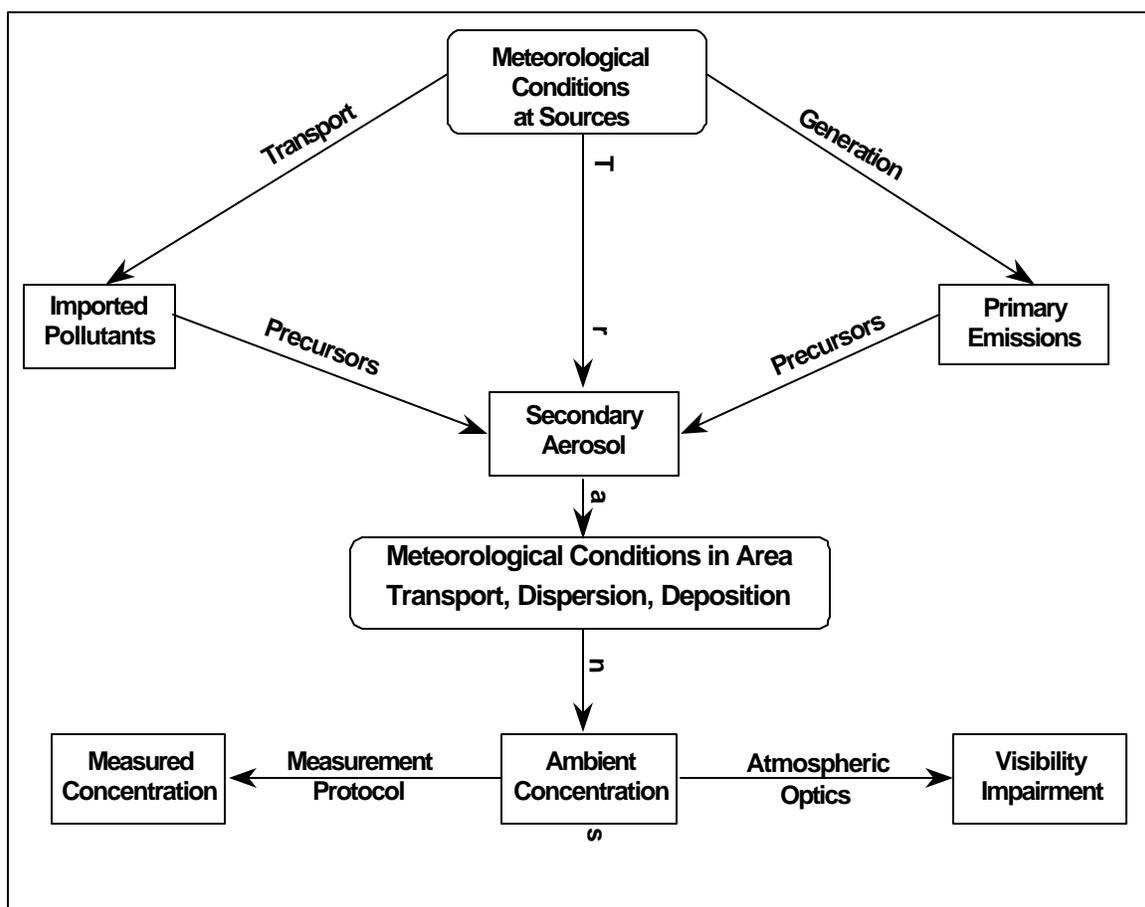
24 Dry deposition rates are expressed in terms of a deposition velocity that varies with particle size,
25 reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter. The wide ranges of
26 reported dry deposition velocities for any given pollutant reflect a combination of experimental
27 uncertainties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

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

37 **3.2.5 Meteorology and Particles**

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

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



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

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

1 monitoring sites. For example, in the San Joaquin Valley, PM10 and PM2.5 episodes in the
2 winter-time are often accompanied by light and variable winds, thus limiting horizontal transport.
3 As a result, pollutants tend to accumulate in local areas; however, a uniform gradient of
4 secondary aerosols was seen valley wide (nitrates in particular). Results of several data
5 analyses, as to the cause of this smooth gradient in secondary particulate concentrations,
6 revealed a shallow mixing layer near the surface with nearly calm winds, but winds of 4 to 8 m/s
7 were observed about 100 meters above the surface. Thus, pollutants trapped near the surface
8 when mixed into this fast moving upper layer, were transported large distances and reacted with
9 sources of ammonia, etc. to form the secondary aerosols.

10 **3.2.6 Fine Mass and Aerosol Light Scattering Relationship**

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

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

36 As was noted earlier in this chapter, the aerosol population is a mixture of different particle
37 sizes, and each size class is composed of an internal and/or external mixture of chemically
38 diverse particles. Hence, it is not possible to express the aerosol concentration as a single
39 number, as is the case for gaseous pollutants. On the other hand, practical considerations
40 dictate that the number of aerosol parameters to be monitored has to be limited. Routine
41 monitoring of aerosol chemical composition in many size classes does not appear to be
42 practical for regulatory purposes. Rather, the aerosol size - chemical composition distribution
43 function needs to be monitored using integral measures such as fine mass concentration
44 (PM2.5) and/or total (or size segregated) light scattering coefficient. PM2.5 is the integral of the
45 aerosol mass - size distribution up to about 2.5 μm . The total light scattering is also an integral
46 of the aerosol mass size distribution but also weighed by the size-dependent scattering
47 efficiency factor.

1 Numerous field investigations have been performed on the correlation between scattering
2 coefficient and particulate volume and mass concentration. Most of the earlier studies (1970s)
3 were based on "high volume" (non-particle size selective sampler) total suspended particle
4 (TSP) mass concentration measurements whose uncertainties and ill-defined upper particle size
5 limits resulted in questionable data. As attention focussed on fine particle monitoring during the
6 1980s, similar comparison field tests restricted to smaller particles were conducted. It is well
7 established that the fine particle mass concentration measured by size segregated filter
8 sampling has a strong statistical correlation with total aerosol light scattering. The main reason
9 for this relationship is that both the fine particle mass as well as the light scattering efficiency
10 factor have a peak in the size range 0.3 - 0.6 μm . Exception to this relationship occurs when the
11 characteristic aerosol size is either smaller (e.g., primary automobile exhaust) or larger (wind
12 blown dust) than the above size range.

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

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

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

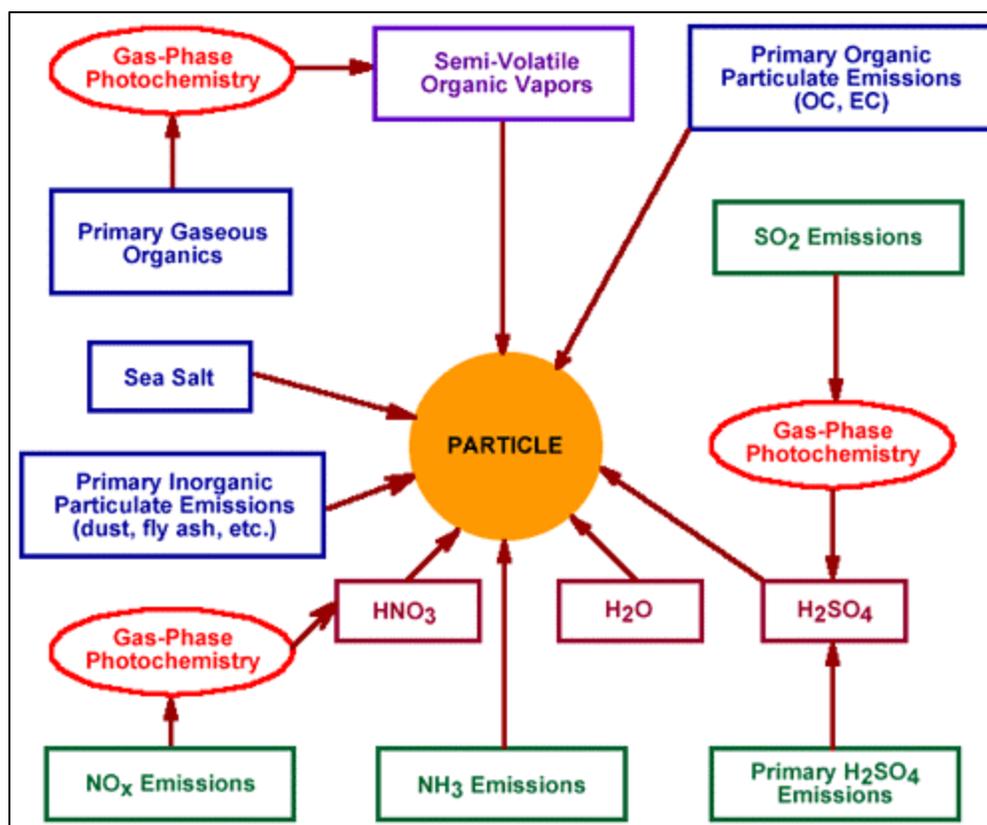
36 The results of several studies of the contribution of various particle components to light
37 scattering and light absorption suggest that sulfate and organic species are major contributors
38 to light scattering, with the contribution of nitrate being more variable. Relative humidity
39 influences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

43 Finally, although results of several studies are strongly suggestive of common optical properties
44 for the fine particle fraction, it would be disingenuous to claim that PM_{2.5} mass and light
45 scattering coefficient are always equivalent, either temporally and spatially. The high-time
46 resolution (i.e., hourly measurements) light scattering data clearly indicate that aerosol variation
47 is significant in both seasonal and monthly time scales. There is also a measurable diurnal
48 variation of up to 50% of the daily average values where primary particle emissions are

1 significant. The light scattering-humidity relationship depends on the particle composition,
 2 microstructure (i.e., internally or externally mixed aerosols) as well as the history of relative
 3 humidity values previously experienced by the particles. Hence the relationship between fine
 4 particle mass and light scattering can be obscured by many physical/ chemical factors and
 5 sampling errors. All of these factors should be examined carefully before the use of any
 6 scattering data for estimating fine mass concentration.

7 3.3 Chemical Properties of Particles

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



12 **Figure 3.4. Schematic diagram of particle formation.**

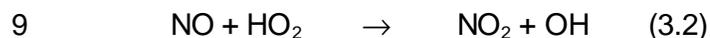
13 Fine PM is derived from combustion material that has volatilized and then condensed to form
 14 primary PM, or from precursor gases (such as sulfur dioxide, nitrogen oxides, and certain
 15 organic compounds) reacting in the atmosphere to form secondary PM. Fine particles typically
 16 are comprised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

18 Coarse particles, in contrast, are formed by crushing, grinding, and abrasion of surfaces, which
 19 breaks large pieces of material into smaller pieces. These particles are then suspended by wind
 20 or by anthropogenic activity such as construction, mining, and agricultural activities. As the
 21 particles respond to conditions in their atmospheric environment, their chemical and physical

1 properties - and hence their characteristics, such as light scattering and toxicity - can change by
 2 accumulation of atmospheric gas-phase chemical reaction products or through heterogeneous
 3 reactions with gas-phase species.

4 **3.3.1 Nitrate Chemistry**

5 The atmospheric chemistry leading to formation of particulate nitrate is fairly complicated. Fresh
 6 NO_x emissions, which primarily consist of nitric oxide (NO) undergo reactions with ozone and
 7 peroxy radicals to form nitrogen dioxide (NO₂), via the reactions shown below.



10 The NO₂ can be directly converted to nitric acid via the homogenous gas phase reaction with
 11 the hydroxyl radical (OH).



13 This is the principal formation mechanism for nitric acid in the daytime (Finlayson-Pitts and Pitts,
 14 1999). Modeling calculations suggest that more than 90% of the daylight HNO₃ formation occurs
 15 via this reaction. It involves the OH radical, which is the key species in the photochemical
 16 oxidation cycle. The OH radical concentration is controlled by the amount of sunlight and the
 17 ambient concentrations of ozone, water vapor, NO, NO₂, and reactive organics.

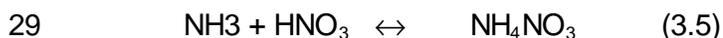
18 The second major formation pathway for nitric acid is the reaction of N₂O₅ with water vapor and
 19 liquid water.



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

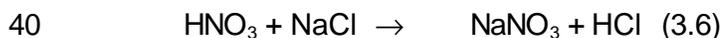
23 There is a wide range of conversion rates for nitrogen dioxide to nitric acid, ranging from less
 24 than 1 percent per hour to 90 percent per hour. Although they vary throughout a 24-hour period,
 25 these rates are significant during both daytime and nighttime hours. This is in contrast to the
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

27 The principal chemical loss process for gas-phase nitric acid is its reaction with gaseous
 28 ammonia to form ammonium nitrate (NH₄NO₃).



30 This reversible reaction is believed to be the primary source of fine (<2.5 μm diameter) nitrate
 31 aerosol in California's urban air. The equilibrium constant for the reaction is both temperature
 32 and relative humidity dependent. High humidity and low temperature favor NH₄NO₃ formation.
 33 Aqueous NH₄NO₃ is formed at relative humidities above the relative humidity of deliquescence
 34 (62%).

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



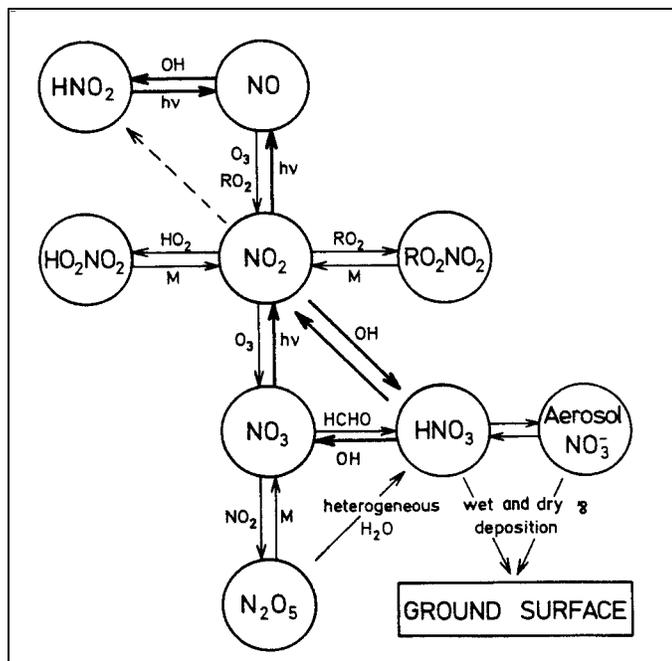
41 Reaction (3.6) may be the principal source of coarse (2.5 to 10 μm) nitrate, and plays an
 42 important role in atmospheric chemistry because it is a permanent sink for gas-phase nitrogen

1 oxide species. This reaction is one of the most extensively studied heterogeneous chemical
2 reactions in the laboratory, and the extent to which this occurs is affected by many factors,
3 including gas-phase and particle-phase concentrations, temperature, relative humidity, and
4 reaction time.

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

13 The atmospheric chemistry leading to formation of particulate nitrate is complicated. The rate of
14 formation depends on the concentrations of many intermediate species (including ammonia and
15 radical species) involved in the reactive organic gases and NO_x photochemical system. Figure
16 3.5 summarizes chemical pathways involving nitrogen oxides in the atmosphere (Warneck
17 1999). Photochemically induced reaction pathways are indicated by bold arrows. These
18 processes are active only during the day, whereas the others occur at all times.

19 Until recently it was assumed that the end product of tropospheric NO_x was nitric acid. However,
20 a recent research project conducted under ARB sponsorship (Mochida and Finlayson-Pitts
21 2000) has shown that nitric acid on a surface can react with NO to regenerate NO_2 which can
22 then form ozone and particulate nitrate. Preliminary modeling studies suggest that this reaction
23 may increase the formation of particulate nitrate and that existing models underestimate the
24 benefit of NO_x controls for reducing PM and ozone. This finding may have very serious
25 implications as to the effectiveness of control strategies for both ozone and PM. An additional
26 research contract is continuing with a focus on providing a more complete understanding of the
27 effect of heterogeneous nitrogen chemistry on ozone and particle formation. The information
28 gained in this project may have very serious implications as to the effectiveness of control
29 strategies for both ozone and PM.



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

3 Ambient concentrations of secondary particles are not necessarily proportional to the quantities
 4 of their precursor emissions, since the rates at which they form and their gas/particle equilibria
 5 may be controlled by factors other than the concentration of the precursor gases. The rate of
 6 NO_x oxidation and the branching ratio between inorganic and organic nitrates depends on the
 7 specific environmental conditions in addition to reactant concentrations (Seinfeld and Pandis
 8 1998). The partitioning of inorganic nitrate between gaseous nitric acid, ammonium nitrate, and
 9 nonvolatile nitrate is known to depend on a number of factors, such as relative humidity,
 10 temperature, and ammonia, in a nonlinear manner.

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

21 **3.3.2 Sulfate Chemistry**

22 Sulfur dioxide emissions result almost exclusively from the combustion of sulfur-containing
 23 fuels. Other sulfur compounds, such as sulfur trioxide (SO_3), sulfuric acid (H_2SO_4), and sulfates,
 24 may also be directly emitted during combustion of sulfur-containing fuels, although usually only
 25 in small amounts. In the atmosphere, sulfur dioxide is chemically transformed to sulfuric acid,
 26 which can be partially or completely neutralized by ammonia and other alkaline substances in
 27 the air to form sulfate salts (Warneck 1999; Seinfeld and Pandis 1998).

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

6 3.3.2.1 Aqueous-Phase Sulfur Dioxide Reactions

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

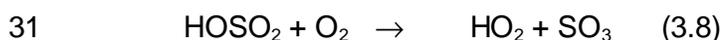
14 The effects of season and time of day suggest the importance of photochemistry, and perhaps
 15 temperature, in the oxidation rate of SO₂. This does not necessarily imply that oxidation
 16 reactions themselves are photochemical in nature, but rather they may involve oxidants such as
 17 H₂O₂ which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

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

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

27 3.3.2.2 Gas-Phase Sulfur Dioxide Reactions

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



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

36 Because of its extremely low vapor pressure (<10⁻⁷ atmospheres), sulfuric acid quickly adheres
 37 to existing particles. Sulfuric acid reacts irreversibly with ammonia to form ammonium bisulfate,
 38 NH₄HSO₄ and ammonium sulfate, (NH₄)₂SO₄. Since the sedimentation velocity of these
 39 submicron particles is very low, sulfate can be transported long distances. In the absence of
 40 precipitation or fog, the typical atmospheric lifetime of fine particulate sulfate is on the order of
 41 several days. Washout by precipitation and accelerated sedimentation resulting from
 42 incorporation of sulfate particles into fog droplets are important sinks.

43 In power-plant or smelter plumes containing SO₂ and NO_x, the gas-phase chemistry depends on
 44 plume dilution, sunlight, and volatile organic compounds, either in the plume or in the ambient

1 air mixing into and diluting the plume. For the conversion of SO_2 to H_2SO_4 , the gas-phase rate in
2 such plumes during summer midday conditions in the eastern United States typically varies
3 between 1 and 3% h^{-1} but in the cleaner western United States rarely exceeds 1% h^{-1} . For the
4 conversion of NO_x to HNO_3 , the gas-phase rates appear to be approximately three times faster
5 than the SO_2 conversion rates. During the winter rates for SO_2 conversion are approximately an
6 order of magnitude lower than during the summer.

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

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

32 **3.3.3 Organic Particles**

33 Atmospheric particulate carbon consists of both elemental carbon (EC) and organic carbon
34 (OC). Elemental carbon has a chemical structure similar to impure graphite and is emitted
35 directly by sources. Organic carbon can either be emitted directly by sources (primary OC) or
36 can be the result of the condensation of low vapor pressure products of the gas-phase reactions
37 of hydrocarbons onto the existing aerosol (secondary OC). Atmospheric carbon particles are
38 emitted from more than 70 different types of air pollution sources (Gray and Cass 1998).
39 Obvious sources include gasoline-powered motor vehicles, heavy-duty diesel vehicles, railroad
40 engines, boilers, aircraft and many other combustors that burn fossil fuel. To the emissions from
41 fuel combustion are added carbon particles from woodsmoke, food cooking operations, and
42 even an ambient concentration increment from such minor sources as cigarette smoke. In
43 addition, there are fugitive sources including the organic carbon content of paved road dust, tire
44 dust and vehicular brake wear particles.

45 Although the mechanisms and pathways for forming inorganic secondary particulate matter are
46 fairly well known, those for forming secondary organic PM are not as well understood. Ozone
47 and the hydroxyl radical are thought to be the major initiating reactants. Pandis et al. (1992)
48 identified three mechanisms for formation of secondary organic PM: (1) condensation of

1 oxidized end-products of photochemical reactions (e.g., ketones, aldehydes, organic acids,
2 hydroperoxides), (2) adsorption of organic gases onto existing solid particles (e.g., polycyclic
3 aromatic hydrocarbons), and (3) dissolution of soluble gases that can undergo reactions in
4 particles (e.g., aldehydes). The first and third mechanisms are expected to be of major
5 importance during the summertime when photochemistry is at its peak. The second pathway
6 can be driven by diurnal and seasonal temperature and humidity variations at any time of the
7 year. With regard to the first mechanism, Odum et al. (1996) suggested that the products of the
8 photochemical oxidation of reactive organic gases are semivolatile and can partition themselves
9 onto existing organic carbon at concentrations below their saturation concentrations. Thus, the
10 yield of secondary organic PM depends not only on the identity of the precursor organic gas but
11 also on the ambient levels of organic carbon capable of absorbing the oxidation product.

12 The formation of atmospheric aerosols from biogenic emissions has been of interest for many
13 years. Recent laboratory and field studies support the concept that nonvolatile and semivolatile
14 oxidation products from the photo-oxidation of biogenic hydrocarbons could contribute
15 significantly to ambient PM concentrations in both urban and rural environments. A number of
16 multifunctional oxidation products have been identified in laboratory studies (Yu et al. 1998;
17 Glasius et al. 2000; Koch et al. 2000; Rao et al. 2001). Many of these compounds have
18 subsequently been identified in field investigations (Yu et al. 1999; Kavouras et al. 1998,
19 1999a,b). However, further investigations are needed to accurately assess their overall
20 contributions to fine PM concentrations.

21 Generally, organic PM concentrations, composition, and formation mechanisms are poorly
22 understood. Particulate organic matter is an aggregate of hundreds of individual compounds
23 spanning a wide range of chemical and thermodynamic properties (Saxena and Hildemann,
24 1996). Some of the organic compounds are "semivolatile" such that both gaseous and
25 condensed phases exist in equilibrium in the atmosphere. The presence of semivolatile or
26 multiphase organic compounds complicates the sampling process. Understanding the
27 mechanisms of formation of secondary organic PM is important because secondary organic PM
28 can contribute in a significant way to ambient PM levels, especially during photochemical smog
29 episodes. Experimental studies of the production of secondary organic PM in ambient air have
30 focused on the Los Angeles Basin. Turpin and Huntzicker (1991, 1995) and Turpin et al. (1991)
31 provided strong evidence that secondary PM formation occurs during periods of photochemical
32 ozone formation in Los Angeles and that as much as 70% of the organic carbon in ambient PM
33 was secondary in origin during a smog episode in 1987. Schauer et al. (1996) estimated that on
34 an annually averaged basis 20 to 30% of the total organic carbon PM in the <2.1 μ m size range
35 in the Los Angeles airshed was secondary in origin.

36 A high degree of uncertainty is associated with all aspects of the calculation of secondary
37 organic PM concentrations. Currently, it is not possible to fully quantify the concentration,
38 composition, or sources of the organic components. Many of the secondary organic aerosol
39 components are highly oxidized, difficult to measure, multifunctional compounds. This is
40 compounded by the volatilization of organic carbon from filter substrates during and after
41 sampling as well as potential positive artifact formation from the absorption of gaseous
42 hydrocarbon on quartz filters. In addition, no single analytical technique is currently capable of
43 analyzing the entire range of organic compounds present in the atmosphere in PM. Even
44 rigorous analytical methods are able to identify only 10 to 20% of the organic PM mass on the
45 molecular level (Rogge et al. 1993a; Schauer et al. 1996).

46 Environmental smog chambers can be useful in elucidating the chemical mechanisms
47 associated with the formation of compounds found in organic PM; however, significant
48 uncertainties always arise in the interpretation of smog chamber data because of wall reactions.
49 Limitations also exist in extrapolating the results of smog chamber studies to ambient conditions

1 found in urban airsheds. Additional laboratory studies are needed to comprehensively identify
2 organic compounds, strategies need to be developed to sample and measure such compounds
3 in the atmosphere, and models of secondary organic aerosol formation need to be improved
4 and added to air quality models in order to address compliance issues related to reducing PM
5 mass concentrations that affect human exposure.

6 **3.3.4 Particle-Vapor Partitioning**

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

21 A recent ARB final research report (Ashbaugh et al. 1998) describes analysis of three data sets
22 to evaluate the extent of mass loss on Teflon filters due to ammonium nitrate volatilization. The
23 results indicated that the effect on measured mass is site-dependent, and depends on the
24 meteorological conditions and the fraction of PM mass that consists of ammonium nitrate
25 particles. There is no straightforward method to correct for the mass loss without measuring it.
26 The highest mass loss occurred during summer daytime in southern California, amounting to
27 30-50% of the gravimetric mass. This study of ammonium nitrate suggests potentially significant
28 nitrate or semivolatile organic compounds loss using the Federal Reference Method sampler for
29 fine particle sampling because it uses Teflon filters for mass concentrations. This may lead to
30 control strategies that are biased toward sources of fugitive dust and other primary particle
31 emission sources.

32 **3.4 Summary**

33 Atmospheric particles originate from a variety of sources and possess a range of morphological,
34 chemical, physical, and thermodynamic properties. Atmospheric size distributions show that
35 most atmospheric particles are quite small, below 0.1 μm , whereas most of the particle volume
36 (and therefore most of the mass) is found in particles greater than 0.1 μm . Several processes
37 influence the formation and growth of particles. New particles may be formed by nucleation from
38 gas phase material. Existing particles may grow by condensation as gas phase material
39 condenses onto existing particles. Particles may also grow by coagulation as two particles
40 combine to form one. Gas phase material condenses preferentially on smaller particles and the
41 rate constant for coagulation of two particles decreases as the particle size increases.
42 Therefore, nuclei mode particles grow into the accumulation mode but accumulation mode
43 particles do not grow into the coarse mode.

44 The lifetimes of particles vary with particle size. Coarse particles can settle rapidly from the
45 atmosphere within minutes or hours, and normally travel only short distances. However, when
46 mixed high into the atmosphere, as in dust storms, the smaller-sized, coarse-mode particles
47 may have longer lives and travel greater distances. Accumulation-mode fine particles are kept
48 suspended by normal air motions and have very low deposition rates to surfaces. They can be

1 transported thousands of kilometers and remain in the atmosphere for a number of days.
2 Accumulation-mode particles are removed from the atmosphere primarily by cloud processes.
3 Coarse mode particles of less than 10 μm diameter as well as accumulation-mode and nuclei-
4 mode (or ultrafine) particles all have the ability to penetrate deep into the lungs and be removed
5 by deposition in the lungs.

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

13 Most of the sulfate and nitrate and a portion of the organic compounds in atmospheric particles
14 are secondary (i.e., they are formed by chemical reactions in the atmosphere). Secondary
15 aerosol formation depends on numerous factors including the concentrations of precursors; the
16 concentrations of other gaseous reactive species such as ozone, hydroxyl radical, peroxy
17 radicals, or hydrogen peroxide; atmospheric conditions, including solar radiation and relative
18 humidity; and the interactions of precursors and preexisting particles within cloud or fog
19 droplets, or on or in the liquid film on solid particles. As a result, it is considerably more difficult
20 to relate ambient concentrations of secondary species to sources of precursor emissions than it
21 is to identify the sources of primary particles.

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

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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 area-wide, stationary, mobile, and natural sources. For air pollution, the particulates of concern are those that are 10 microns or less in size (PM₁₀), and, those that are 2.5 microns or less in size (PM_{2.5}, 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 area-wide, stationary, mobile, 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 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 2.5 micron 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.

4.1.2 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. Combustion exhaust from stationary sources produces mostly PM_{2.5}. Other stationary sources, such as those handling mineral products, also produce emissions of PM₁₀ particles.

4.1.3 Mobile Sources

The contributions of directly emitted particulates from mobile vehicles vary substantially within California. Sources of mobile emissions include gasoline and diesel powered vehicle exhaust emissions, tire wear, break wear, trucks, busses, heavy equipment, and other mobile sources such as trains and aircraft. Like most combustion sources, the particulate emissions from mobile

1 sources are nearly all in the PM_{2.5} size fraction. (This category does not include the road or soil
2 dust created by car, truck, or equipment operations, which are included in the areawide source
3 category.)

4 **4.1.4 Natural Sources**

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

9 **4.2 Secondary Particulate Sources**

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

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

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

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

30 **4.3 Regional Dependence of Source Contributions**

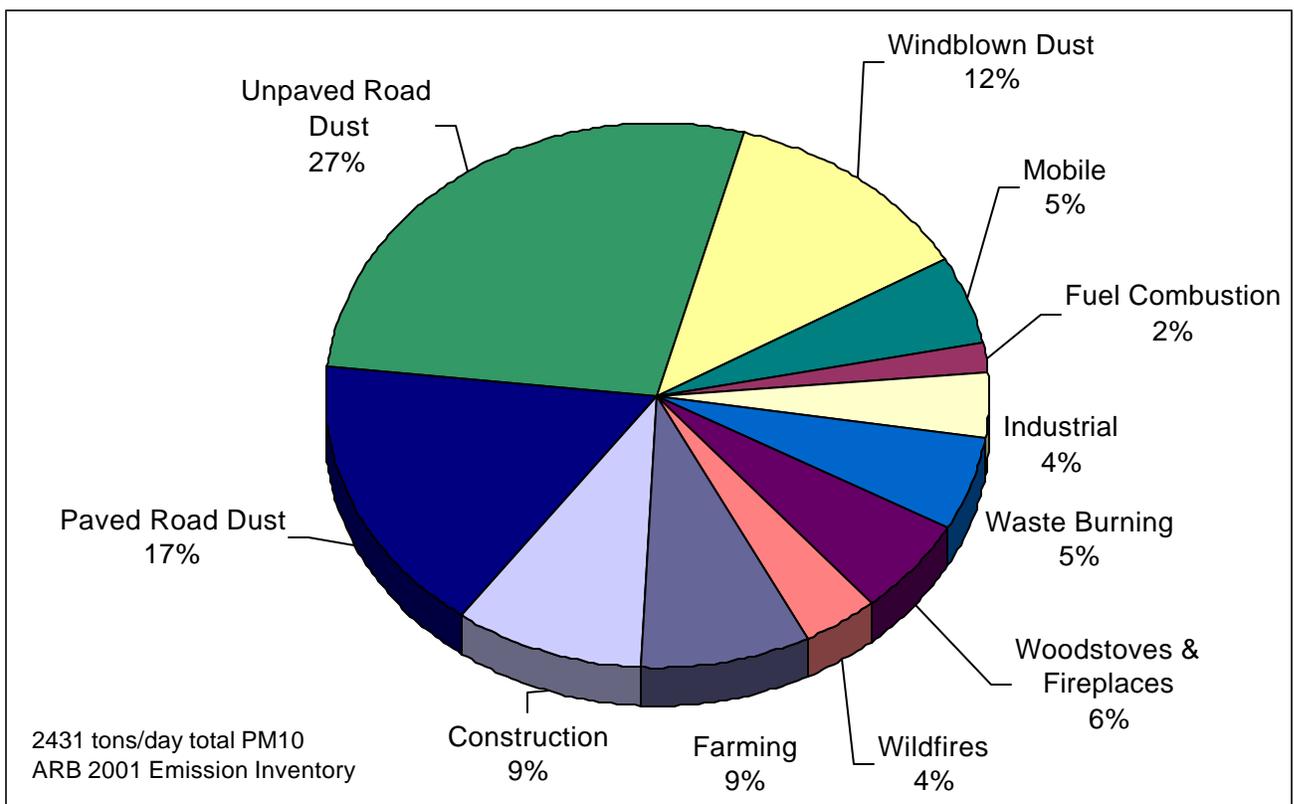
31 The contributors to primary PM vary regionally in the State. Urban areas are typically dominated
32 by paved road dust and construction related emissions for directly emitted PM. More rural
33 regions include paved and unpaved road dust, farming operations, and windblown dust as major
34 contributors.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

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

1 **4.4 Temporal Dependence of Source Contributions**

2 Regional monitoring shows that many areas in the state show seasonal trends in ambient PM
 3 concentrations. For example, in the Sacramento Valley, PM values peak during October to
 4 January and July to August. In the San Joaquin Valley there are both winter and late fall peaks.
 5 The winter PM is predominantly fine particulate (PM2.5 and smaller secondary particulates),
 6 while the fall season PM has a more significant PM10 emission component due to directly
 7 emitted geologic dust. In Southern California high PM levels occur at several times of the year
 8 based on meteorological conditions. In the Owens Valley, windstorms create short-term
 9 episodic high PM concentrations. And in places like Mammoth Lakes and Lake Tahoe, high
 10 particulate levels typically occur in the winters due to woodstove emissions and application of
 11 anti-skid materials to icy roads.

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



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

19 **4.5 References**

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5 Measurement of Particulate Matter

5.1 Introduction

On December 9, 1982, the California Air Resources Board (Board) revised the State PM Standard by rescinding the total suspended particulate standard and adding standards for fine particles. The Board approved amendments to the California Administrative Code, 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 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. Though the Standard provides for the use of equivalent samplers, there have been no requests for equivalent sampler determinations. This is due to the emphasis placed on meeting Federal standards and using Federal PM10 sampling methods.

In December 2000, the Board determined that the State ambient air quality standards for PM10 and 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.

At this time, the State is seeking to eliminate confusion between PM10 sampler types, and recognize the Federal reference method for PM2.5 as the State's method. But most importantly, the State is moving ahead to officially identify continuous monitoring method(s) for measuring PM to determine attainment with the revised State Ambient Air Quality Standard. Continuous monitoring for either PM10 or PM2.5 would better characterize PM emission patterns and exposure, and could reduce the cost of the air monitoring network. Continuous data can be used for a variety of critical functions such as to enhance public health research, to study diurnal variation, to evaluate short-term peak exposure, to provide more data for establishing model variation, to aid in identifying air pollution source(s), and to more accurately reflect dispersion patterns. Adopting these methods officially will promote further proliferation of continuous samplers.

5.2 Existing Monitoring Requirements

5.2.1 State Method P for PM10

Method P (Title 17, Barclays California Code of Regulations, Subarticle 9, Appendix B) describes the design and performance requirements for the PM10 sampler to be used to determine compliance with the State Ambient Air Quality Standard. Method P is given as Appendix A to this document. These requirements are:

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 which collects 50 percent (referred as D50) of all particles of 10 μm aerodynamic diameter, and which collects a declining fraction of particles as their diameter increases and an increasing fraction of particles as their diameter decreases. 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

1 with the same size and shape but with different densities will have different aerodynamic
2 diameters.

3 The factors affecting sampling efficiency are wind speed and direction. The performance of a
4 PM10 sampler should be independent of wind speed to simulate human respiration. The inlet
5 design and its internal configuration shall be such that it shows no dependency on wind
6 direction and wind speed when operated within 2 to 24 kilometers-per-hour wind speeds. To do
7 this, the inlet should be omnidirectional, that is, the inlet should be symmetrical about the
8 vertical axis.

9 Suspended particulate matter refers to atmospheric particles, solids, or liquids, except
10 uncombined water. The upper cutpoint is defined as a 50 percent collection efficiency at 10 ± 1
11 μm aerodynamic diameter determined at normal wind speeds. Dry, free flowing particles should
12 be sampled with the same efficiency as liquid, sticky particles. The expected mass
13 concentrations of liquid particles should be within limits of that predicted by the ideal sampler.
14 For solid particles, the expected mass concentration should be no more than 5 percent above
15 that obtained for liquid particles of the same size. The sampler must have less than 15 percent
16 variation in the measurements produced by 3 collocated samplers.

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

29 The sampler must possess an automatic flow control device which maintains a constant flow
30 rate to within ± 10 percent of the recommended range for the sampler inlet over normal
31 variations in line voltage and filter pressure drop during the sampling period. Change in flow
32 velocity will result in change in nominal particle size collected. Therefore, it is important that the
33 flow rate through the inlet be maintained at a constant value that is as close as possible to the
34 inlet design flow rate.

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

44 **5.2.2 State Method for Sulfates**

45 Currently Section 70200 of Title 17 of the California Health and Safety Code lists the State
46 Ambient Air Quality Standard for Sulfates. Sample collection is to be done by high-volume
47 sampling, and analysis by Turbidimetric Barium Sulfate spectrometry, AIHL Method 61, or any

1 equivalent procedure which can be shown to the satisfaction of the ARB to give equivalent
2 results at or near the level of the air quality standard.

3 The current TSP sulfate method (which employs a high volume sampling with analysis by ion
4 chromatography) is described in the ARB method MLD 033. There is also an existing method,
5 MLD 007, for PM₁₀ sulfates. MLD 007 is based on high-volume SSI sampling and ion
6 chromatography.

7 **5.2.2 Federal Methods for PM₁₀**

8 The primary use of a designated standard measurement method is to determine whether a
9 given geographical area is in attainment or non-attainment with the National Ambient Air Quality
10 Standards (NAAQS). For monitoring methods to be used in State and local air monitoring
11 station networks for this purpose, the methods must be designated by the U.S. EPA as either
12 reference or equivalent methods.

13 Federal reference methods (FRM) use the measurement principles and specifications described
14 below. A Federal equivalent method (FEM) is based on the performance of the method relative
15 to a reference method in rigorous field tests. Measurements using an equivalent method, when
16 compared to measurements produced by collocated reference method samplers, must meet
17 strict performance criteria.

18 The requirements for an FRM for PM₁₀ are described in Appendix M, Title 40, Code of Federal
19 Regulations Part 50, 1997, and are provided here as Appendix B to this document. These
20 requirements are for the most part the same as the California Method P. This is understandable,
21 as Method P was adopted in consultation with the U.S. EPA as they were preparing to propose
22 methods for the upcoming NAAQS for PM₁₀. A comparison of the two methods, item-by-item, is
23 given in Appendix C. There are differences in a few specific requirements, which are highlighted
24 in the table. The discussion below focuses only on those differences. The purpose of presenting
25 this information is to highlight the need to update Method P.

26 The FRM requires PM₁₀ sampler to simulate particle penetration of the human respiratory
27 system as described by the Chan-Lippmann (1980), penetration model. The D₅₀ cutpoint of the
28 sampler is 10 μm with a tolerance of ± 0.5 μm, compared to the tolerance of 1.0 μm for Method
29 P.

30 The alkalinity of filter medium should be less than 2.5 microequivalents/gram for FRM as
31 opposed to less than 5 microequivalents/gram for Method P. The filters should be equilibrated at
32 constant relative humidity of between 20 percent and 45 percent ± 5 percent for FRM instead of
33 <50 percent relative humidity for Method P before weighing.

34 The precision of collocated FRM samplers must be 5 μg/m³ for PM concentration below
35 80 μg/m³ and 7 percent for PM₁₀ concentration above 80 μg/m³ for FRM, as opposed to 15
36 percent for all concentrations for Method P.

37 The FRM requires the air flow rate through the sampler remain stable over a 24-hour period,
38 regardless of filter loading; the specific requirements are ±5 percent of the initial reading for the
39 average flow, and ±10 percent of the initial flow rate for any instantaneous flow measurement.
40 For Method P, the flow rate should be within 10 percent at all times.

41 Typically, an analytical balance with a sensitivity of 0.1 mg is required for hi-vol samplers (flow
42 rates >0.5 m³/min, large filters). Lo-vol samplers (flow rates <0.5 m³/min, smaller filters) require
43 a more sensitive balance, which is not indicated in Method P.

1 The other major difference between the State and Federal method is the designation of Federal
2 Equivalent Method (FEM) test protocols, not included in Method P, although method
3 equivalency is referred to in general terms in State regulations.

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

10 **5.2.3 Federal Methods for PM2.5**

11 The U.S. EPA promulgated rigorous design and performance specifications for the PM2.5 FRM
12 samplers. The FRM for PM2.5 specifies sampler design, performance characteristics, and
13 operational requirements. These specifications are contained in 40 CFR part 50, Appendix L; 40
14 CFR part 53, Subpart E; and 40 CFR part 58, Appendix A. These are given in Appendices, D, E,
15 and F, respectively, of this document.

16 Only measurements made using U.S. EPA-designated FRM samplers may be used to
17 determine an area's compliance status with the PM2.5 NAAQS. The definition of PM2.5 is
18 determined by particles collected on this sampler. The sampler uses the PM10 lo-vol impactor
19 followed by the Well Impactor Ninety-Six (WINS) inertial impactor. The WINS impactor removes
20 particles larger than 2.5 μm . PM2.5 and smaller particles proceed beyond the WINS and are
21 deposited on a filter.

22 Design specifications: All of the sampler components that come in contact with the sampled air
23 stream (which are the first stage inlet, the downtube, the second stage separator (WINS), the
24 upper filter holder, the filter cassette, and the filter support screen) are specified by design (40
25 CFR part 50, Appendix L). Design of other components of FRM samplers are left to
26 manufacturers, as long as resulting samplers meet all the prescribed performance
27 specifications.

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

35 The State of California does not have its own PM2.5 monitoring method at this time. The PM2.5
36 samplers in use in the State's air monitoring network, and the operational guidance used, are
37 those developed and funded by the U.S. EPA. The PM2.5 method requires strict adherence to
38 the associated performance and operational guidance. The PM2.5 samplers have been in
39 service for two years, and generally perform to their intended specification. Staff propose
40 adopting the FRM sampler and the performance and operational requirements associated with
41 the methods for any State PM2.5 standard. The State is not proposing to adopt the U.S. EPA's
42 FEM criteria.

43 To allow the use of continuous method(s), U.S. EPA has issued a policy creating a correlated
44 acceptable continuous (CAC) monitor classification by which continuous methods can be used
45 to measure PM2.5 for attainment assessment purposes, on an area-specific basis. The CAC
46 approach allows a PM2.5 measurement at a single site in a Community Monitoring Zone to
47 deviate from the spatial average of Core sites within that zone by up to 20 percent. During the

1 first year of monitoring, CAC monitors must be collocated with the FRMs at core(s) site to
2 establish the sampler performance relationship.

3 **5.3 Available PM Sampling Methods**

4 There are two fundamental methods commonly used to measure atmospheric PM₁₀ and PM_{2.5}
5 that are potentially useable Statewide. The first is the gravimetric method, in which particles
6 segregated by size are collected on a pre-weighed filter medium and assessed to determine PM
7 mass. PM concentration is calculated by dividing the weight gain on the filter by the total volume
8 of air (at ambient conditions) that passed through the filter. The second incorporates non-
9 gravimetric means and includes devices such as beta ray attenuation.

10 Other sampling methods are available. Some have been tested and found to disagree with the
11 FRM samplers, or rely on site-specific relationships. These can include samplers that are based
12 on particle size distribution, optical properties, or parameters that can vary by site or season.
13 The State is proposing that reference samplers not be overly influenced by environmental
14 factors. Such samplers are not suitable for a Statewide network.

15 Filter-based monitoring methods are used to compare data from region to region and to
16 determine compliance with the State and Federal standards. Their limitations are that mass is
17 only available on 24-hour average basis, and operation is time and labor intensive compared to
18 real time, continuous samplers. The time-lag inherent in data availability in conventional filter-
19 based methods precludes the use of these methods to provide the general public with timely
20 warnings about episodic air pollution hazards. Filter-based systems can also have problems
21 with loss of volatile chemical species, and particle loss during handling and transport, although
22 these effects have been minimized by having strict operational protocols.

23 **5.3.1 General Description and Limitations of Gravimetric Methods**

24 5.3.1.1 High Volume Size Selective Inlet Sampler

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

28 The high volume (hi-vol) SSI sampler used in the State and Federal PM₁₀ networks consists
29 basically of a PM₁₀ inlet, an impactor, a flow control system recorder, and a pump. The
30 automatic flow control system consists of either a mass flow controller or a volumetric flow
31 controller, which controls the flow to 40 ft³/min (1132 liters per minute or lpm). The flow rate
32 through the impactor is used with the elapsed time to determine the volume of air sampled.
33 According to one manufacturer of the SSI, its inlet has a cutpoint of 9.7 μm in winds up to
34 22 miles per hour (36 kilometers per hour) (Andersen, Inc.).

35 PM₁₀ hi-vol samples are collected on an 8x10 inch (20 cm x 25 cm) quartz filter that offers high
36 collection efficiencies and is resistant to absorbing artifacts related to the collection of sulfates
37 and nitrates. Volatile constituent losses are known to exist, however, prompt sample removal
38 can minimize these losses. Losses due to poor cleaning of the impactor have also been
39 reported.

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

43 The SSI sampler provides a direct measurement of PM₁₀ mass concentration. The large filter
44 size provides two benefits. First, it increases the precision and accuracy of mass measurement,

1 and second, it provides sufficient PM that can be analyzed for many of the primary constituents
2 of interest.

3 5.3.1.2 Low Volume Sampler

4 PM10

5 Low volume (lo-vol) PM10 FRM samplers are manual devices, which collect PM of a specific
6 size range on a filter. They consist of a PM10 inlet, an impactor, a pump, a flow rate controller,
7 and a timer. Fundamentally, the operational principles of the lo-vol and the hi-vol (SSI) samplers
8 are the same. The differences occur with features such as the inlet size, flow rate, and filter
9 size. These differences are discussed below.

10 Approved lo-vol samplers are equipped with either a flat or tilted PM10 inlet, as specified in
11 Appendix L of 40 CFR Part 50 (Figures L-2 through L-19). These inlets are smaller than the inlet
12 for the hi-vol sampler.

13 The lo-vol samplers use a small teflon or teflon-coated fiber filter for collection efficiency,
14 alkalinity, and chemical stability, and stability throughout a wide temperature range. The
15 sampler may have a manual or an automatic filter-changing mechanism. It is required to be able
16 to measure 24-hour PM10 mass concentrations of at least $300 \mu\text{g}/\text{m}^3$, while maintaining the
17 operating flow rate within the specified limits.

18 FRM lo-vol samplers operate for 24 hours at a flow rate of 16.67 lpm. They use gravimetric
19 means to determine ambient PM mass concentrations. The teflon filters used in the samplers
20 limit the analyses of constituents of primary concern. The FRM lo-vol samplers have the same
21 labor-intensive limitations of the hi-vol samplers which, in air monitoring networks, reduce the
22 number of sampling days to 1-in-6, and which limit the sampling period to 24 hours.

23 PM2.5

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

27 The WINS is a particle separator, where suspended PM2.5 is separated from the PM10. The
28 WINS impactor is a single jet impactor, which impacts into a "well" holding a 37 mm glass fiber
29 substrate impregnated with 1 mL of tetramethyltetraphenyltrisiloxane (silicon oil) single-
30 compound diffusion oil. The WINS impactor inertially separates fine particles of an aerodynamic
31 diameter of $2.5 \mu\text{m}$ or less from PM10. Larger particles are captured in the oil-impregnated
32 substrate in the wells of the impactor, and the PM2.5 and smaller particles are collected on a 47
33 mm filter.

34 The filter is made of a polytetrafluoroethylene (Teflon), and has a particle collection efficiency of
35 greater than 99.7 percent. Prior to its use, the filter is equilibrated for 24 hours at a temperature
36 range of 20 to 23°C and at a relative humidity in the range of 20 to 40 percent, and preweighed
37 in a laboratory.

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

40 Dichotomous Sampler

41 The dichotomous sampler draws air at an actual flow rate of $1 \text{ m}^3/\text{hour}$ (16.67 actual lpm).
42 Ninety percent of the air (15.00 lpm) flows through the fine particulate filter, and the remaining
43 10 percent (1.67 lpm) flows through the coarse particulate filter.

1 The dichotomous sampler uses a virtual impactor (region of stagnant air) to segregate the air
2 sample into two fractions. The virtual impactor particle separator accelerates the air sample
3 through a nozzle and then deflects the air at a right angle. Most particles smaller than 2.5
4 micrometers (fine fraction) will follow the higher air flow path and collect on a fine particulate
5 filter. Particles between 2.5 and 10 micrometers (coarse fraction) have sufficient inertia to
6 impact into the chamber below the nozzle and are collected on a coarse particulate filter. Ten
7 percent of the sample air flows through the coarse particulate filter and because of this,
8 approximately 1/10 of the fine particulates are collected on the coarse particulate filter.

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

12 PM2.5 measurement made using the dichot and the virtual separation technique do not meet
13 U.S. EPA requirements for PM2.5 sampling in terms of the impactor type, filter size and flow
14 rate. The dichot utilizes a PM10 inlet similar to a lo-vol sampler, but the flow rate is only 10
15 percent of the total flow rate, hence introducing a potential source of difference from the lo-vol
16 PM10 sampler. Therefore, the use of this method for PM2.5 produces data that are not usable
17 for compliance designation with the NAAQS for PM2.5.

18 **5.3.2 General Description and Limitations of Continuous Methods**

19 Continuous methods produce hourly average PM concentrations in real time on a daily basis.
20 As contrasted with the intermittent sampling frequency of filter-based methods, a complete
21 record of PM has many advantages over periodic sampling, principally, the ability to assess air
22 quality on the vast number of non-sampled days. Arnold et al., (1992) collected daily 24-hour
23 PM10 samples with an automated monitor and noted that 80 percent of the highest 10 daily
24 concentrations in 1989 and 1990 were not encountered by the commonly used every-sixth-day
25 sampling schedule.

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

31 Several continuous sampler technologies were considered in developing the staff's
32 recommendation for PM10 and PM2.5. These include the tapered element oscillating
33 microbalance (TEOM), the beta attenuation monitor (BAM), and the continuous ambient mass
34 monitor (CAMM).

35 The BAM and the TEOM are the two most commonly used commercially available, continuous
36 PM analyzers in California. Both have been used to measure ambient PM10 and PM2.5 mass
37 concentrations. These two technologies were designated as FEMs for PM10. Because of their
38 widespread use, a discussion of each is provided below. There are no continuous FEMs for
39 PM2.5 at this time.

40 The continuous ambient mass monitor (CAMM), which was designed to measure PM2.5
41 concentration, utilizes the principle of pressure drop as particles are collected on a membrane
42 filter (Babich, et al. 2000). The change in pressure is assumed to be proportional to PM2.5 mass
43 concentration. The results of tests in California need further examination.

44 **5.3.2.1 Beta Attenuation Monitor**

45 Several researchers (Jaklevic, et al. 1981 and Kim, et al. 1999) have used the measurement
46 principle of absorption of beta radiation by PM on a filter as an indicator of particulate matter

1 mass to provide real-time measurement of atmospheric PM. A Beta Attenuation Monitor (BAM)
2 uses a lo-vol size selective inlet, a filter tape, a beta attenuation source and detector, a lo-vol
3 flow controller, and a timer. The sampler contains a source of beta radiation (^{14}C or ^{85}Kr) and a
4 detector to measure the beta absorption of PM accumulated on a filter. The filter material is a
5 roll or cassette, which advances automatically on a time sequence. When particles are placed
6 between the beta source and the detector, the beta rays are attenuated or absorbed by particles
7 in their path. The difference in attenuation before and after the segment of the tape used to
8 collect PM is attributed to the PM deposited on the filter. The reduction in beta ray intensity
9 passing through the collected PM is a function of the mass of material between the source and
10 the detector. The degree of beta radiation attenuation is converted to PM concentration.

11 PM2.5

12 Instrument intercomparison studies of BAM PM2.5 units (a Met One model 1020) were
13 conducted at Bakersfield (1998 – 1999) and Fresno (1999 – 2000) (Appendix G). The results at
14 the Fresno Supersite were good (regression coefficient [R^2] of 0.97, slope of 1.07, intercept of
15 7.06). At Bakersfield, the PM2.5 BAM study compared one BAM equipped with a standard
16 PM2.5 WINS inlet and one with sharp cut cyclone with the PM2.5 FRM. The comparison at
17 Bakersfield also showed very good agreement (an R^2 of 0.99 in both cases, slope of 0.91 and
18 0.97, and intercepts of 0.8 and 3.25 were obtained, respectively). A minimum of 20 data pairs
19 were gathered at each location.

20 PM10

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

25 5.3.2.2 Element Oscillating Microbalance

26 The Tapered Element Oscillating Microbalance (TEOM) uses gravimetric technology in a real-
27 time monitor to measure airborne particle mass. A TEOM consists basically of a size- selective
28 inlet, sample filter, microbalance, flow controller (at 16.67 lpm), timer, and software that makes
29 the operation of the instrument fully automatic. In practice, the TEOM collects PM on a filter
30 located on the top of a hollow, oscillating tapered tube. A small portion of the incoming air flow is
31 drawn through the filter and through the tube. The oscillation frequency of the tapered inlet tube
32 is inversely proportional to the mass of the sample that is deposited on the collection filter. The
33 frequency decreases as mass accumulates on the filter, providing a direct measure of inertial
34 mass. The typical measurement is collected over a period of ten minutes. The sample chamber
35 is maintained above ambient temperatures ($30\text{-}50^\circ\text{C}$) to minimize the effect of temperature
36 changes and thermal expansion of the tapered element that may affect the oscillation
37 frequency, and to reduce particle-bound water (Patashnick et al. 1991).

38 Several studies (Allen et al. 1997, Chung, et al. 2001, Cook et al. 1995) have shown that the
39 concentration of PM10 or PM2.5 mass using the TEOM are often lower than PM measurements
40 produced by other methods. Analysis of the constituents typically found in such cases indicates
41 this is caused by loss of semi-volatile PM, ammonium nitrate, and/or low molecular weight
42 organic compounds in the heated sample chamber. While most of the volatile components are
43 found in the fine PM fraction (PM2.5), the discrepancies between PM10 samplers can be
44 significant.

45 Cook et al., (1995) studied the performance of the PM2.5 TEOM with a candidate FRM PM2.5
46 sampler at the Bakersfield monitoring station. The TEOM was operated at two temperatures,

1 30°C and 50°C, to determine the effect of temperature on measurement of PM mass. At both
2 temperature settings, the TEOM measured lower PM_{2.5} mass than the dichot or a single-stage
3 lo-vol gravimetric sampler. PM concentrations from the TEOM at 50°C were much lower
4 (negative bias) compared to 30°C, confirming the effect of temperature at that location on semi-
5 volatile organics and nitrates from the filter.

6 In a recent study in Bakersfield, PM₁₀ SSI (an FRM) and TEOM samplers operated in parallel
7 from November 1999 to February 2000 (Appendix G). This is a period when PM, and in
8 particular volatile components, are high. The samplers correlated well, but again, the TEOM
9 showed a significant negative bias (R^2 of 0.95 with slope of 0.37). At the Fresno Supersite, for
10 the same sampling period, similar samplers correlated as well, and less bias relative to the FRM
11 was seen (R^2 of 0.95 and slope of 0.83).

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

16 In general, TEOMs of the design used to date do not perform well in the two areas of the State
17 with the most persistent PM problem, the San Joaquin Valley Air Basin and the South Coast Air
18 Basin. The TEOM's disadvantage is that the temperature necessary for the proper operation of
19 the microbalance volatilizes a substantial component of the PM as part of the measurement
20 process. This is more pronounced for measurement of fine PM fraction where volatile
21 components of the PM are the dominant fraction.

22 New versions of the TEOM are being developed. One, the SES, conditions the sample stream
23 to a lower humidity and temperature level, to reduce losses of volatile species (Meyer, et al.
24 2000). The SES utilizes a Nafion dryer designed to lower the humidity level of the sample
25 stream. At the time this draft staff report was being prepared, the Board was soliciting candidate
26 samples to evaluate and is soliciting interest from vendors with samplers that may be compared
27 with FRMs.

28 **5.4 Recommendations**

29 The staff recommends the following changes to Title 17, California Administrative Code,
30 Sections 70100(j) and 70200:

- 31
- Delete the existing Method P entitled "Ambient Air Analysis Method...".
 - Create a new Method P entitled "Measurement Method for Particulate Matter in Ambient
32 Air". This method is divided into two parts, "Measurement of PM₁₀" and "Measurement of
33 PM_{2.5}", which are summarized below.

34

35 Measurement of PM₁₀ shall be accomplished by one of the three following techniques:

- 36
- A sampler which meets the requirements of the FRM for PM₁₀, as specified in 40 CFR Part
37 50, Appendix M, and which employs an inertial impactor; or,
 - A continuous PM₁₀ sampler which, at the time of the standard adoption, produces
38 measurements of PM₁₀ which correlate to the FRM-produced values to a high degree of
39 statistical significance; or,
 - A sampler which has been demonstrated to the satisfaction of the Air Resources Board to
40 produce measurements equivalent to the FRM.

41

42

43 Measurement of PM_{2.5} shall be accomplished by one of the following three techniques:

- 1 • A sampler which meets the requirements of the FRM for PM_{2.5}, as specified in the 40 CFR
2 Part 50, Appendix L; or,
- 3 • A continuous PM_{2.5} sampler which, at the time of the standard adoption, produces
4 measurements of PM_{2.5} which correlate to the FRM-produced values to high degree of
5 statistical significance; or,
- 6 • A sampler which has been demonstrated to the satisfaction of the Air Resources Board to
7 produce measurements equivalent to the FRM.

8 The rationale for these recommendations is given below:

9 PM₁₀

- 10 • There is a need to update the State PM₁₀ method, Method P, to reflect advancements and
11 improvements in sampler technology. The FRM for PM₁₀ is quite similar to Method P and
12 includes requirements that are more up-to-date. The FRM sampler operations requirements
13 are currently used in the State and local air monitoring network. Incorporating the FRM into
14 the AAQS will simply change legal requirements to reflect practice.
- 15 • Using hi-vol and lo-vol filter-based FRM to measure PM₁₀ to judge attainment of the State
16 AAQS will allow the FRM samplers that perform well, but are not approved for use in
17 California, to be used for both State and Federal regulatory activities. This will eliminate
18 unnecessary confusion caused by having State and Federal methods.
- 19 • Allowing the use of the lo-vol PM₁₀ method for the State PM₁₀ standard offers the
20 advantage of having one PM₁₀ sampler produce data for both the State PM₁₀ standard and
21 the potential future Federal PM coarse standard.

22 PM_{2.5}

- 23 • Using the PM_{2.5} FRM as the method to measure PM_{2.5} for the State standard takes
24 advantage of the more than 80 FRM samplers that are operating in California as part of the
25 State and local PM_{2.5} monitoring network.
- 26 • Adopting a continuous sampler technology that corresponds to a high degree with the FRM
27 for PM_{2.5} has many programmatic and public health benefits to the State.
- 28 • Continuing to allow the future identification of samplers found to be acceptable to the Board
29 will allow the use of advanced sampler technology, including continuous samplers not now
30 available.

31 **5.5 Estimated Costs and Impacts**

32 The State of California has had an extensive PM₁₀ network for years. The proposal reaffirms
33 and enhances the role FRM samplers play for the State AAQS. A substantial PM_{2.5} network,
34 largely funded by the U.S. EPA, is also now in place in California, and the U.S. EPA is in the
35 process of implementing the last stages of the build-up of the PM_{2.5} network. Both networks
36 meet Federal sampler siting and other guidelines considering Metropolitan Statistical Areas,
37 geography, meteorology, and previous air monitoring information. Appendix H is a list of the
38 PM₁₀ and PM_{2.5} monitoring sites and includes the various types of samplers that are being
39 used at these sites as of June 2001.

40 The State's PM₁₀ sampling method (Method P) has been the State ambient air monitoring
41 method since 1985. The sampler of choice at that time was the hi-vol SSI. Implementing the
42 proposed changes in Method P to explicitly acknowledge all FRM samplers would not incur any

1 cost to either government entities or private businesses, because it would allow the operators of
2 the PM samplers the option of retaining the current sampling method. In fact, it would expand
3 the number of acceptable samplers now in use to include heretofore unrecognized methods.

4 At this time, the State does not have an ambient air quality standard for PM_{2.5}. The staff
5 recommendation is that with the adoption of such a standard for California, the Board adopt the
6 Federal method for measuring PM_{2.5}. The FRM was adopted by the U.S. EPA in July 1997
7 (40CFR Parts 50, 53, and 58).

8 The existing network of PM_{2.5} samplers is extensive and would be the primary network for a
9 State ambient standard. Little extra expense is anticipated if the State adopts a similar standard
10 method. The recommended changes to Method P may result in cost saving to the extent that
11 continuous PM₁₀ monitoring methods are used in place of conventional filter-based methods.
12 Continuous methods are less labor intensive than Method P and generate substantially more
13 data. The staff cannot quantify any cost saving since it is unknown to what extent local agencies
14 would choose to use to continuous samplers, instead of the conventional filter-based samplers
15 used now.

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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.

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.

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



1 Air districts with areas designated nonattainment for the State PM10 standards are not required
2 by State law to develop plans for attaining the State PM10 standards. However, H&SC sections
3 40001 and 40913 require such districts to adopt and enforce rules and regulations to
4 expeditiously attain the PM10 standards.

5 **6.2 Monitoring Network**

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

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

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

1 **Figure 6.2. PM10 Mass Monitoring Sites**



1 **Figure 6.3. PM2.5 FRM Mass Monitoring Sites**



1

Figure 6.4. Dichotomous Sampler Sites

2 **6.3 Characterization of Ambient Air Quality**

3 **6.3.1 Overview**

4 This section describes the characteristics of PM₁₀ and PM_{2.5} by each air basin in California,
 5 including: ambient concentrations; seasonal variations; identification of sources leading to the
 6 observed ambient particle concentrations; and the frequency distribution of the observed
 7 concentrations. To assess the spatial and temporal characteristics of PM₁₀ and PM_{2.5}
 8 concentrations, we analyzed the following ambient air quality data: PM₁₀ observations from
 9 Size Selective Inlet (SSI) monitors (from 1998 to 2000) (ARB 1998, ARB 2000a); PM_{2.5}
 10 information from the newly deployed Federal Reference Method (FRM) monitors, available only
 11 for two years (1999 and 2000) (ARB 2000b); and PM_{10-2.5} and PM_{2.5} data from dichotomous
 12 (dichot) samplers (from 1988 to 1999) (ARB 1998). The data were extracted from the U.S.
 13 Environmental Protection Agency (U.S. EPA) Aerometric Information Retrieval System (AIRS)
 14 on May 18, 2001. For assessing the chemical composition of ambient PM₁₀ and PM_{2.5}, we
 15 reviewed information available from: the State's PM₁₀ and PM_{2.5} monitoring networks; Two-
 16 Week Samplers (TWS) used in the California Children's Health Study (Taylor et al. 1998); the
 17 Interagency Monitoring of Protected Visual Environments (IMPROVE) program; and from
 18 special studies conducted in Imperial Valley, Sacramento, San Francisco Bay Area, San
 19 Joaquin Valley (1995 Integrated Monitoring Study, IMS95), Santa Barbara County, and South
 20 Coast Air Basin (1995 PM₁₀ Enhancement Program, PTEP95).

1 6.3.1.1 PM10 and PM2.5 Ambient Concentrations

2 Table 6.1 lists maximum 24-hour and annual average PM10 concentrations in micrograms per
3 cubic meter ($\mu\text{g}/\text{m}^3$) recorded in each air basin in the last three years and PM2.5 concentrations
4 in the last two years – since federally approved PM2.5 monitors have been in operation in
5 California. The table also shows the number of days with measured concentrations over the
6 PM10 State Standard and the number of days with measured concentrations over the federal
7 PM2.5 standard. Detailed data by monitoring station for each air basin are presented in
8 Appendices 6-A and 6-B. We used SSI data for PM10 and FRM data for PM2.5 to generate
9 these tables. Monitoring data are presently being evaluated for occurrences of exceptional
10 events, consequently the data listed in Table 6.1 and Appendices 6-A and 6-B include data that
11 in the future may be removed from AIRS.

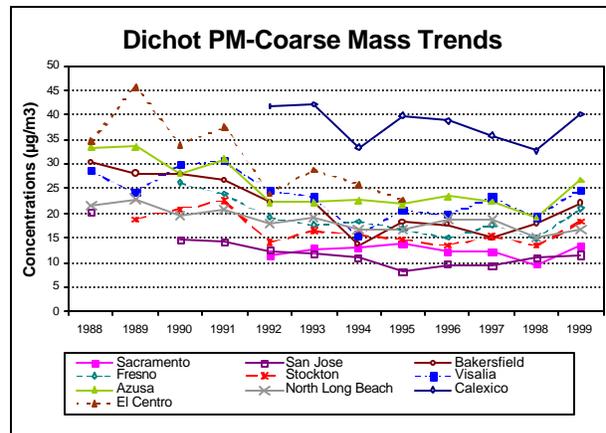
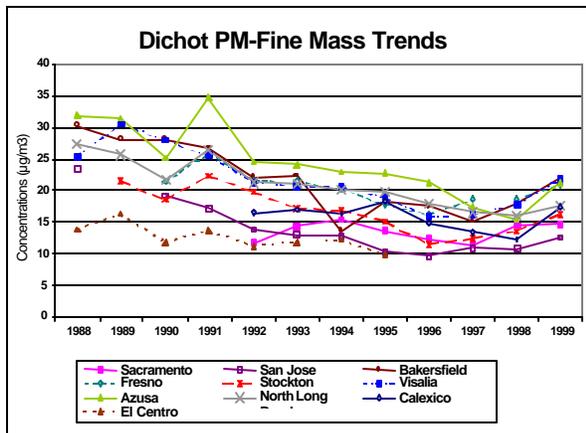
12 As shown in Table 6.1, with the exception of Lake County, all air basins exceed the current
13 State 24-hour PM10 standard of $50 \mu\text{g}/\text{m}^3$. Only Salton Sea, San Diego, San Joaquin, and
14 South Coast air basins exceed the current State annual standard of $30 \mu\text{g}/\text{m}^3$. The Salton Sea
15 Air Basin recorded two of the three highest 24-hour PM10 levels in the State, $1613 \mu\text{g}/\text{m}^3$ in
16 2000 and $1342 \mu\text{g}/\text{m}^3$ in 1999, while Great Basin Valleys registered $1116 \mu\text{g}/\text{m}^3$ in 1998. Salton
17 Sea also had the highest PM10 annual averages in the State, $183 \mu\text{g}/\text{m}^3$ in 2000 and $130 \mu\text{g}/\text{m}^3$
18 in 1999. In air basins exceeding both State PM10 standards, the ratios of maximum 24-hour and
19 annual concentrations compared to the respective standards suggest that the 24-hour State
20 standard is controlling (Table 6.2). Currently, eight air basins (Great Basin Valleys, Mountain
21 Counties, Sacramento Valley, Salton Sea, San Diego County, San Francisco Bay Area, San
22 Joaquin Valley, and South Coast) recorded 24-hour concentrations over the federal PM2.5
23 standard. Values over the 24-hour standard in Mountain Counties in 1999 may have been
24 caused by extensive wildfires. With the exception of Great Basin Valleys and Mountain
25 Counties, the other six air basins also recorded maximum annual average concentrations above
26 the federal annual PM2.5 standard.

27 As part of California's PM2.5 program, three locations have been selected to measure
28 background particulate matter concentrations: Point Reyes National Seashore in Northern
29 California, and San Rafael Wilderness and San Nicholas Island in Southern California. These
30 sites are located away from populated areas and other significant sources of particulate and
31 particulate precursor emissions. The sites have been in operation since December 2000. Data
32 from these sites are not yet available. However, data obtained from the IMPROVE program for
33 Point Reyes from March 1996 through February 1999 indicate that annual average
34 concentrations were $4.55 \mu\text{g}/\text{m}^3$ for PM2.5 and $10.97 \mu\text{g}/\text{m}^3$ for PM10 (Malm et al. 2000). PM10
35 and PM2.5 data collected at San Nicolas Island as part of PTEP95 program show that 24-hour
36 PM10 concentrations ranged from 4.7 to $69.19 \mu\text{g}/\text{m}^3$, with an annual average of $18.7 \mu\text{g}/\text{m}^3$
37 and PM2.5 levels ranged from 2.4 to $14.5 \mu\text{g}/\text{m}^3$, with an annual average of $6.82 \mu\text{g}/\text{m}^3$ (Kim et
38 al. 2000).

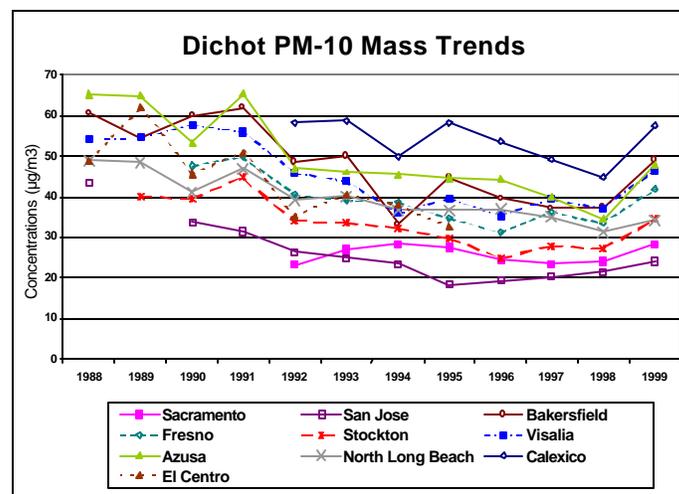
39 6.3.1.2 Historical Trends

40 We determined PM concentration trends using dichot PM2.5, PM2.5-10, and PM10 data
41 collected from 1988 through 1999 at selected urban sites. The dichot sampler uses a low-
42 volume PM10 inlet followed by a virtual impactor, which splits ambient air samples into fine
43 (PM2.5) and coarse (PM10-2.5) particle fractions. The sum of these two fractions provides a
44 measure of total PM10. We estimated annual arithmetic mean concentrations, by averaging
45 quarterly (January through March, April through June, July through September, and October
46 through December) arithmetic means. Data illustrated on the figure below indicate that, overall,
47 the annual means of PM2.5 decreased until 1998, increasing in 1999 at most sites. Monthly
48 rainfall data obtained from National Weather Service stations indicate 1999 was a much drier

1 year than 1997 and 1998, contributing to higher particulate matter concentrations in 1999. The
 2 coarse PM10-2.5 and the PM10 annual means exhibited similar trends, with a slightly less
 3 pronounced decrease in coarse fraction concentrations in the 1994 to 1999 period.
 4



5



6

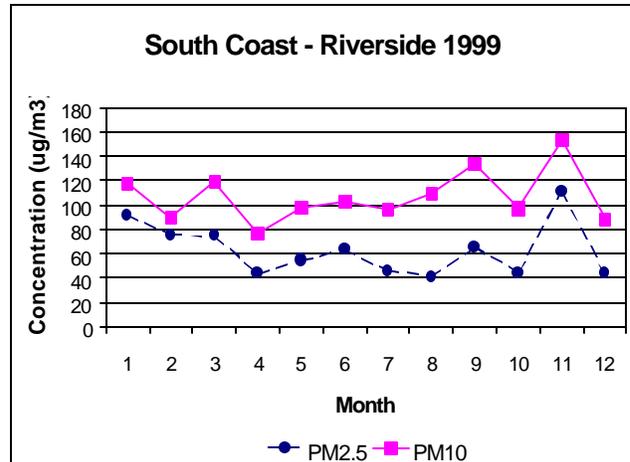
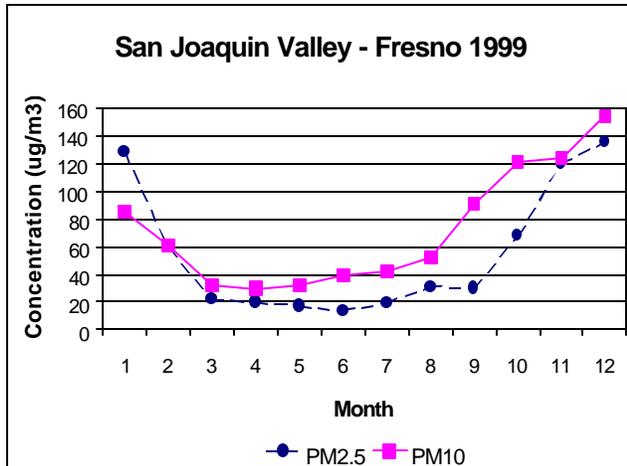
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8

9 6.3.1.3 Seasonality

10 Plots showing seasonal variation in ambient particulate matter concentrations were generated
 11 using FRM data for PM2.5 and SSI data for PM10. These seasonality plots are included in the
 12 subsections of this chapter describing particulate matter air quality in each air basin. The data
 13 represent the peak monthly concentration for each size fraction. In some cases PM2.5 is higher
 14 than PM10. This can occur for two reasons. First, the measurements are made on two different
 15 sampling systems and therefore have different levels of accuracy, precision, and uncertainty.
 16 Second, in some cases peak PM10 and PM2.5 concentrations do not occur on the same day.
 17 The plots were generated to provide an understanding of the seasonality of peak
 18 concentrations, not to compare specific PM10/PM2.5 concentrations to each other.

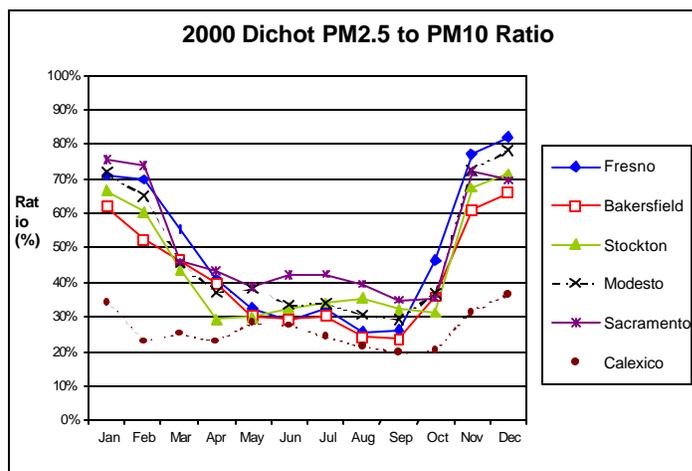
1 In general, there are a number of air basins, which exhibit strong seasonal patterns. Areas such
 2 as Sacramento, the San Joaquin Valley, and the San Francisco Bay Area record much higher
 3 PM2.5 and PM10 concentrations in the winter months. During this time of year, the PM2.5 size
 4 fraction drives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



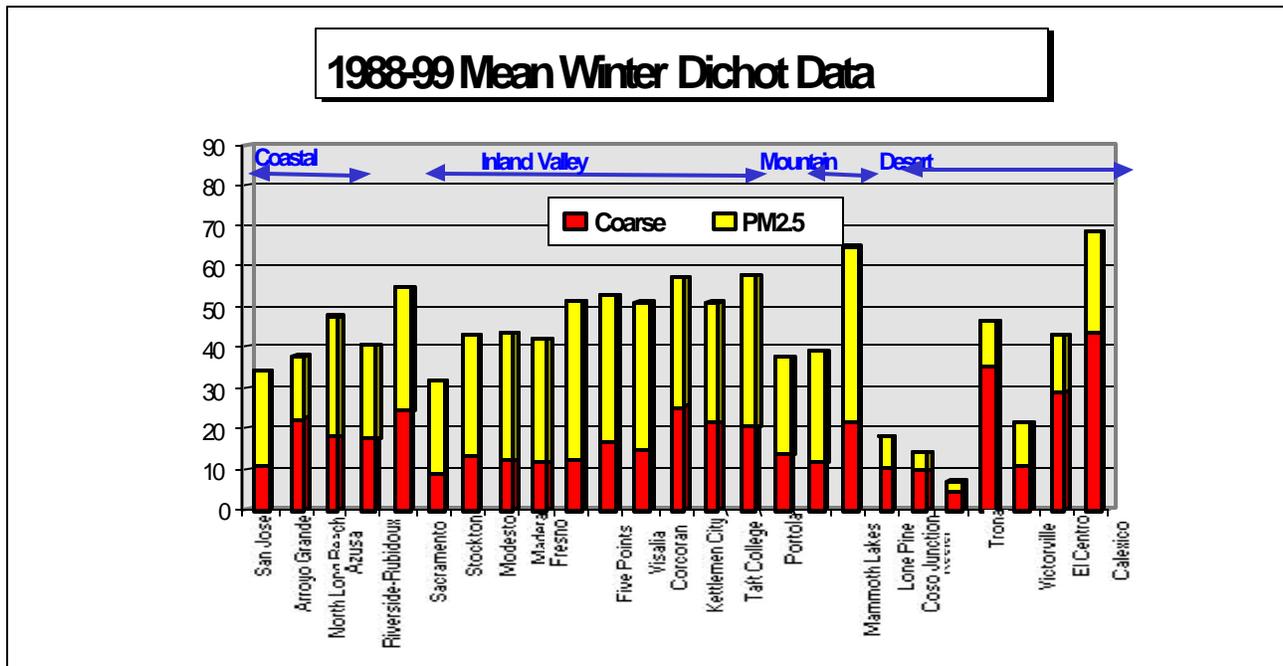
5
 6 Other areas such as the South Coast have a much more uniform distribution. In the South
 7 Coast, PM10 and PM2.5 concentrations remain high throughout the year.

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

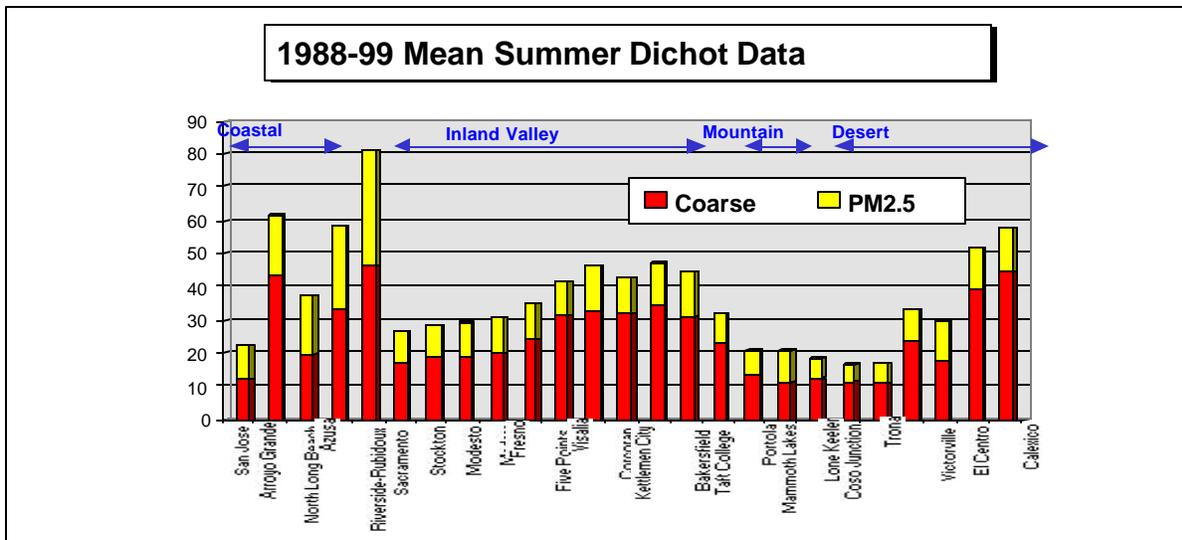
10 We used data collected with dichot samplers from 1998 to 2000 to estimate the ratios of PM2.5
 11 to PM10 concentrations (e.g., Table 6.3). In general, the average PM2.5 portion of PM10 was
 12 higher in the winter (November to February) than during the rest of the year (March to October).
 13 These seasonal differences were most pronounced in the San Joaquin Valley (75% in the winter
 14 and 38% during the rest of the year) and least prominent in the Mojave Desert (46% in winter
 15 and 39% during the rest of the year). No seasonal differences were apparent in the Great Basin
 16 Valleys Air Basin.



1 Seasonal variations in meteorological conditions and in the activity of emissions sources cause
 2 the size, composition, and concentration of particulate matter to vary in space and time.
 3 Because air typically flows inland from the Pacific Ocean, the percentage of days exceeding the
 4 California 24-hour standard is generally lower along the coast than in inland areas. As the air
 5 parcel moves downwind across areas with significant anthropogenic activities, fresh emissions
 6 and gas-to particle conversion cause PM concentrations to increase with distance (e.g., along



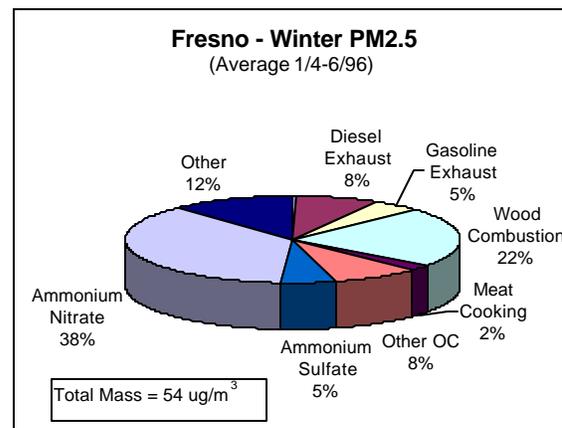
7
 8 the North Long Beach, Azusa, Riverside-Rubidoux corridor). PM2.5 concentrations are highest
 9 during the winter months (November to February). Cool temperatures, low inversion layers, and
 10 humid conditions favor the formation of secondary nitrate and sulfate particles, which are found
 11 predominantly in the fine fraction. Residential wood combustion also leads to higher PM2.5
 12 concentrations during the winter. From 1988 to 1999, in the San Joaquin Valley, 97 % of the
 13 four highest 24-hour PM2.5 concentrations and 68% of the four highest PM10 concentrations
 14 occurred during the winter. In the South Coast 53% of the four highest PM2.5 and 58% of the
 15 highest PM10 levels occurred in the winter season. Soil dust is the dominant contributor to
 16 PM10 in the summer. A desert environment generally has low PM concentrations, but on
 17 occasion high winds cause significant increases in dust.



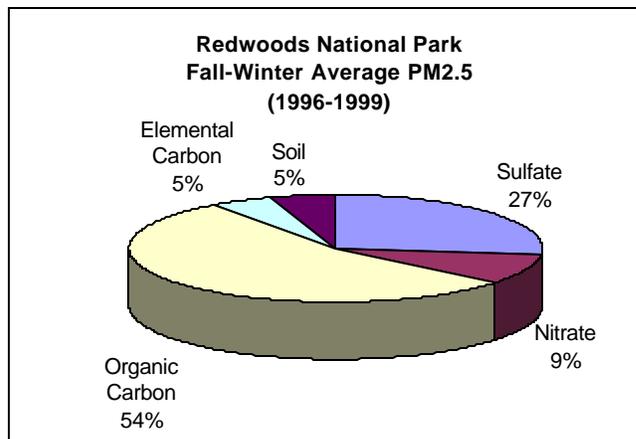
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2 6.3.1.4 Source Apportionment

3 Chemical Mass Balance models are used to establish which sources and how much of their
 4 emissions contribute to ambient particulate matter concentrations and composition. The models
 5 use chemical composition data from ambient PM samples and from emission sources. The
 6 source attribution data presented in this report was derived from a variety of studies with
 7 differing degrees of chemical speciation. In general however, the source categories can be
 8 interpreted in the following manner: The soil, woodsmoke, cooking, motor vehicle, and marine
 9 categories represent primary, or directly emitted particulate matter. The marine category
 10 represents sea salt. Soil represents the combination of mechanically disturbed soil (paved and
 11 unpaved roads, agricultural activities) and windblown dust. Woodsmoke or burning represents
 12 residential wood combustion, and can sometimes also represent other biomass burning such as
 13 agricultural or prescribed burning. The motor
 14 vehicle category represents direct motor vehicle
 15 exhaust from both gasoline and diesel vehicles.
 16 Nitrate (or ammonium nitrate) and sulfate (or
 17 ammonium sulfate) represent secondary species,
 18 i.e., they form in the atmosphere from the primary
 19 emissions of NO_x, SO_x, and ammonia.
 20 Combustion sources such as motor vehicles
 21 contribute to the NO_x that forms ammonium
 22 nitrate. The "other" category represents the mass
 23 that cannot be accounted for by the identified
 24 source categories. It can include water, as well as
 25 sources not included in the source apportionment
 26 analysis.



1 For some areas, such as the sites represented by the IMPROVE network, specific source
2 apportionment analysis has not been conducted. Instead, the primary chemical components are
3 shown. As discussed above, nitrate and sulfate are secondary species. Soil, elemental carbon,
4 as well as much of the organic carbon are primary species.



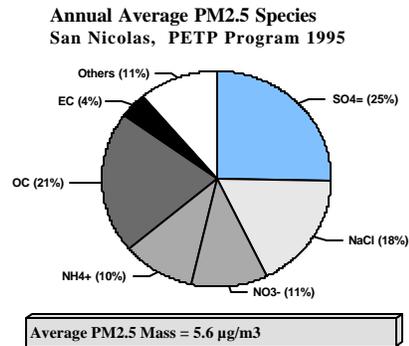
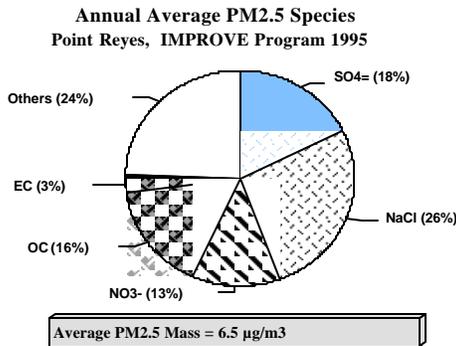
5
6 New data that is becoming available will allow for better, and more consistent source
7 apportionment. For example, the PM2.5 speciation samplers measure the species needed for
8 source apportionment analysis on the same sampler. Previously, ions and carbon were
9 measured on the SSI, and elements on the dichotomous samplers, requiring data from different
10 samplers to be combined for a complete picture. Data from special studies such as the
11 California Regional PM10/PM2.5 Air Quality Study (CRPAQS) and the 1997 Southern California
12 Ozone Study (SCOS97) will also provide more detailed speciation data for source
13 apportionment analysis

14 In many urban areas (e.g., Fresno and Bakersfield in the San Joaquin Valley, and San Jose in
15 the San Francisco Bay Area) during the winter, the major component of PM2.5 is nitrate –
16 predominantly formed in the atmosphere from reactions from motor vehicle exhaust and other
17 combustion sources - followed by wood combustion – mostly in fireplaces and wood stoves -
18 and primary emissions from motor vehicles. In the San Joaquin Valley rural areas, in the winter,
19 nitrate is the largest contributor, while vegetative burning and direct motor vehicle exhaust are
20 not as prominent as in urban sites. In the town of Mammoth Lakes in the Great Basin Valleys Air
21 Basin, total carbon – from residential wood combustion and motor vehicles - comprised 30% to
22 50% of the measured PM10 during the winter, In the Mountain Counties town of Quincy, high
23 levels of organic carbon are observed during the winter and fall. During the summer, in locations
24 such as San Jose and Sacramento soil dust is a significant component of PM10, and in coastal
25 San Jose sea salt makes up about one fourth of PM2.5. High levels of soil dust also contribute
26 to PM10 concentrations in rural, agricultural Corcoran during the fall months. On an annual
27 basis, in South Coast cities secondary nitrate is the major particulate constituent, while in
28 coastal Santa Barbara primary emissions from motor vehicles are most prominent, followed by
29 sea salt and soil dust. In the desert city of Calexico, soil comprises two thirds of PM10, while
30 motor vehicle exhaust contributes one fourth throughout the year.

31 Background sites often exhibit very different profiles. In national parks like Redwoods, Lake
32 Tahoe, and Pinnacles, organic carbon is the major component of annual average fine
33 particulate matter. The charts below show the PM2.5 chemical composition at two of the PM2.5
34 program background sites.

35

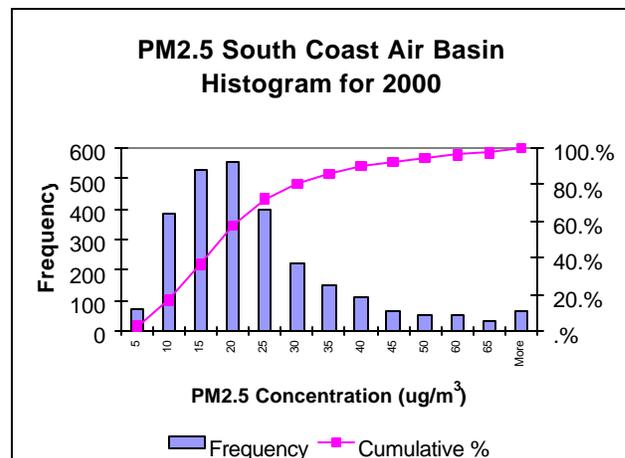
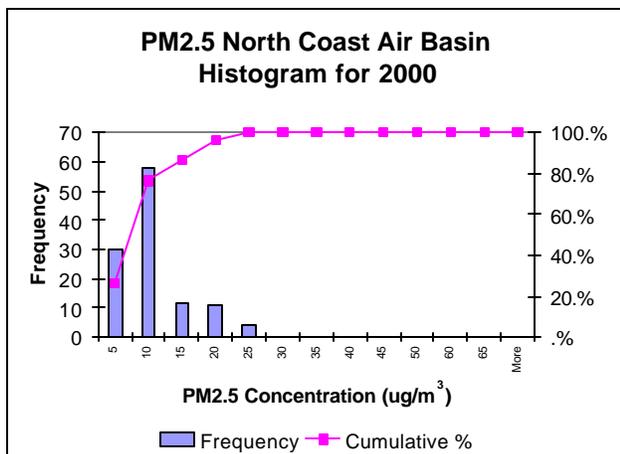
- 1 Data for Point Reyes are from analysis of ambient air collected in 1995 as part of the IMPROVE
- 2 program. Composition data for San Nicholas Island were collected as part of the PTEP95 study.
- 3 The data show sea salt, sulfate, and organic carbon are the largest contributors to PM_{2.5} at
- 4 both sites.



5 6.3.1.5 Frequency of Measured PM₁₀ and PM_{2.5} Concentrations

6 We generated histograms that represent the frequency distribution of observed particulate
 7 matter concentrations at all sites within an air basin. Separate histograms were plotted for 1998-
 8 2000 for PM₁₀ (Appendices 6-C1 to 6-C3) and 1999-2000 for PM_{2.5} observations (Appendices
 9 6-D1 and 6-D2). As with previous analyses, the PM₁₀ data is derived from the SSI monitor and
 10 the PM_{2.5} data from the FRM monitor. Each bar represents the number of observations within
 11 the specified range. For example, for PM_{2.5} the first bar is the number of observations between
 12 0 and 5 µg/m³, the second between 5 and 10 µg/m³ and so on. The histograms provide
 13 information on the frequency of high concentrations within each air basin, as well as the most
 14 frequent, or predominant concentration levels, and can provide insight into the impact of setting
 15 the standards at varying levels.

16 In many of the air basins, 80% of the PM₁₀ observations are below 30 to 35 µg/m³. However,
 17 other air basins, such as the San Joaquin Valley and the South Coast, have significant numbers
 18 of observations that are much higher. In these areas, the 80% cumulative frequency is not
 19 reached until about 70 µg/m³. For PM_{2.5}, in many of the air basins, most of the observations
 20 are below 10 to 20 µg/m³. However, as with PM₁₀, areas such as the San Joaquin Valley and
 21 the South Coast exhibit a distribution such that the 80% cumulative frequency is reached at 35
 22 to 40 µg/m³.



1 6.3.1.6 Diurnal Variation in PM10 levels

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

16 6.3.1.7 Particle Size Distribution

17 Data on particle size distribution is limited. During the IMS95 winter study in San Joaquin Valley,
18 air samples using a Micro-Orifice Uniform Deposit Impactor (MOUDI) sampler were collected at
19 Bakersfield (Chow et al. 1997). The MOUDI partitions ambient PM samples into nine size cuts
20 between 0.054 and 15 μm . We used these data to study the size distribution of PM10
21 components. Soil components were concentrated mainly in the larger size fractions ($>3.16 \mu\text{m}$),
22 the coarse component of PM10. The size of nitrate particles peaked between 1 and 1.78 μm ,
23 while organic carbon particles appeared in both larger (peak between 0.37 and 1 μm) and
24 smaller ($<0.054 \mu\text{m}$) size fractions.

25 **6.3.2 Characterization of Ambient Particulate Matter by Air Basin**

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

34

1 **Table 6.1. Maximum PM10 and PM2.5 Concentrations per Air Basin**

Air Basin	Year	PM10 ($\mu\text{g}/\text{m}^3$)			PM2.5 ($\mu\text{g}/\text{m}^3$)*		
		Days over State Std.	Max. 24-hour (Std.=50)	Max Annual Geometric Mean (Std.=30)	Days over Federal Std.	Max 24-hour (Std.=65)	Max Annual Average of Quarters (Std.=15)
Great Basin Valleys	1998	29	1116	20			
	1999	1	514	14		41	7
	2000	14	572	20	2	68	9
Lake County	1998		35	6			
	1999		43	11		15	4
	2000		22	10		9	Incomplete data
Lake Tahoe	1998	2	59	20			
	1999		41	17		21	8
	2000		50	18		23	7
Mojave Desert	1998	8	165	24			
	1999	12	109	28		48	12
	2000	11	80	30		39	8
Mountain Counties	1998	11	92	23			
	1999	13	125	23	4	92	14
	2000	8	98	22		48	8
North Central Coast	1998	5	76	26			
	1999	9	103	28		31	8
	2000	4	74	27		23	Incomplete data
North Coast	1998		50	20			
	1999	11	100	22		37	9
	2000	2	51	20		24	9
Northeast Plateau	1998	4	66	13			
	1999	12	100	30		40	8
	2000	10	80	18		38	7

2 * No conclusions on attainment for the federal PM2.5 standard should be drawn from these data, since attainment designations will
 3 be based on three years of data.

4 **Monitoring data are presently being evaluated for occurrences of exceptional events, consequently the table includes data that in
 5 the future may be identified as recorded during an exceptional event and be removed from consideration.

1 **Table 6.1. Maximum PM10 and PM2.5 Concentrations per Air Basin (continuation)**

Air Basin	Year	PM10 ($\mu\text{g}/\text{m}^3$)			PM2.5 ($\mu\text{g}/\text{m}^3$)*		
		Days over State Std.	Max. 24-hour (Std.=50)	Max Annual Geometric Mean (Std.=30)	Days over Federal Std.	Max 24-hour (Std.=65)	Max Annual Average of Quarters (Std.=15)
Sacramento Valley	1998	17	68	19			
	1999	27	171	26	11	108	19
	2000	18	86	25	5	98	12
Salton Sea	1998	62	568	79			
	1999	68	1342	130		53	15
	2000	97	1613	183	1	84	17
San Diego County	1998	18	89	39			
	1999	24	121	48		64	18
	2000	25	139	42	2	66	16
San Francisco Bay Area	1998	5	92	22			
	1999	12	114	25	4	91	16
	2000	7	76	24	1	67	14
San Joaquin Valley	1998	51	159	34			
	1999	64	183	50	42	136	28
	2000	66	145	45	29	160	23
South Central Coast	1998	18	73	24			
	1999	18	90	27		65	14
	2000	25	113	28		55	15
South Coast	1998	59	116	49			
	1999	55	183	65	15	121	30
	2000	74	126	52	23	120	28

2 * No conclusions on attainment for the federal PM2.5 standard should be drawn from these data, since attainment designations will
 3 be based on three years of data.

4 **Monitoring data are presently being evaluated for occurrences of exceptional events, consequently the table includes data that in
 5 the future may be identified as recorded during an exceptional event and be removed from consideration.

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

Air Basin	Year	Max 24-hour/Std. (Std. = 50 µg/m ³)	Max Annual Avg./Std. (Std. = 30 µg/m ³)
Salton Sea	1998	11.4	2.6
	1999	26.8	4.3
	2000	32.0	6.1
San Diego	1998	1.8	1.3
	1999	2.4	1.6
	2000	2.8	1.4
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	2.5	1.7

3

4

1 **Table 6.3. Ratios of monthly average PM_{2.5} to PM₁₀ mass with a reported minimum**
 2 **and maximum at each location, 1999**

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

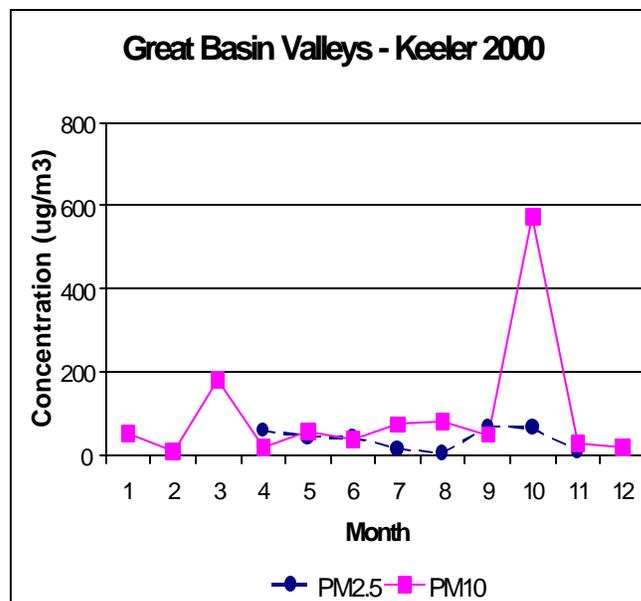
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1 On an annual basis, particulate levels are low in the Great Basin Valleys Air Basin (PM10 = 14 to 20 $\mu\text{g}/\text{m}^3$ and PM2.5 = 7 to 9 $\mu\text{g}/\text{m}^3$). Eighty percent of the 24-hour PM10 observations were below 25 to 30 $\mu\text{g}/\text{m}^3$ and 80% of the 24-hour PM2.5 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 dry lakebed produces extremely high concentrations of particulate in the air, reaching 1116 $\mu\text{g}/\text{m}^3$ in 1998. Particulate levels exceeded the 24-hour State PM10 standard 44 times in the last three-year

13 period and two observations over the federal PM2.5 standard were recorded in the last two
 14 years. The Great Basin Valleys Air Basin did not exceed either the PM10 or PM2.5 annual
 15 standards.

16 The chart below illustrates the monthly variation of the maximum daily PM10 and PM2.5
 17 concentrations at Keeler in 2000. Keeler is located near the Owens dry lakebed. High PM10
 18 concentrations can occur at any time of the year, though more frequently in the spring and fall.
 19 PM2.5 concentrations are relatively uniform most of the year.



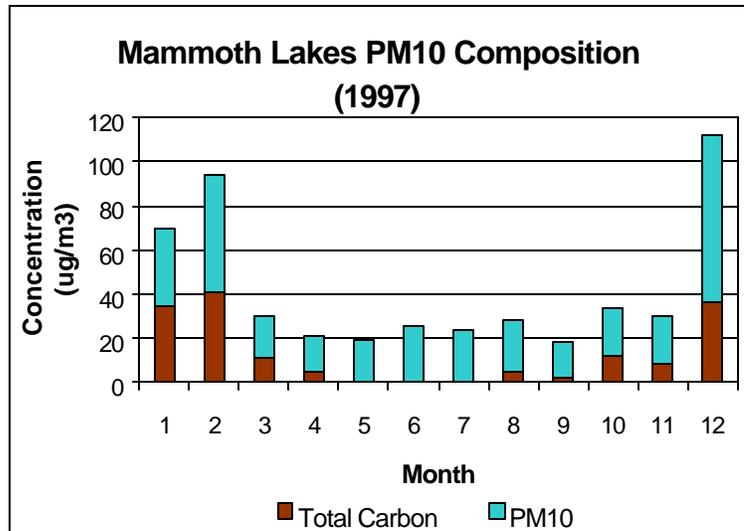
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*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

21 Data obtained from the Keeler and Coso Junction dichotomous samplers in 1999 indicate the
 22 PM2.5 component of PM10 ranges from 14% to 89%, with an annual average of 33%.

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

1 In the town of Mammoth Lakes, high
2 PM10 concentrations usually occur
3 during the winter months (December
4 – February). The graph on the right
5 shows the monthly variation of the
6 maximum daily PM10
7 concentrations in 1997. The chart
8 also illustrates how much of the
9 measured PM10 is total carbon.
10 During the winter, total carbon
11 comprises 30% to 50% of the
12 measured PM10. Sources of carbon
13 include residential wood combustion
14 and motor vehicles.



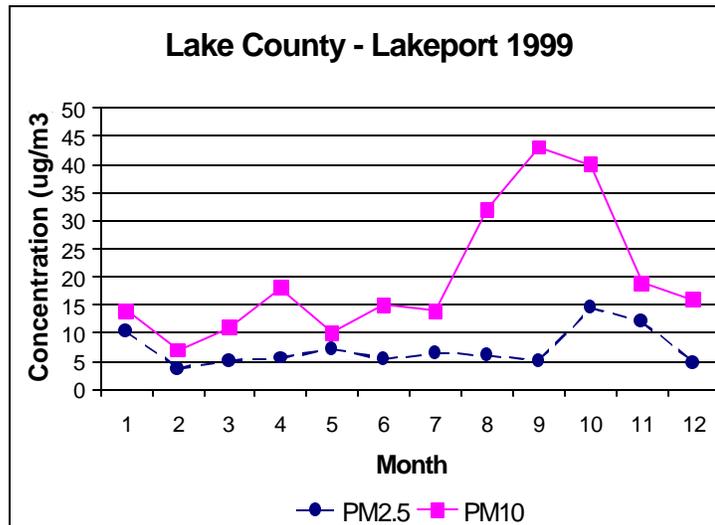
**Lake County
Air Basin**



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.

The chart below 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.



17

18

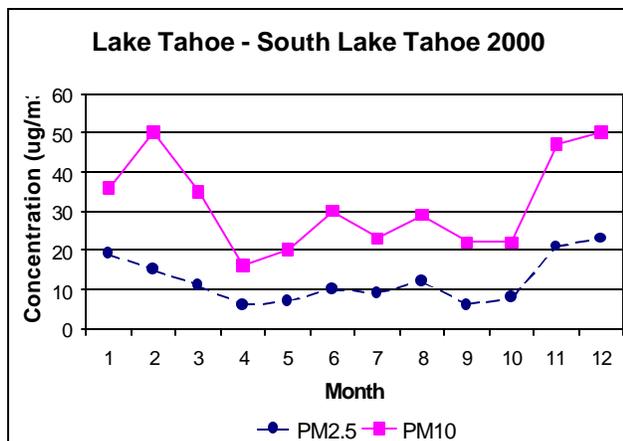
*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

Lake Tahoe Air Basin

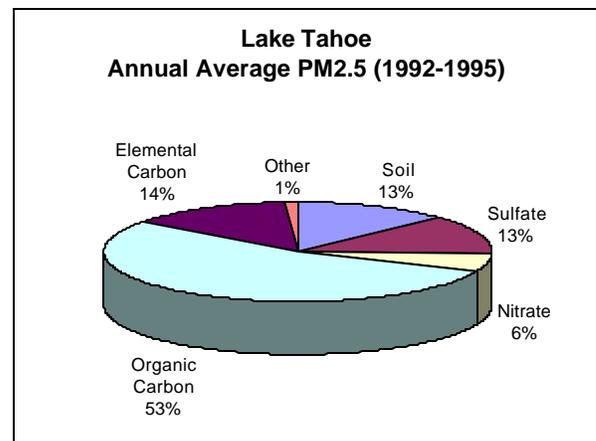


In the Lake Tahoe Air Basin, particulate levels exceeded the 24-hour State PM10 standard two times in the last three-year period, but fine particulate levels were well below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. In 1998, 80% of the PM10 observations were below 45 to 50 $\mu\text{g}/\text{m}^3$. In the last two years, 80% of the PM2.5 observations were below 10 to 15 $\mu\text{g}/\text{m}^3$.

The chart on the left below illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in South Lake Tahoe in 2000. PM10 as well as PM2.5 levels are highest during the late fall and winter (November through February), and are lowest in the in spring and summer.



14



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

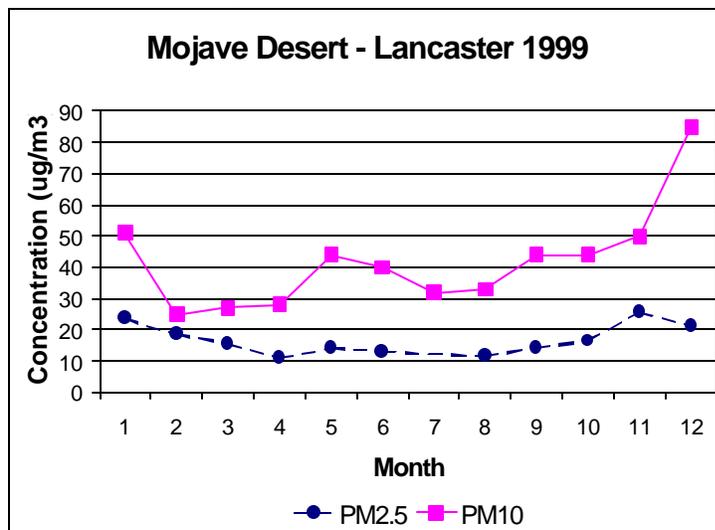
17 Data for the illustration shown on the right above are from analysis of ambient air collected in
 18 Lake Tahoe from 1992 through 1995 as part of the IMPROVE program (Sisler 1996). The
 19 constituents shown can vary substantially daily and seasonally based on a variety of factors
 20 such as meteorology and which particulate sources are most active. The data show large
 21 carbon contributions, mostly from residential wood combustion in fireplaces and other
 22 combustion sources, including motor vehicles. The nitrates and sulfates shown are
 23 predominantly formed from reactions between motor vehicle exhaust - nitrogen oxides and
 24 sulfur oxides – and other combustion sources. The soil component originates from sources such
 25 as paved and unpaved road dust.

Mojave Desert Air Basin



In the Mojave Desert Air Basin, particulate levels exceeded the 24-hour State PM10 standard 31 times in the last three-year 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 $\mu\text{g}/\text{m}^3$.

- 10 The chart below illustrates the monthly variation of the maximum daily PM10 and PM2.5
- 11 concentrations in Lancaster in 1999. PM10 as well as PM2.5 levels are highest during the winter
- 12 months - December and January. During the rest of the year, PM2.5 levels are quite low, while
- 13 PM10 levels fluctuate with no distinct pattern.
- 14 Data from the dichotomous sampler at Victorville in 1999 indicate the PM2.5 component of



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

- 15 PM10 ranges from 19% to 75%. The average PM2.5 fraction of PM10 is 46% from November to
- 16 February and 39% from March to October.
- 17 Ambient air quality data from 1997 through 1999 show low levels of secondary nitrate and
- 18 sulfate particulate in the Mojave Desert, indicating that most of the particulate matter is primary
- 19 in origin.
- 20 Based on the 2000 annual PM10 emission inventory, the major contributors to primary
- 21 particulates in the Mojave Desert Air Basin are unpaved road dust, windblown dust, paved road
- 22 dust, and construction related dust. A few point source categories, such as mineral processing
- 23 facilities, also contribute significant emissions.

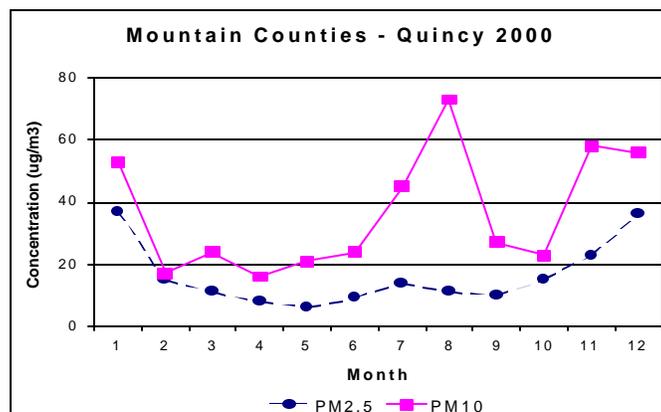
**Mountain Counties
Air Basin**



In the Mountain Counties Air Basin, particulate levels exceeded the 24-hour State PM10 standard 32 times in the last three-year 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 $\mu\text{g}/\text{m}^3$.

The chart below 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.

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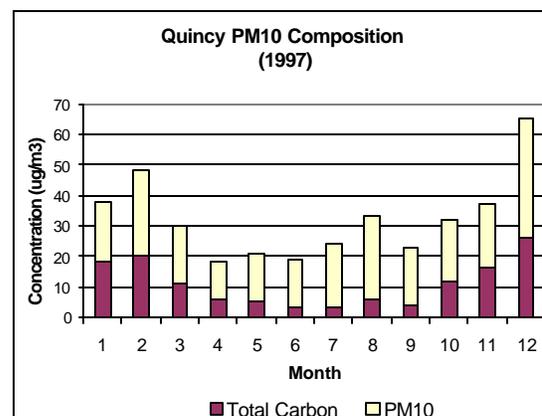


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

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

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

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



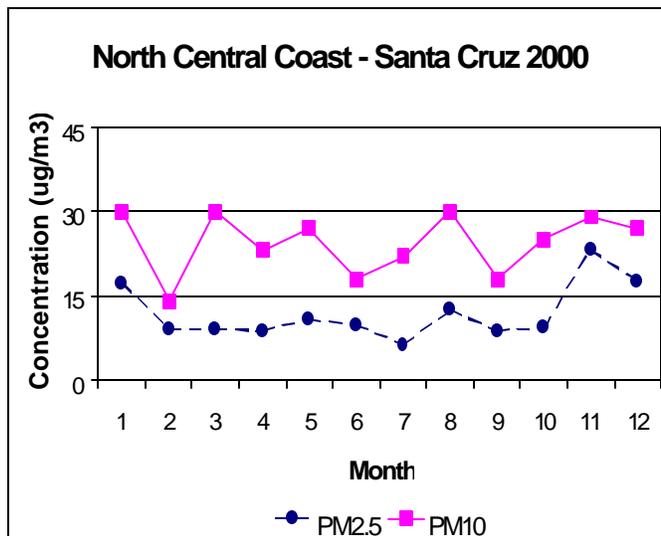
North Central Coast Air Basin



In the North Central Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 18 times in the last three-year 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 $\mu\text{g}/\text{m}^3$.

14

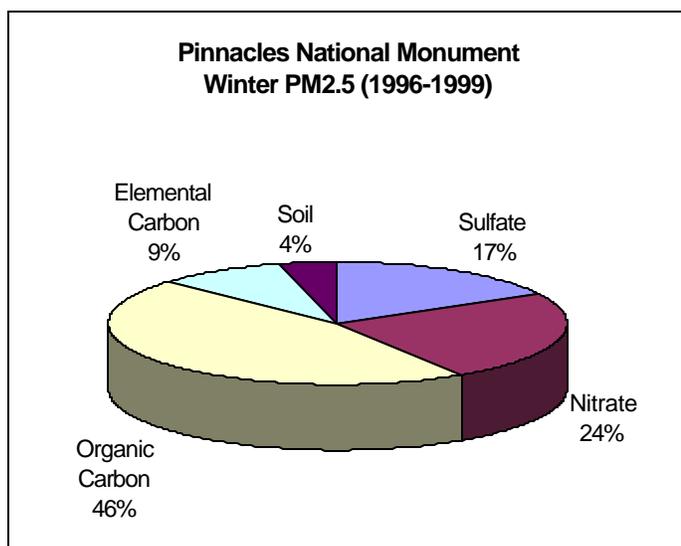
15 The chart on the right illustrates the
 16 monthly variation of the maximum daily
 17 PM10 and PM2.5 concentrations in Santa
 18 Cruz in 2000. Fine particulate levels are
 19 highest from November through January
 20 and are very low the rest of the year.
 21 PM10 levels fluctuate throughout the year,
 22 with no distinct seasonal pattern.



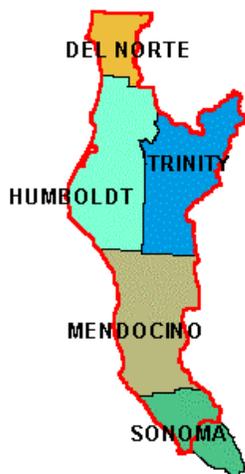
23 Based on the 2000 annual PM10 emission
 24 inventory, the major sources of directly
 25 emitted particulates in the North Central
 26 Coast Air Basin are unpaved roads,
 27 windblown dust, dust from farming
 28 operations, paved road dust, and
 29 residential wood burning.

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

30 Data for the illustration shown at right
 31 are from analysis of ambient air
 32 collected in the Pinnacles National
 33 Monument from 1996 through 1999 as
 34 part of the IMPROVE program (Malm et
 35 al. 2000). The constituents shown can
 36 vary substantially daily and seasonally
 37 based on a variety of factors such as
 38 meteorology and which particulate
 39 sources are most active. The data show
 40 carbon as the largest component of fine
 41 particulate matter. Smaller contributions
 42 are also seen from secondary nitrate
 43 and sulfate formed from reactions in the
 44 atmosphere of nitrogen oxides and sulfur
 45 oxides from motor vehicle exhaust and
 46 other combustion processes.



North Coast Air Basin

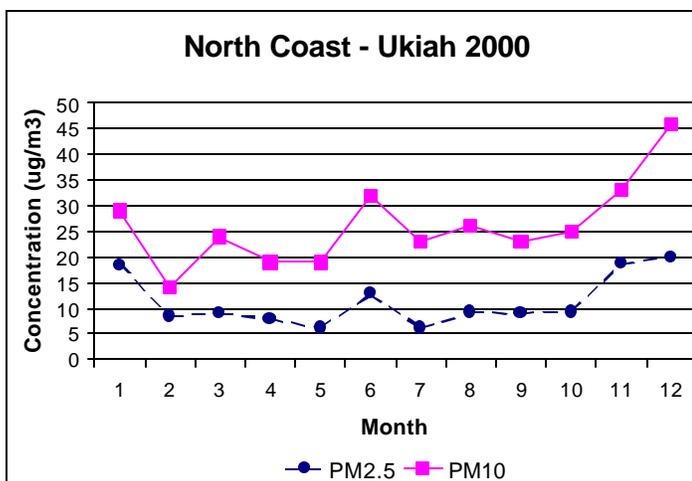


In the North Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 13 times in the last three-year period, but fine particulate levels were below the federal PM2.5 standards. The State annual PM10 standard was also not exceeded. In the North Coast Air Basin, 80% of the PM10 observations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

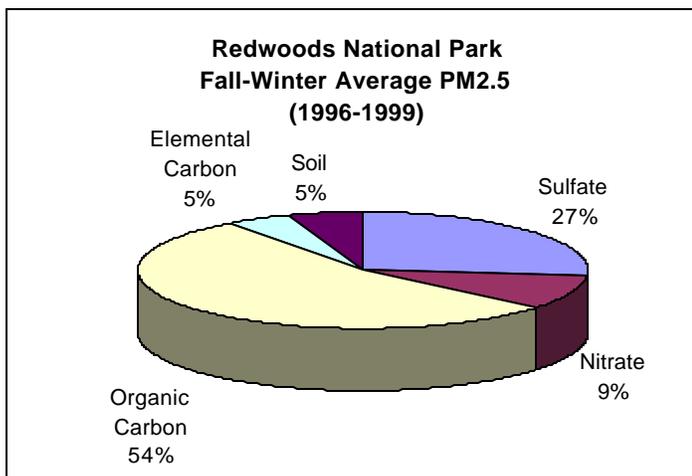
The chart below illustrates the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Ukiah in 2000. PM10 as well as PM2.5 levels are highest during the months of November through January, with a smaller peak in June.

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

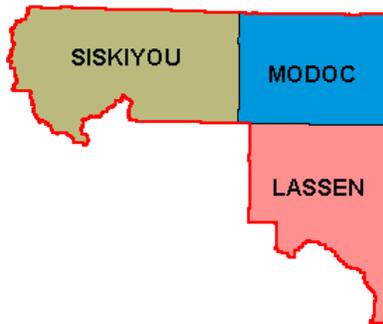
23 Data for the illustration shown at right
 24 are from analysis of ambient air
 25 collected in the Redwoods National
 26 Park from 1996 through 1999 as part
 27 of the IMPROVE program (Malm et
 28 al. 2000). The constituents shown can
 29 vary substantially daily and
 30 seasonally based on a variety of
 31 factors such as meteorology and
 32 which particulate sources are most
 33 active. The data show substantial
 34 contributions from organic and
 35 elemental carbon, as well as
 36 secondary sulfate and nitrate formed
 37 from reactions in the atmosphere of
 38 nitrogen oxides and sulfur oxides
 39 from motor vehicle exhaust and other
 40 combustion processes.



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



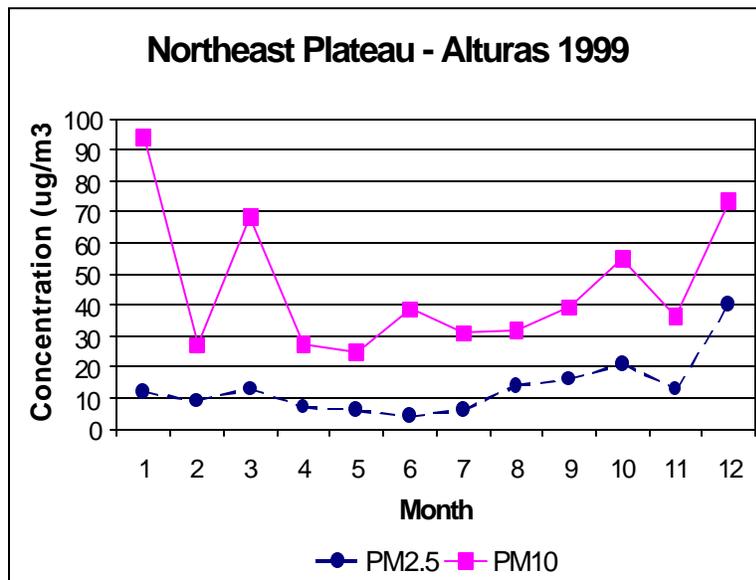
Northeast Plateau Air Basin



In the Northeast Plateau Air Basin, particulate levels exceeded the 24-hour State PM10 standard 26 times in the last three-year 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 $\mu\text{g}/\text{m}^3$.

The chart below 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

12 the spring and summer. PM2.5 levels are highest in December.

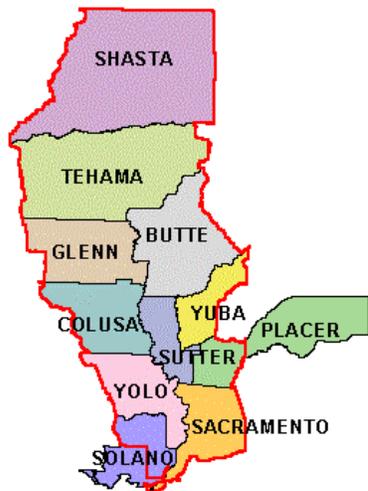


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

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

16

Sacramento Valley Air Basin

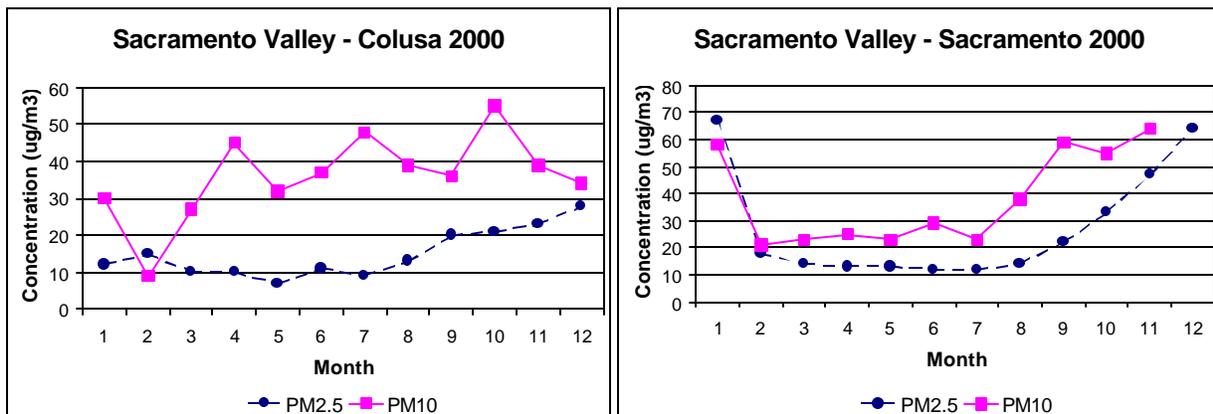


In the Sacramento Valley Air Basin, particulate levels exceeded the 24-hour State PM10 standard 62 times in the last three-year period and PM2.5 concentrations over the federal PM2.5 standard were recorded 16 times in the last two years. Particulate levels also exceeded both the State PM10 and federal PM2.5 annual standards. In the Sacramento Valley Air Basin, 80% of the PM10 observations are below 45 to 50 µg/m³ and 80% of the PM2.5 measurements are below 20 to 25 µg/m³.

The charts below 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. 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,

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

22

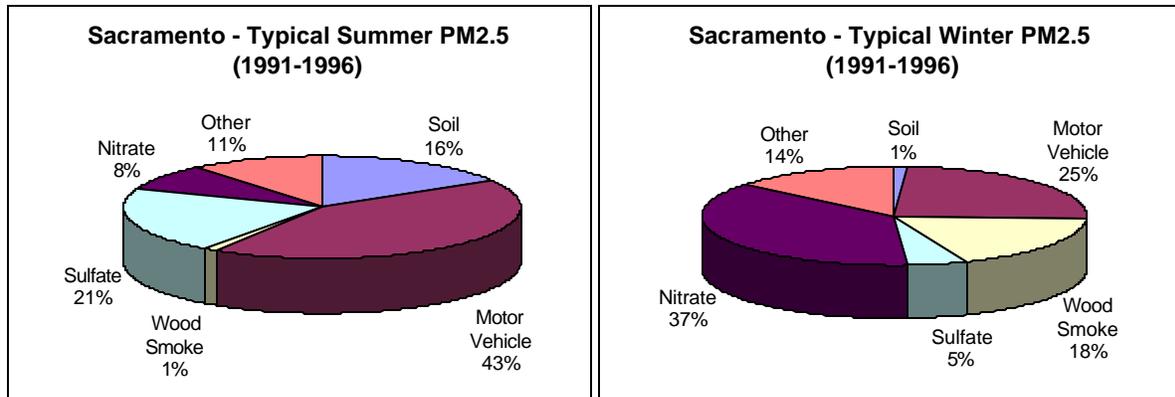


***The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.**

23

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

28 Data for the illustrations shown below are from analysis of ambient air collected in the summer
 29 (June through September) and winter (November through January) from 1991 through 1996 in
 30 Sacramento (Motallebi 1999, Motallebi 2001). The constituents shown can vary based on a
 31 variety of factors such as meteorology and which particulate sources are most active.

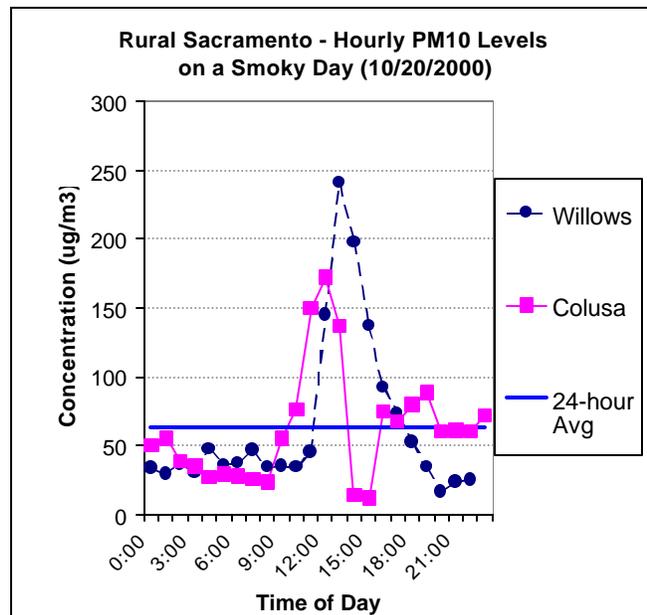


1

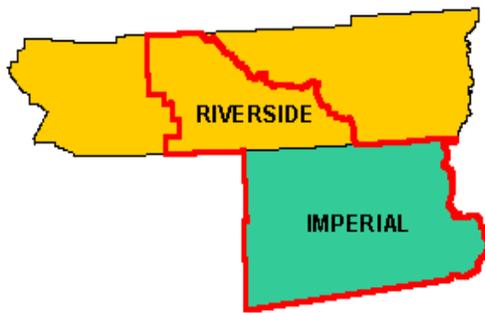
2 In the summer, directly emitted particles from motor vehicle exhaust and dust from paved roads
 3 and construction activities are major contributors to fine particulate ambient levels. The data
 4 also show contributions from secondary sulfate and nitrate formed from reactions in the
 5 atmosphere of nitrogen oxides and sulfur oxides from motor vehicle exhaust and other
 6 combustion processes. During the winter, wood smoke from residential fireplaces becomes a
 7 significant source of fine particulates. Winter conditions - cool temperatures, low wind speeds,
 8 low inversion layers, and high humidity – also favor the formation of nitrates.

9 The northern Sacramento Valley can be
 10 impacted by seasonal agricultural burning,
 11 mostly during the fall. The chart on the right
 12 illustrates the hourly variation in PM10
 13 levels on a rice straw burning day in
 14 Willows and Colusa in 2000. PM10 levels
 15 reached 4 to 5 times the level of the State
 16 24-hour PM10 standard for two hours in
 17 Willows and an average of 3 times the level
 18 of the standard for three hours in Colusa.

19



Salton Sea Air Basin

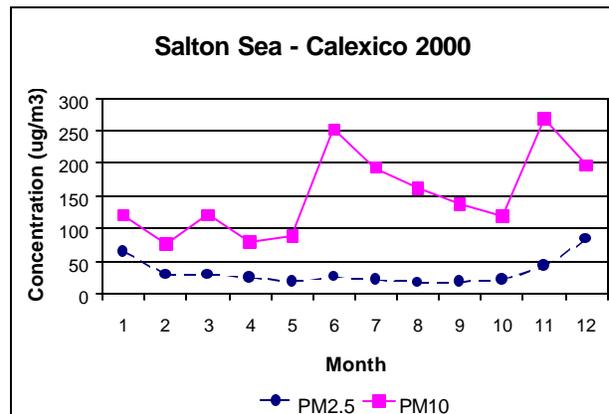


The Salton Sea Air Basin registered the highest 24-hour PM10 concentrations in the State in 1999 and in 2000. Particulate levels exceeded the 24-hour State PM10 standard 227 times in the last three-year period, but only one observation over the 24-hour federal PM2.5 standard was recorded last year. Particulate levels also exceeded both the State PM10 and federal PM2.5 annual standards. Eighty % 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 $\mu\text{g}/\text{m}^3$.

12

13 The chart on the right illustrates the monthly
 14 variation of the maximum daily PM10 and
 15 PM2.5 concentrations in Calexico in 2000.
 16 PM10 levels peak in the summer and fall. Fine
 17 particulates show a small increase in the fall and
 18 winter.

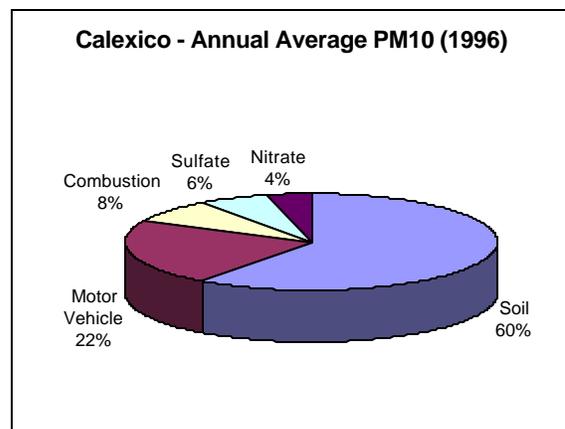
19 Data obtained from the Calexico dichotomous
 20 sampler in 2000 indicate the PM2.5
 21 component of PM10 ranges from 13% to 49%.
 22 The average PM2.5 fraction of PM10 from
 23 November to January is 34% and from
 24 February to October is 24%.



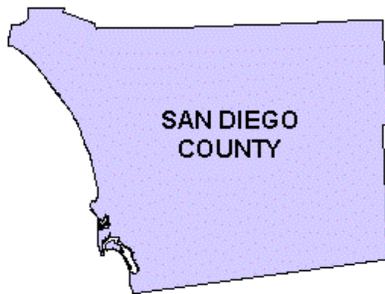
*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 greater than PM10.

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

30 A detailed chemical analysis of the particulate
 31 components in ambient air was used to provide
 32 the illustration of the sources of particulate matter
 33 in Calexico in 1996 (Woodhouse 2001). Dust is
 34 the major component of PM10. The figure also
 35 shows significant contributions from motor vehicle
 36 exhaust. The observed results could partially be
 37 due to transported pollutants from the
 38 neighboring city of Mexicali, which has high traffic. Secondary sulfate and nitrate formed from
 39 reactions in the atmosphere of nitrogen oxides and sulfur oxides from motor vehicle exhaust
 40 and other combustion processes also are small contributors to particulate matter levels in the air
 41 basin.



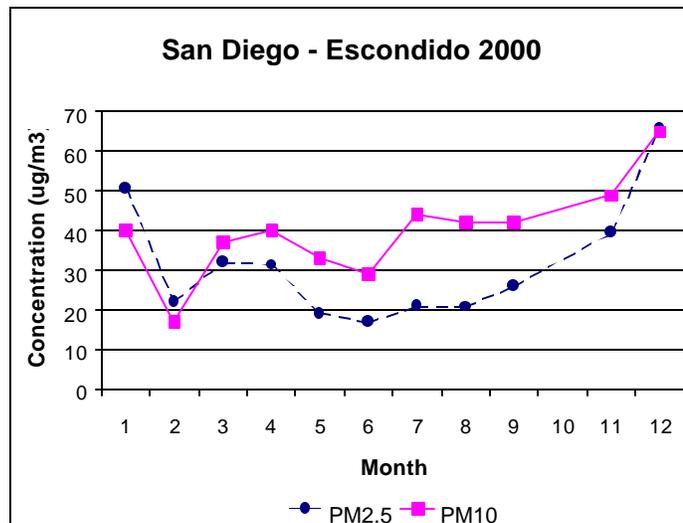
San Diego Air Basin



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 last three years. Ambient particulate levels also exceeded the State 24-hour PM10 standard 67 times in the last three years and two PM2.5 observations over the federal PM2.5 standard were recorded in the last two years. 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 $\mu\text{g}/\text{m}^3$.

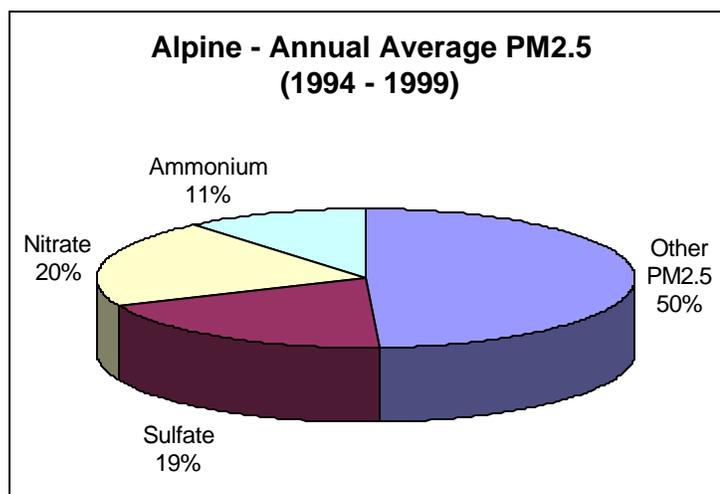
11 The chart on the right illustrates the
 12 monthly variation of the maximum daily
 13 PM10 and PM2.5 concentrations in
 14 Escondido in 2000. PM10
 15 concentrations exhibit no distinct
 16 seasonal pattern, while PM2.5
 17 concentrations are highest during the fall and
 18 winter.

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



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

27 Data for the illustration shown at right
 28 are from analysis of ambient data
 29 collected in Alpine from 1994 through
 30 1999 as part of the Southern
 31 California Children's Health Study.
 32 The data show substantial
 33 contributions from secondary nitrate
 34 and sulfate formed from reactions in
 35 the atmosphere of nitrogen oxides
 36 and sulfate oxides from motor vehicle
 37 exhaust and other combustion
 38 processes. The other PM2.5
 39 represents soil sources and total
 40 carbon. Carbon sources include wood
 41 smoke, other combustion sources,
 42 and motor vehicles (Salmon et al.
 43 2001).



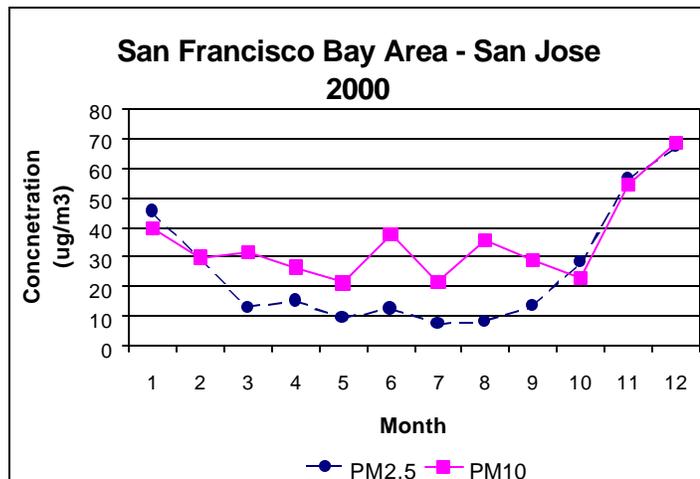
San Francisco Bay Area Air Basin



In the San Francisco Bay Area Air Basin, particulate levels exceeded the 24-hour State PM10 standard 24 times in the last three-year period and five PM2.5 observations over the 24-hour federal PM2.5 standard were recorded in the last two years. Particulate levels also exceeded the federal PM2.5 annual standard in 1999. Eighty % 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 $\mu\text{g}/\text{m}^3$.

The chart below 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.

16 Data obtained from the San Jose
 17 dichotomous sampler in 1999 indicate
 18 the PM2.5 portion of PM10 ranges from
 19 30% to 80%. The average PM2.5
 20 portion of PM10 from November to
 21 January is 61%, dropping to 46% from
 22 February to October.

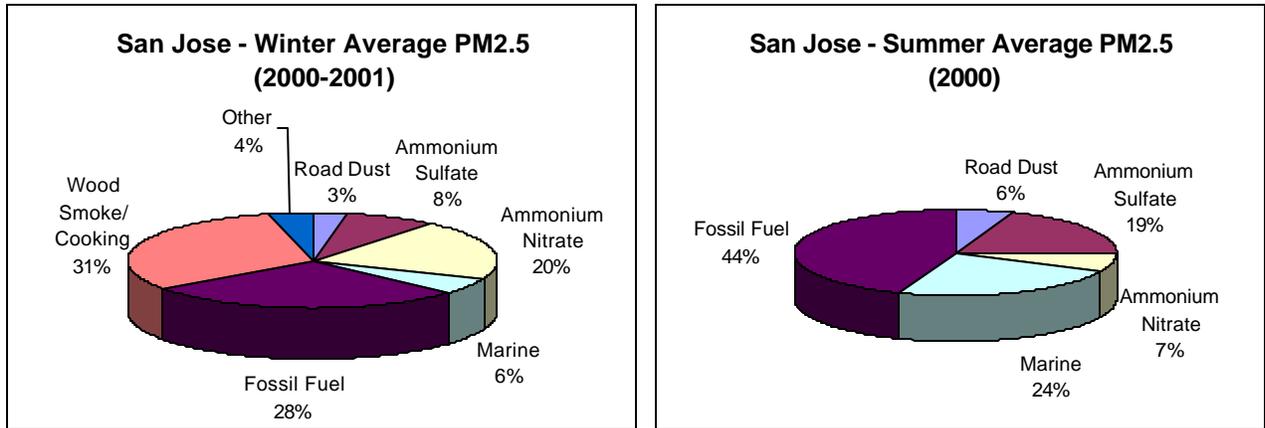


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

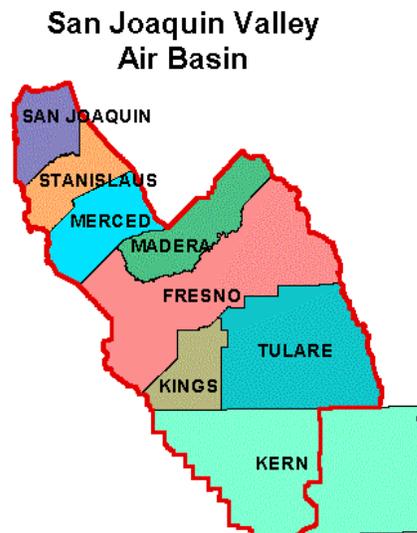
29
 30 Based on the 2000 annual PM10 emission inventory of directly emitted particulate matter, major
 31 sources include smoke from residential wood combustion, dust from construction operations,
 32 and the dust created by vehicles traveling on paved roads. There are also significant emissions
 33 from unpaved road dust in some counties and motor vehicle exhaust from cars and trucks.

34 Detailed chemical analyses of the fine particulate components in ambient air were used to
 35 provide the illustrations below (Fairly 2001). For this study, “summer” includes April through
 36 September and “winter” includes October through March. The constituents shown can vary
 37 depending on a variety of factors, such as meteorology and which particulate sources are most
 38 active.

39
 40



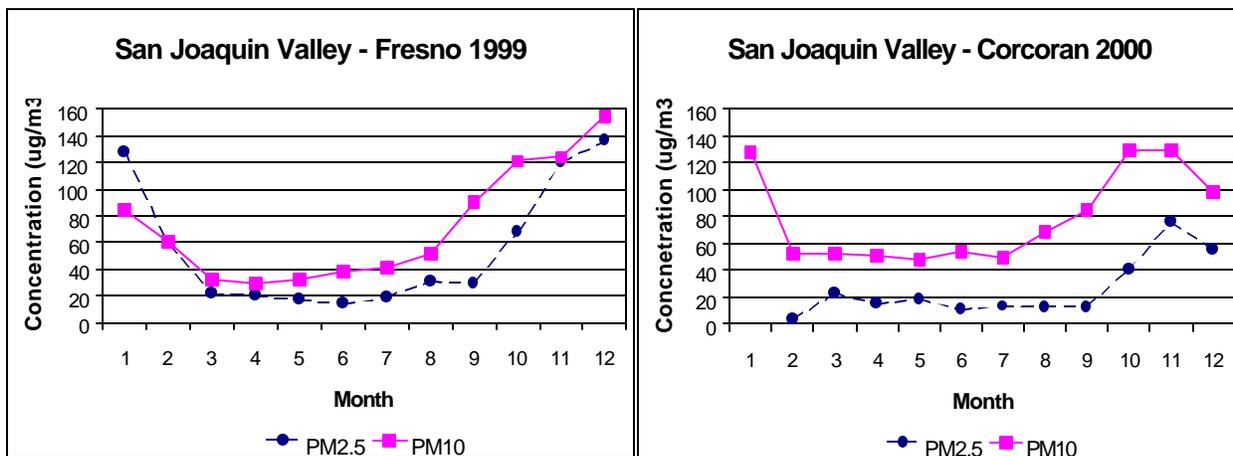
1
 2 During the summer, fossil-fueled sources – motor vehicles, refineries, power plants – contribute
 3 most significantly to fine particle levels in the region. Secondary ammonium sulfate and
 4 ammonium nitrate, formed from reactions in the atmosphere of nitrogen oxides and sulfur
 5 oxides from motor vehicle exhaust and other combustion processes, constitute one fourth of
 6 PM2.5. Marine air (sea salt) is also a significant contributor. In the winter wood smoke from
 7 residential wood combustion and cooking becomes the main component of fine particulate
 8 matter, followed by fossil fuel sources and secondary ammonium nitrate. Winter conditions -
 9 cool temperatures, low wind speeds, low inversion layers, and high humidity - favor the
 10 formation of nitrates.



In the last two years, the San Joaquin Valley Air Basin recorded the highest PM2.5 levels in the State – more than twice the federal standard - and 71 PM2.5 observations over the federal standard were recorded. Particulate levels exceeded the 24-hour State PM10 standard 181 times in the last three-year period. Particulate concentrations also exceeded both the State PM10 and federal PM2.5 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 PM2.5 measurements were below 35 to 40 $\mu\text{g}/\text{m}^3$.

The charts below illustrate the monthly variation of the maximum daily PM10 and PM2.5 concentrations in Corcoran in 2000 and in Fresno in 1999. In Corcoran, PM10 levels are highest in October and November, with PM2.5 peaking in November. In Fresno, PM10 and

17 PM2.5 are highest from October through January. PM2.5 drives PM10 concentrations during the
 18 wintertime in Fresno. The PM2.5 fraction of PM10 is smaller in Corcoran with fall peaks driven
 19 by PM10.

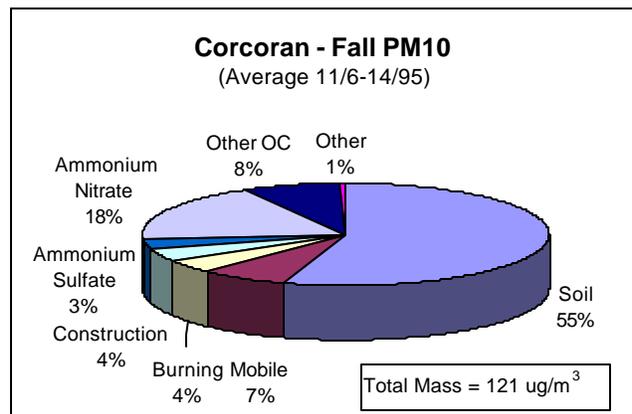
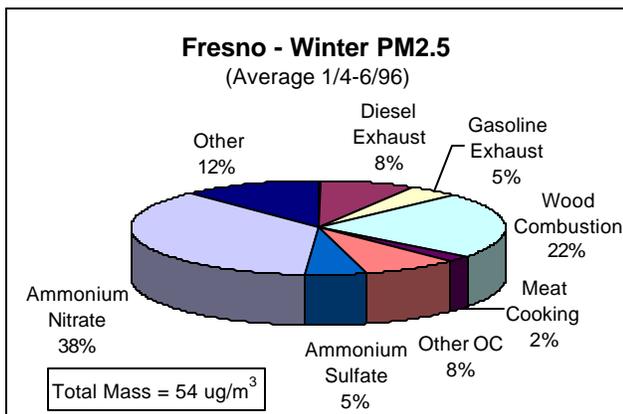
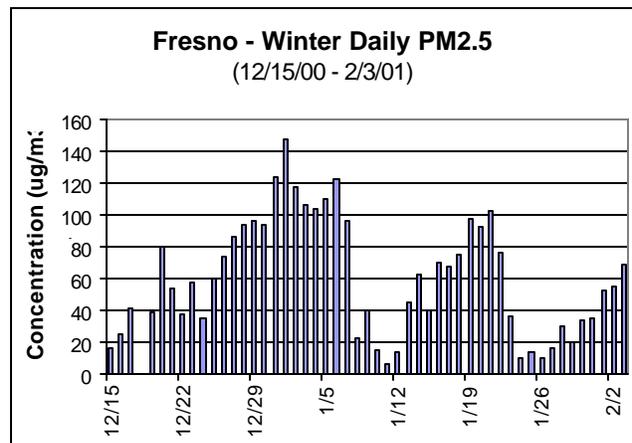


*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

20
 21 Data obtained from the Fresno dichotomous sampler from 1998 through 1999 indicate the
 22 PM2.5 component of PM10 ranges from 19% to 88%. The November through February average
 23 PM2.5 fraction is 75% of PM10 and the March through October average is 38%. Data obtained
 24 from the Corcoran dichotomous sampler from 1998 and 1999 show that the PM2.5 component
 25 ranges from 12% to 90%. The November through February average PM2.5 portion of PM10 is
 26 62% and the March through October average is 28%.

27 The chart below shows the daily variations in PM2.5 levels in Fresno during the winter of 2000
 28 to 2001. The data were obtained as part of the CRPAQS study. PM2.5 concentrations were
 29 over the federal 24-hour PM2.5 standard close to 40% of the time.

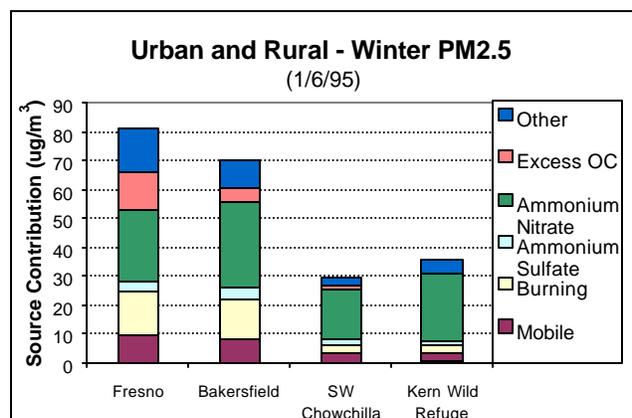
1 Based on the 2000 annual PM10 emission
 2 inventory, the major sources of directly
 3 emitted particulates in the San Joaquin
 4 Valley are agricultural and unpaved road
 5 dust, paved road dust, and windblown dust.
 6 Other less significant sources include
 7 stationary industrial activities, residential
 8 wood combustion, and particulates emitted
 9 by mobile sources such as cars and trucks.
 10 Detailed chemical analyses of the particle
 11 components in ambient air data collected
 12 during the 1995-Integrated Monitoring Study
 13 (IMS95), were used to provide the



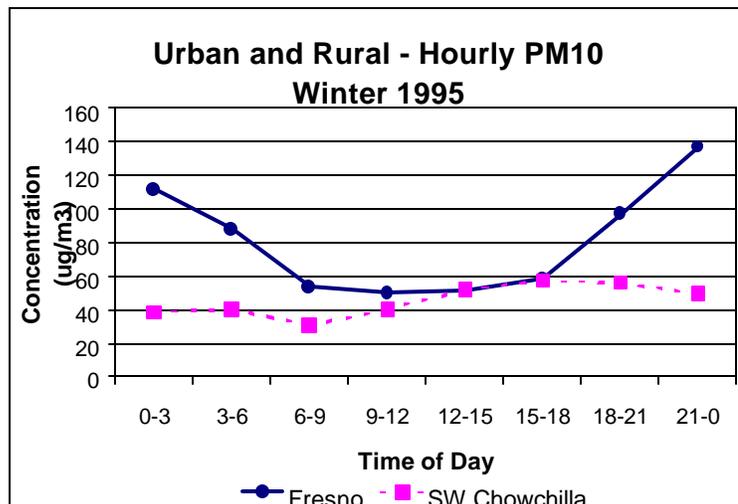
14 illustrations of the sources of particle matter in the San Joaquin Valley during the fall and winter
 15 (Magliano et al. 1999; Schauer et al. 1998).

16 In the fall at Corcoran, high particulate levels were associated with high levels of soil dust.
 17 During the winter in Fresno, emissions from biomass burning (primarily residential wood
 18 combustion), direct motor vehicle emissions, organic carbon, and secondary nitrate – formed
 19 from reactions in the atmosphere of nitrogen oxides and sulfate oxides from motor vehicle
 20 exhaust and other combustion processes - are major contributors to ambient particulate matter.
 21 Winter conditions – cool temperatures, low wind speeds, low inversion layers, and high humidity
 22 – favor the formation of nitrates.

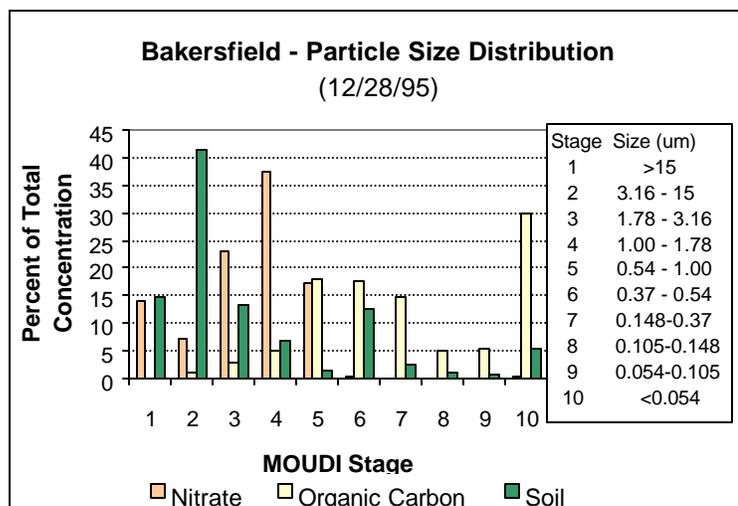
23 The Bakersfield and Fresno sites were
 24 located in large urban areas; the Kern Wild
 25 Refuge site was located amidst natural
 26 vegetation, while the SW Chowchilla site
 27 was in a rural area, surrounded by
 28 agricultural fields. At the peak of a winter
 29 PM2.5 episode, PM2.5 concentrations at the
 30 two rural sites were about half of the PM2.5
 31 levels at the two urban sites. Secondary
 32 ammonium nitrate was the largest contributor
 33 at all four sites. Vegetative burning and direct
 34 mobile source exhaust contributed 19% and
 35 12% of the PM2.5 mass in the urban areas,
 36 but only an average of 8% and 9% at the rural sites. The excess organic carbon resulting from
 37 combustion sources other than vegetative burning and mobile sources as well as secondary
 38 organic carbon – was significant at the urban, but not at the rural sites.



1 In the winter, PM10 levels varied
 2 significantly during the course of the day,
 3 with the highest concentrations
 4 occurring during the nighttime. In
 5 contrast, in rural SW Chowchilla
 6 PM10 levels did not vary much
 7 within a day. Chemical composition
 8 data indicate diurnal variations in
 9 ammonium nitrate were the primary
 10 cause of the PM10 variations in SW
 11 Chowchilla. The rise in PM10
 12 concentration in Fresno
 13 corresponded mostly to significant
 14 nighttime peaks in vegetative
 15 burning, mobile sources, and
 16 excess organic carbon (Magliano et
 17 al. 1999).



18 Data for the illustration shown at
 19 right are from air samples collected
 20 with a Micro-Orifice Uniform Deposit
 21 Impactor (MOUDI) sampler at
 22 Bakersfield during IMS95 (Chow et
 23 al. 1997). The size distribution of
 24 nitrate particles peaked between 1
 25 and 1.78 μm . Organic carbon
 26 particles appeared in both larger
 27 (peak between 0.37 and 1 μm) and
 28 smaller ($<0.054 \mu\text{m}$) stages. The
 29 ultrafine carbon particles (< 0.08
 30 μm) result from direct emissions
 31 from combustion sources or from
 32 the condensation of gases cooled
 33 down soon after they are emitted.



34 The soil components were concentrated mainly on the larger particle size fractions ($>3.16 \mu\text{m}$),
 35 the coarse fraction of PM10.

36

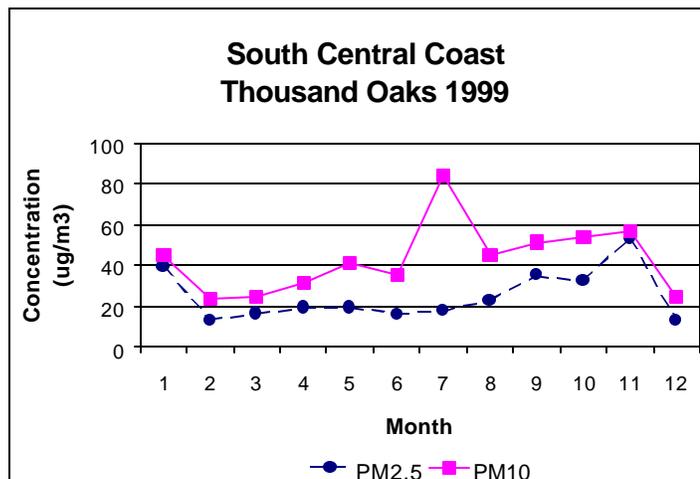


In the South Central Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 61 times in the last three years. Neither of the federal PM2.5 standards or the State annual PM10 were exceeded in the last few years. Eighty percent of the 24-hour PM10 observations were below 30 to 35 $\mu\text{g}/\text{m}^3$ and 80% of the 24-hour PM2.5 measurements were under 10 to 15 $\mu\text{g}/\text{m}^3$.

The chart below 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.

13

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



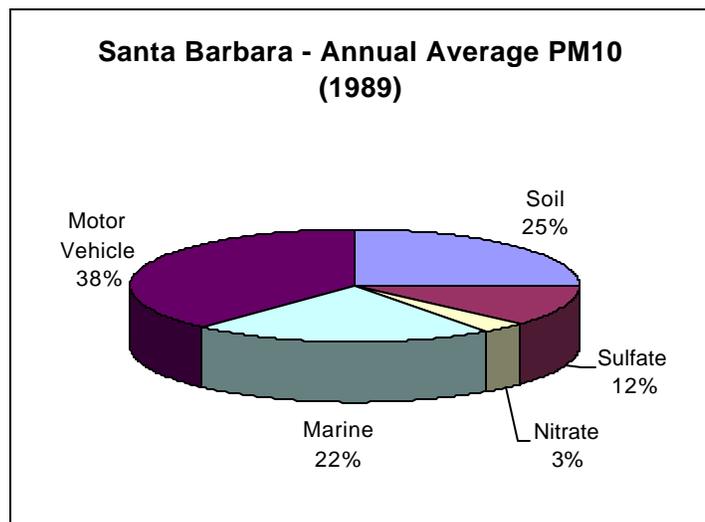
23 A detailed chemical analysis of particle
 24 components in ambient air was used to
 25 provide the following illustration of the
 26 sources of particulate matter in Santa
 27 Barbara County (Chow et al. 1996).

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

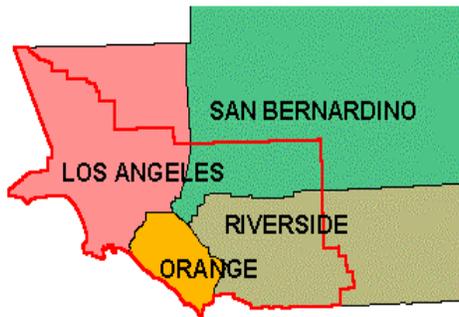
28

29 The constituents shown can vary
 30 substantially daily and seasonally based
 31 on a variety of factors such as
 32 meteorology and which particulate
 33 sources are most active.

34 Motor vehicles are the major contributor
 35 to PM10 levels in the region. Marine
 36 aerosols and soil each account for one
 37 fourth of the PM10 composition.
 38 Secondary ammonium nitrate and
 39 sulfate are relatively small contributors.



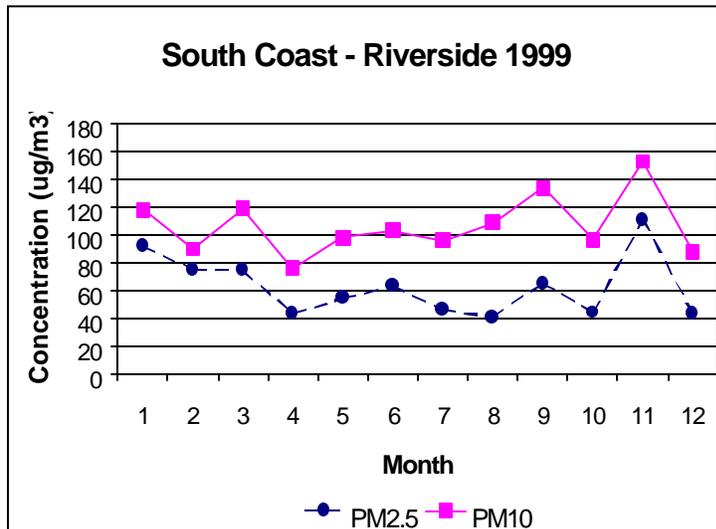
South Coast Air Basin



In the South Coast Air Basin, particulate levels exceeded the 24-hour State PM10 standard 188 times in the last three-year period, and 38 PM2.5 observations over the 24-hour federal PM2.5 standard were recorded in the last two years. Particulate levels also exceeded both the State PM10 and federal PM2.5 annual standards. The South Coast recorded some of the highest levels of PM2.5 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 PM2.5 measurements were below 35 to 40 $\mu\text{g}/\text{m}^3$.

13 The chart at right illustrates the
 14 monthly variation of the
 15 maximum daily PM10 and
 16 PM2.5 concentrations in
 17 Riverside in 1999. Both PM10
 18 and PM2.5 concentrations
 19 exhibit no distinct seasonal
 20 pattern, with high concentrations
 21 throughout the year.

22 Data obtained from the Long
 23 Beach dichotomous sampler in
 24 1999 indicate the PM2.5 portion
 25 of PM10 ranges from 30% to
 26 96%. The average PM2.5
 27 portion of PM10 from November
 28 to February is 59% dropping to



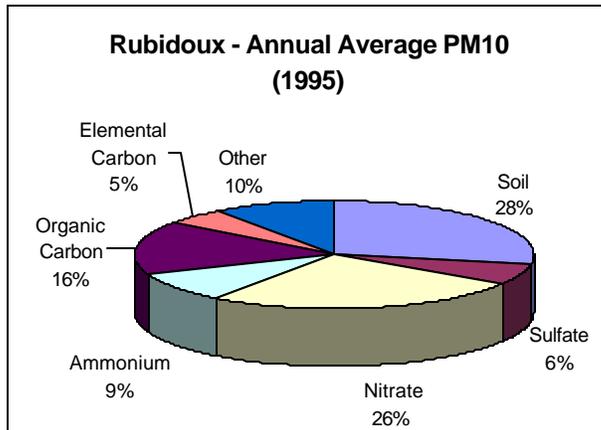
*The monitors used to measure PM10 and PM2.5 are different and occasionally recorded concentrations of PM2.5 which are greater than PM10.

29 45% from February to October.

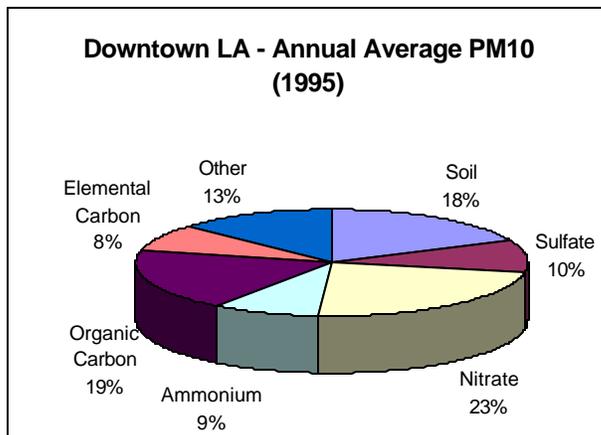
30 The 2000 annual PM10 emission inventory shows that the major sources of directly emitted
 31 particulates in the South Coast Air Basin are paved road dust, unpaved road dust,
 32 construction related dust, and the general categories of motor vehicle emissions and
 33 industrial emissions.

34 Data for the illustrations shown below are from analysis of ambient data collected during a
 35 one-year special study conducted from January 1995 to February 1996 as part of the PM10
 36 Technical Enhancement Program (PTEP) (Kim et al. 2000). The constituents shown can vary
 37 substantially daily and seasonally based on a variety of factors such as meteorology and
 38 which particulate sources are most active. The figures show that secondary nitrates – formed
 39 from reactions in the atmosphere of nitrogen oxides from motor vehicle exhaust and other
 40 combustion processes - contribute most significantly to particulate matter in the region.
 41 Carbon - elemental and organic - also derived from motor vehicles and other combustion
 42 sources contributes approximately one fourth of the particulate levels. Dust from soil is more
 43 prevalent in Riverside (Rubidoux site) as compared to Downtown Los Angeles.

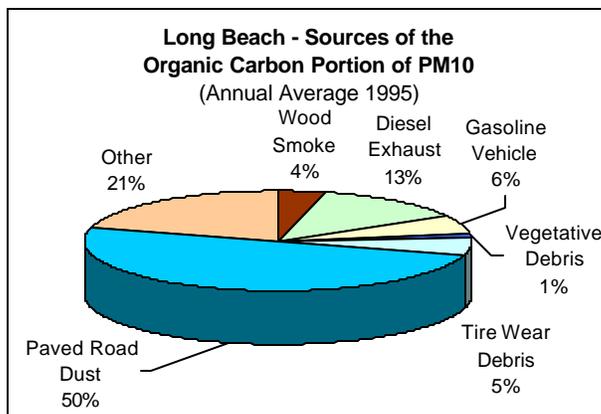
44



1



2



3

4 Data from a detailed chemical analysis conducted as part of the Children's Health Study were
 5 used to provide the illustration on the sources of the organic compound portion of PM10 in
 6 Long Beach in 1995 (Salmon et al. 2001). Road dust is the major contributor to the organic
 7 carbon portion of PM10 in Long Beach, followed by diesel- and gasoline-powered vehicle

1 exhaust. The “other” category – resulting from combustion sources other than vegetative
2 burning and mobile sources, as well as secondary organic carbon - is also significant.

3 **6.4 Ambient Air Quality Population Exposure**

4 **6.4.1 Introduction**

5 This section addresses two main questions: 1) what percent of the population in each air
6 basin is exposed to different concentrations of ambient PM10 and PM2.5 levels? 2) is the
7 population weighted average PM10 and PM2.5 concentration in each air basin?

8 **6.4.2 Exposure Model Details and Assumptions**

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

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

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

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

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

33 **6.4.3 Data Used**

34 Exposure calculations were performed for three metrics: annual arithmetic mean (AAM),
35 annual geometric mean (AGM), and peak 24-hour concentration, represented by the
36 Expected Peak Day Concentration (EPDC) for PM10. For PM2.5 the annual average of
37 quarters (AOQ) was used instead of the annual geometric mean. We chose the AGM and the
38 EPDC for PM10 and the AOQ for PM2.5, because these are the relevant metrics for the
39 existing State PM10 and the federal PM2.5 standards. PM10 data from 1998 through 2000
40 and PM2.5 data from 1999 through 2000 were obtained from all monitors in the State meeting
41 quality assurance criteria for valid data. For each metric, different numbers of monitors were
42 available which met the specified validity criteria. Therefore the population represented for
43 each metric is slightly different. For PM10 the population used in the analysis represented 99
44 percent of the 1990 statewide total population, while for PM2.5 it ranged from 62% to 66%.
45 For variations among air basins see Appendices 6-G1 to 6-G3 and 6-H1 to 6-H3.

1 As mentioned in Section 6.1, the EPDC for a monitoring site is the peak 24-hour PM10 (or
 2 PM2.5) concentration expected to occur no more than once per year. The EPDC is a highly
 3 precise estimate of the 99.7th percentile (364/365th percentile) of the 24-hour PM10 (or PM2.5)
 4 concentrations measured at the monitoring site. Since the sampling frequency for PM10
 5 concentrations is usually once every six days and for PM2.5 it varies by monitoring site (once
 6 every six days, once every three days or daily), the method used for calculating the EPDC
 7 automatically compensates for sampling frequencies that are less than daily. To calculate the
 8 EPDC, we use the highest twenty percent of all measurements during the last three years. An
 9 “exponential-tail” model is used for this purpose (Larsen and Nystrom, 1992; Breiman et al.,
 10 1978). The computer program to determine the EPDC is available to the public upon request
 11 (Contact: Larry Larsen, ARB).

12 1990 census data reported by census tract were used as the 2000 data were not yet available
 13 in the census tract format. The census data contains the shape, size, and centroid of each
 14 census tract, as well as the population count.

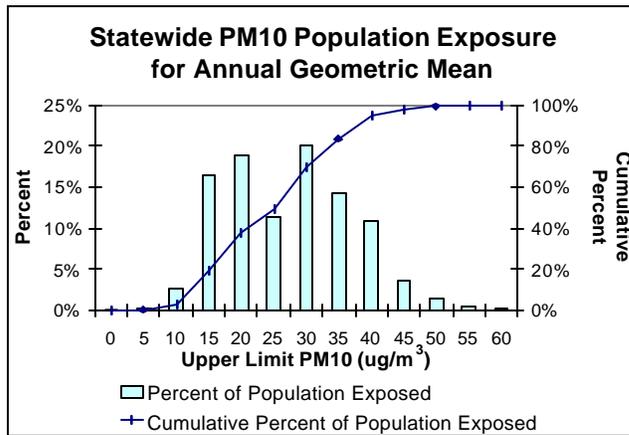
15 **6.4.4 Discussion of Exposure Model Results**

16 The detailed output of the exposure model for each of the three PM10 metrics is provided in
 17 Appendices 6-E1 to 6-E6 and for the PM2.5 metrics in Appendices 6-F1 to 6-F6. For each
 18 metric there is a statewide summary as well as a summary by air basin. The concentration
 19 data are shown in 5 $\mu\text{g}/\text{m}^3$ increments with the associated population exposed to
 20 concentrations within that range. An additional column is provided to indicate the percent of
 21 the population that is above the relevant standards. The table below summarizes the results
 22 of the PM10 statewide assessment.
 23

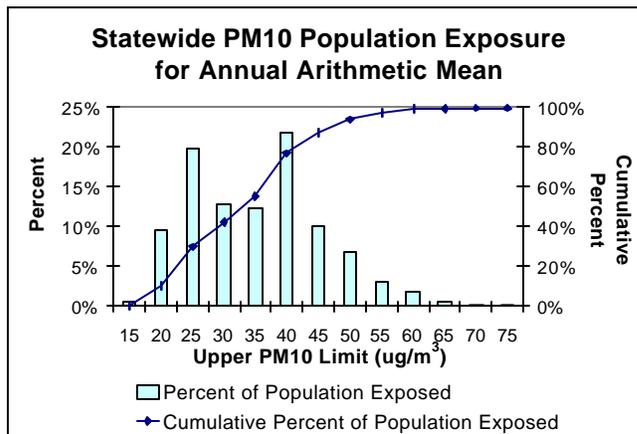
Form of Standard for PM10	Percent Population* Exposed to >30 $\mu\text{g}/\text{m}^3$ for annual means or >50 $\mu\text{g}/\text{m}^3$ for EPDC	1990 Population* Exposed to >30 $\mu\text{g}/\text{m}^3$ for annual means or >50 $\mu\text{g}/\text{m}^3$ for EPDC (million)
Annual Arithmetic Mean	56.9%	16.5
Annual Geometric Mean	50.7%	14.7
24-Hour Expected Peak Day Concentration	98.9%	28.6

24
 25 * This represents the percent of the 1990 population used in the exposure analysis. The total
 26 population used in the analysis varied by metric, since the number of monitors with data
 27 meeting specified validity criteria was different for each metric (Appendices VI-G1 to VI-G3).

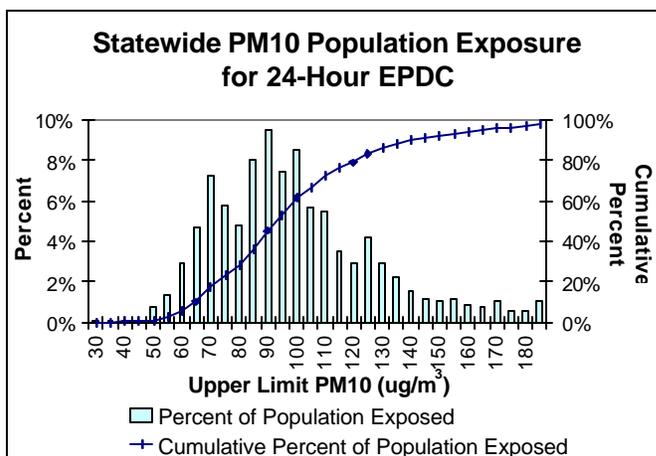
- 1 The charts below show the distribution of the statewide population exposed to different PM10
- 2 concentration ranges.



3



4



5

- 6 The AAM statistics show that 57% of the statewide population is exposed to PM10
- 7 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
- 8 statistics indicate 47% of the people in the State are exposed to annual PM10 levels between

1 15 and 30 $\mu\text{g}/\text{m}^3$. Based on the EPDCs, essentially the whole State has PM10 levels
 2 exceeding the 24-hour State PM10 standard.

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

13 The 24-hour EPDC analysis illustrates in most air basins, 80% to 100% of the population is
 14 exposed to PM10 levels above 50 $\mu\text{g}/\text{m}^3$. Lake County is an exception, with its entire
 15 population exposed to concentrations below the current standard.

16 The following table summarizes the results of the PM2.5 statewide assessment.

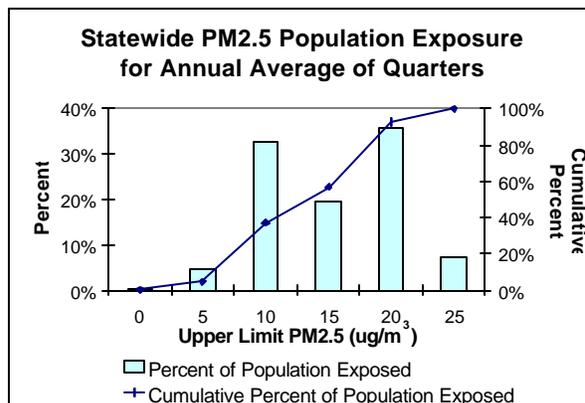
17

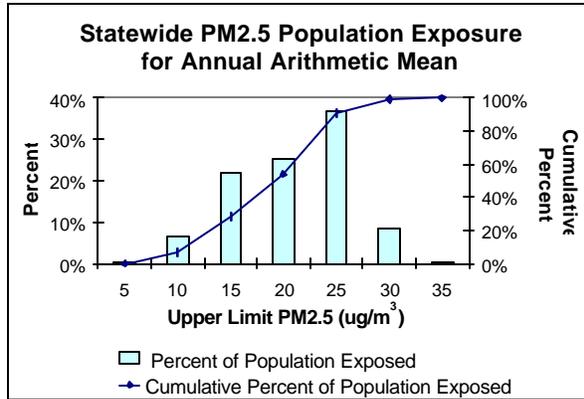
Form of Standard for PM2.5	Percent Population* Exposed to 15 $\mu\text{g}/\text{m}^3$ for annual or 65 $\mu\text{g}/\text{m}^3$ for EPDC	1990 Population* Exposed to 15 $\mu\text{g}/\text{m}^3$ for annual or 65 $\mu\text{g}/\text{m}^3$ for EPDC (million)
Annual Arithmetic Mean	71.2 %	13.5
Annual Average of Quarters	62.8 %	11.7
24-Hour Expected Peak Day Concentration	80.1 %	15.1

18

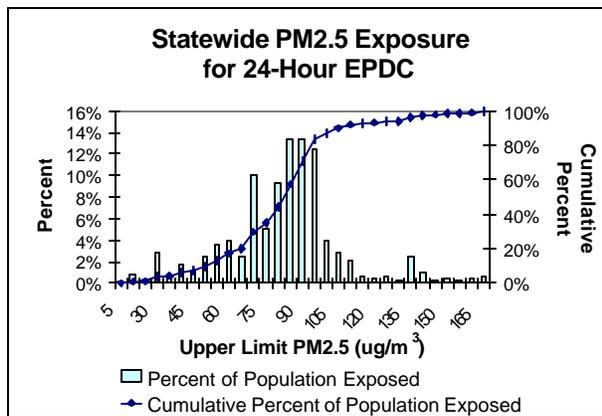
19 * This represents the percent of the 1990 population used in the exposure analysis. The total
 20 population used in the analysis varied by metric, since the number of monitors with data
 21 meeting specified validity criteria was different for each metric (Appendices 6-H1 to 6-H3).

22 The charts below show the distribution of the statewide population exposed to different PM2.5
 23 concentration ranges.





1



2

3 The AAM statistics show that 71% of the statewide population is exposed to PM2.5
 4 concentrations above 15 µg/m³, while 22% is exposed to concentrations between 10 µg/m³
 5 and 15µg/m³. The AOQ statistics indicate 63% of the people in California are exposed to
 6 concentrations above 15 µg/m³ and 33% to concentrations between 10 µg/m³ and 15 µg/m³.
 7 Based on the EPDCs, 80% of the State's population is exposed to 24-hour PM2.5 levels
 8 above the federal PM2.5 standard.

9 The air basin summary statistics in Appendices 6-F1 to 6-F3 show that for the two forms of
 10 the PM2.5 annual average the percent of the population exposed to 15 µg/m³ and above is
 11 98% in the South Coast and 89% in the San Joaquin Valley. About 60% of the San Diego and
 12 28% of the Sacramento Valley population is exposed to annual average PM2.5
 13 concentrations above the level of the federal PM2.5 standard, while 10% to 20% of the people
 14 in the Salton Sea are exposed to concentrations above this level. Based on the AAM, close to
 15 55% of the San Francisco Bay Area population and 36% of the Mountain Counties population
 16 is exposed to concentrations above 15 µg/m³, while based on the AOQ only 9% of the people
 17 in the in the San Francisco Bay Area and no one in the Mountain Counties is.

18 The 24-hour EPDC analysis shows that the percent of the population exposed to peak PM2.5
 19 concentrations of greater than 65 µg/m³, is: over 90% in the South Coast, San Francisco Bay
 20 Area, San Joaquin Valley, and Sacramento Valley; over 17% in the Great Basin Valleys and
 21 Mountain Counties; and 7% in the Salton Sea.

1 From the data presented in Appendices 6-E1 to 6-E3 and 6-F1 to 6-F3, we also estimated
 2 PM10 and PM2.5 annual and 24-hour population weighted concentrations for each air basin.
 3 We assumed that the population in a specific concentration bin is exposed to the midpoint
 4 concentration in that bin. The table below lists the results of the analysis for PM10.

5

Population Weighted Metrics for PM10			
Air Basin	Annual Arithmetic Mean	Annual Geometric Mean	Expected Peak Day Concentration
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

6

7 The annual statistics show that in three air basins - South Coast, San Joaquin Valley, and
 8 Salton Sea - the basinwide population weighted average PM10 concentrations are above 30
 9 $\mu\text{g}/\text{m}^3$. The Salton Sea has the highest PM10 annual averages in the State (AAM of 70 $\mu\text{g}/\text{m}^3$
 10 and AGM of 58 $\mu\text{g}/\text{m}^3$). The South Coast (with an average AAM of 41 $\mu\text{g}/\text{m}^3$ and AGM of 37
 11 $\mu\text{g}/\text{m}^3$) and the San Joaquin Valley (with AAM of 39.5 $\mu\text{g}/\text{m}^3$ and AGM is 34.3 $\mu\text{g}/\text{m}^3$) follow.

12 The results of the 24-hour PM10 concentration analysis show that, with the exception of Lake
 13 County, the rest of the State has basinwide population weighted average EPDCs over 50
 14 $\mu\text{g}/\text{m}^3$. The desert areas - Great Basin Valleys and Salton Sea - have the highest EPDCs,
 15 around 300 $\mu\text{g}/\text{m}^3$. The South Coast and San Joaquin Air Basins follow, with EPDCs above
 16 100 $\mu\text{g}/\text{m}^3$. The rest of the air basins have EPDCs between 50 and 100 $\mu\text{g}/\text{m}^3$.

1 The table below lists the population weighted statistics calculated for PM2.5.

2

Population Weighted Metrics for PM2.5			
Air Basin	Annual Arithmetic Mean	Average of Quarters	Expected Peak Day Concentration
Great Basin Valleys	8.5	7.5	18
Lake County	2.5	2.5	17.5
Lake Tahoe	7.5	7.5	27.5
Mountain Counties	16.6	9.8	44.9
Mojave Desert	10	12.3	27.6
North Coast	7.5	7.5	35.6
North Central Coast	7.5	7.5	23.8
Northeast Plateau	NA	NA	NA
South Coast	22.2	22.3	87
South Central Coast	11.8	11.8	43.1
San Diego	15.6	15.7	54.3
San Francisco Bay Area	15.8	12.9	71
San Joaquin Valley	22.3	20.3	132
Salton Sea	13.1	13.6	45.3
Sacramento Valley	12.3	12.8	93.1
Statewide	18.3	18.2	81.4

3

4 PM2.5 annual statistics show that while five air basins - the Mountain Counties, South Coast,
 5 San Diego, San Francisco, and San Joaquin Valley - have basinwide population weighted
 6 average AAMs above 15 $\mu\text{g}/\text{m}^3$, only the last three air basins exhibit AOQs higher than the
 7 level of the federal PM2.5 standard.

8 Four air basins have population weighted average 24-hour EPDCs over 65 $\mu\text{g}/\text{m}^3$. The San
 9 Joaquin Valley has the highest EPDC (132 $\mu\text{g}/\text{m}^3$) of about twice the level of the standard,
 10 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
 11 Bay Area (71 $\mu\text{g}/\text{m}^3$).

12 **6.5 Characterization of Personal and Indoor Exposures**

13 **6.5.1 Personal PM Exposures**

14 Peoples' actual exposures to PM, or their "personal exposures," have been shown in
 15 numerous studies to differ notably from outdoor PM concentrations measured at ambient
 16 monitoring stations, and often are much higher than outdoor PM levels. This is primarily due
 17 to people's proximity to sources of PM throughout the day, especially indoor sources such as

1 cigarette smoke, cooking emissions, and re-suspension of house dust. (Personal PM
2 exposures are estimated by measuring pollutant concentrations in a person's breathing zone,
3 the area near their nose and mouth, using portable instruments worn by the individuals.)
4 Because people often spend time close to indoor PM sources, such as when they cook,
5 personal concentrations also are often higher than indoor PM concentrations measured at
6 fixed locations in the indoor environment. The results of recent studies of personal and indoor
7 concentrations of PM most relevant to understanding Californians' exposures are presented
8 in Table 6-E-1 and discussed below.

9 The first major study to demonstrate personal PM concentrations above indoor and outdoor
10 concentrations was the Particle Total Exposure Assessment Methodology (PTEAM) Study,
11 conducted in 1990 in Riverside, California. Investigators measured PM₁₀ and PM_{2.5} for 12-
12 hour daytime and nighttime periods in 178 homes during September to November. They
13 found 12-hour daytime personal PM₁₀ concentrations to be about 50% higher than
14 simultaneously measured daytime residential indoor or outdoor concentrations. Daytime
15 personal concentrations averaged 150 $\mu\text{g}/\text{m}^3$, while indoor and outdoor concentrations both
16 averaged about 95 $\mu\text{g}/\text{m}^3$ (Clayton et al. 1993, Ozkaynak et al. 1996a,b). Most importantly,
17 12-hour daytime personal PM₁₀ concentrations exceeded the California 24-hour ambient air
18 quality standard of 50 $\mu\text{g}/\text{m}^3$ for about 90 percent of the monitoring days and exceeded the
19 federal PM₁₀ standard of 150 $\mu\text{g}/\text{m}^3$ for 25 percent of the monitoring days. During nighttime,
20 personal PM₁₀ concentrations decreased and were similar to concurrent indoor and outdoor
21 concentrations (roughly 80 $\mu\text{g}/\text{m}^3$), reflecting the importance of the proximity of people to PM
22 sources during normal activities in determining personal exposure concentrations.

23 The PTEAM study used a probability sampling design, in which study subjects were carefully
24 chosen to ensure that the sampled population represented the city of Riverside as a whole.
25 These types of studies are large and expensive, and therefore not frequently performed.
26 Three other PM probability studies (Pellizzari et al. 1999; Oglesby et al. 2000; Santos-Burgoa
27 et al. 1998) have been performed since PTEAM; in two, investigators found higher personal
28 concentrations than corresponding outdoor concentrations, while outdoor concentrations were
29 not measured in the third study. In Toronto, the investigators found average personal and
30 outdoor PM_{2.5} concentrations of 28 $\mu\text{g}/\text{m}^3$ and 15 $\mu\text{g}/\text{m}^3$, respectively (Pellizzari et al. 1999).
31 For PM₁₀, average personal and outdoor concentrations were 68 $\mu\text{g}/\text{m}^3$ and 24 $\mu\text{g}/\text{m}^3$,
32 respectively. As part of the EXPOLIS (Air Pollution Exposure Distribution within Adult Urban
33 Populations in Europe) Study, in Basel, Switzerland, average personal and residential outdoor
34 PM_{2.5} concentrations were measured at 24 $\mu\text{g}/\text{m}^3$ and 19 $\mu\text{g}/\text{m}^3$, respectively; for
35 nonsmokers, average personal and residential outdoor concentrations were both 18 $\mu\text{g}/\text{m}^3$,
36 showing the large impact smoking can have on personal PM_{2.5} exposures (Oglesby et al.
37 2000). In Mexico City, personal PM₁₀ concentrations were higher, averaging 97 $\mu\text{g}/\text{m}^3$,
38 although no outdoor measurements were available for comparison (Santos-Burgoa et al.
39 1998).

40 Many smaller-scale particle exposure studies that have not used probability sampling design
41 have been performed, in both the general population and in populations sensitive to PM, such
42 as the elderly or patients with chronic obstructive pulmonary disease (COPD). Recent U.S.
43 studies of personal PM₁₀ and PM_{2.5} in which all or most of the study subjects were elderly
44 and/or COPD patients include Evans et al. 2000, Linn et al. 1999, Rojas-Bracho et al. 2000,
45 Sarnat et al. 2000, and Williams et al. 2000a,b,c. Like PTEAM, these smaller studies have
46 also shown that personal exposures can be higher than simultaneously measured residential
47 indoor and outdoor concentrations. However, they have generally shown smaller differences
48 than those found in the PTEAM study, and stronger correlations with ambient levels. This
49 appears to be in part due to the reduced activity levels of many of the study subjects who

1 have pre-existing lung disease (for example, fewer cleaning and cooking activities). These
2 studies have also generally found smaller differences between personal and ambient levels
3 for PM_{2.5} as compared to PM₁₀, and that correlations between ambient and personal levels
4 are generally higher for PM_{2.5} than for PM₁₀. Notable exceptions exist, however, such as the
5 results from two recent studies of elderly subjects in Fresno, CA and Baltimore, MD (Evans et
6 al. 2000, Williams et al. 2000a,b,c) where personal levels were lower than ambient levels, on
7 average. Also, another study of elderly subjects in Baltimore found a lower correlation
8 between personal and ambient levels of PM_{2.5} than for PM₁₀ (Sarnat et al. 2000). Again,
9 these results are likely explained by the reduced activity level of the study participants, as well
10 as seasonal differences in ambient levels and ventilation practices, local variability, and the
11 presence or use of fewer indoor PM sources.

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

18 In summary, in spite of the many studies cited, the ability to accurately estimate PM exposure
19 concentrations for general populations, especially PM_{2.5} exposures, is still limited by the
20 small number of probability design studies and the limited seasonal coverage of the
21 probability studies that have been conducted (which did not include the important seasonal
22 variations in air exchange rates; U.S. EPA, 2001). The PTEAM study remains the only major
23 probability sampling PM exposure study conducted in the U.S. and still provides the most
24 relevant California PM₁₀ exposure data, although it essentially covered just one season in
25 one city. Representative PM_{2.5} data for all Californians are lacking.

26 **6.5.2 Sources of Indoor PM**

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

32 Outdoor air infiltration and indoor combustion sources such as smoking and cooking are
33 typically the greatest sources of indoor PM (Wallace 1996; Ozkaynak et al. 1996a,b; Brauer et
34 al. 2000; Abt et al. 2000). For example, through source apportionment the PTEAM
35 investigators estimated that, on average, about 76% of the PM_{2.5} mass and 66% of the
36 PM₁₀ mass originated outdoors; 5% of PM_{2.5} and 4% of PM₁₀ was attributed to tobacco
37 smoking; 4% of PM_{2.5} and 5% of PM₁₀ was attributed to cooking; and 14% of PM_{2.5} and
38 26% of PM₁₀ were from unexplained sources (Ozkaynak et al. 1996a). Thus, reductions in
39 outdoor PM levels can have a major effect on the indoor concentrations. Abt et al. (2000)
40 found that the relative contribution of outdoor PM to indoor levels varied by particle size, with
41 outdoor air generally contributing a majority of the smaller particles (less than 0.5 microns)
42 measured indoors, while indoor sources contributed more to the larger (2-10 microns) size
43 fraction.

44 In PTEAM, in homes with smokers, it was estimated that 30% of the PM_{2.5} mass and 24% of
45 the PM₁₀ mass came from smoking, while in homes in which cooking occurred during the
46 monitoring period, 25% of the PM_{2.5} and PM₁₀ was estimated to come from the cooking
47 activity (Ozkaynak 1996b). These results are consistent with those found in many previous
48 indoor studies that have examined the impact of cigarette smoking on indoor PM levels, and

1 led to subsequent studies of indoor cooking emissions that have confirmed the high impact
2 that some cooking methods can have on indoor and personal PM levels (Rogge et al. 1997;
3 Abt et al. 2000; Wallace 2000; Brauer et al. 2000; Long et al. 2001). In a study of a variety of
4 cooking activities using gas and electric stoves in a test home in northern California, kitchen
5 PM₁₀ levels ranged to more than 1400 µg/m³ during frying, broiling, and baking activities.
6 During use of the self-cleaning feature, oven cleaning resulted in kitchen PM₁₀ levels up to
7 3661 µg/m³, and indoor PM_{2.5} ranged to 2032 µg/m³, while concurrent outdoor levels ranged
8 only to 20 µg/m³. The burning of wood, incense, and mosquito coils can also be important
9 combustion sources of residential indoor PM, especially in the 2.5 µm size range and below
10 (Brauer et al. 2000; Lofroth et al. 1991).

11 Physical generation or re-suspension of particles also can be an important PM source. Indoor
12 surfaces such as carpets and draperies can attract and re-emit particles (Thatcher and
13 Layton, 1995, Kamens et al. 1991). Particle concentrations from carpets can be high even in
14 homes where good cleaning practices are used, and the particles can become re-entrained in
15 the indoor air when people walk or play on the carpeted surface (Wallace 2000; Roberts et al
16 1992; Abt et al. 2000, Vette et al. 2001). Track-in of particles on shoes and by children and
17 pets has also been shown to contribute significantly to indoor particle concentrations in
18 residences (Roberts et al. 1992, Thatcher and Layton 1995). House dust particles have been
19 found to include vapors, metals, and semi-volatile chemicals of intermediate vapor pressures,
20 such as pesticides and polycyclic aromatic hydrocarbons (Rothenberg et al. 1989; Roberts et
21 al. 1992; Lewis et al. 1999; U.S. EPA, 1999) that have their own toxic properties. These
22 contaminants are often adsorbed onto the surfaces of house dust particles, and are available
23 for re-emission to the air and subsequent inhalation, and for dermal absorption and/or
24 ingestion by children through floor contact and hand-to-mouth behavior (Rothenberg et al.,
25 1989; Lewis et al, 1994). For toxics such as lead, floor dust levels can be a major determinant
26 of exposure.

27 Biological contaminants such as fungi, bacteria, house dust mites, and pollen also can
28 contribute to indoor particle concentrations, especially in buildings with moisture problems
29 from flooding or roof leaks that have not been properly repaired. Many biological
30 contaminants can trigger asthma attacks in sensitive individuals and cause other adverse
31 health effects such as allergy symptoms, sinus and respiratory infections, headaches and
32 irritant effects, many of which would not necessarily occur from exposure to equal mass
33 concentrations of less biologically active types of particles (NAS 1993; NAS 2000).

34 **6.5.3 Relation of Personal PM Concentrations with Ambient Concentrations**

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

40 The complex relationships between personal exposures and outdoor concentrations are
41 reflected in the variable correlations found between personal PM₁₀ concentrations and
42 ambient concentrations. Correlations (r^2) of personal PM₁₀ concentrations with ambient
43 concentrations in studies utilizing a cross-sectional study design (each individual monitored
44 for one day), including PTEAM, have been low, ranging from 0 to about 0.3 (Dockery and
45 Spengler 1981, Sexton et al. 1984a,b, Spengler et al. 1985, Liroy et al. 1990, Clayton et al.
46 1993, Ozkaynak et al. 1996b). In these studies, investigators have generally collected
47 personal exposure samples over durations of 12 or 24 hours.

1 However, for longitudinal studies with seven or more repeated measurements, correlations for
2 a given subject between personal and outdoor concentrations are greater than for a cross
3 section of subjects with a single measurement period (Wallace 1996, Wallace 2000).
4 Additionally, recent studies for PM_{2.5} have found stronger correlations for personal PM_{2.5}
5 concentrations with outdoor particle concentrations than were found for PM₁₀ in earlier PM₁₀
6 studies. In recent studies, the median longitudinal correlation coefficient (r^2) between personal
7 and outdoor PM_{2.5} concentrations for each individual over multiple days was 0.61 in Boston
8 (Rohas-Bracho et al. 2000), and 0.25 and 0.76 for winter and summer, respectively, in
9 Baltimore (Sarnat et al. 2000). Average correlation coefficients (r^2) between personal and
10 outdoor PM_{2.5} concentrations were 0.41 and 0.84 for two studies in Fresno (Evans et al.
11 2000), 0.26 in Los Angeles (Linn et al. 1999), and 0.89 in Baltimore (Williams et al. 2000a,b).
12 However, because some of these studies used elderly and/or ill subjects, the correlations may
13 be greater than would be seen for healthy individuals due to the participants' reduced rates of
14 activities relative to the general population, (see Table 6-E-1 for a description of the
15 demographic group observed in each study), the absence of major indoor PM sources, and
16 seasonal variation.

17 Strong correlations between personal and outdoor concentrations have also been observed in
18 two European studies. In their longitudinal study of 13 children in the Netherlands, Janssen et
19 al. (1999) found longitudinal correlation coefficients between personal and outdoor PM₁₀ of
20 0.75 for all children and 0.84 for children not exposed to environmental tobacco smoke.
21 Correlation coefficients for PM_{2.5} were 0.86 for all children and 0.92 when environmental
22 tobacco smoke exposures were excluded. Personal concentrations averaged 28 $\mu\text{g}/\text{m}^3$, while
23 outdoor concentrations measured 17 $\mu\text{g}/\text{m}^3$. In a study of elderly subjects with cardiovascular
24 disease, the median Pearson's correlation for personal and outdoor PM_{2.5} was 0.79 in
25 Amsterdam and 0.76 in Helsinki (Janssen et al 2000).

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

42 **6.5.4 Contributions of Outdoor Sources of PM to Indoor Concentrations**

43 Outdoor particles enter buildings and other indoor environments and contribute to indoor
44 concentrations. The rate at which particles infiltrate into indoor environments and the ratio of
45 indoor to outdoor concentrations are dependent on many factors, especially the air exchange
46 rate of the building, the use of operable windows and doors, and the aerodynamic size of the
47 particles. Through source apportionment techniques, the PTEAM investigators estimated that,
48 of the total indoor mass of particles, outdoor particles contributed 76% of the PM_{2.5} mass and
49 66% of the PM₁₀ mass (Ozkaynak et al. 1996a,b). Correlations (r^2) between indoor PM_{2.5}

1 and nearby outdoor PM_{2.5} were estimated in studies of elderly subjects to be 0.93 (winter)
2 and 0.75 (spring) in Fresno (Evans et al. 2000), 0.19 in Los Angeles (Linn et al. 1999), and
3 0.96 in Baltimore (Williams et al. 2000a). In a study of four Boston homes with air exchange
4 rates below 1.0 hr⁻¹, Abt et al. (2000) estimated that only 20-43 percent of indoor particles
5 from 2-10 μm were from outdoors, while 63-92 percent of indoor PM from 0.02-0.3 μm were
6 from the outdoors.

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

$$10 \quad C_{in} = C_{out} [P a / (a + k)]$$

11 where P is the particle penetration factor, a is the air exchange rate of the building, k is the
12 particle deposition rate, C_{in} is the concentration of particles of outdoor origin in indoor air (i.e.,
13 those that have infiltrated indoors), and C_{out} is the concentration of particles in outdoor air.
14 Both P and k are dependent on particle size, making the solution to this equation dependent
15 on the particle size fraction considered.

16 Air exchange rate is the rate at which the air in an indoor air space is exchanged with the
17 same volume of outdoor air. In residential buildings, air exchange rates vary widely depending
18 upon building construction, opening of windows and doors, wind-and fan-induced pressure
19 changes, and seasonal changes. A number of investigators have reported air exchange rates
20 for homes in California (Ozkaynak et al. 1996a,b, Sheldon et al. 1993, BSG 1990, Wilson et
21 al. 1993, ADM 1990, Pellizzari et al. 1999, Wilson et al. 1986). Representative values for the
22 mean and standard deviation of air exchange rates in residential buildings in California have
23 been estimated at 1.2 and 1.0, respectively, with a log normal distribution (California Air
24 Resources Board, 1998), and have been measured as high as 5 or more air changes per
25 hour.

26 The penetration factor denotes, for a given volume of air that enters the building, the fraction
27 of the outdoor contaminant mass that moves through the building shell to the indoor space
28 without interception. For residential buildings, the main route of entry of outdoor air is through
29 open windows and doors and cracks in the building shell. Penetration factors are calculated
30 based on measurements of other parameters, mainly indoor and outdoor particle mass
31 concentrations, and can vary depending on the size fraction of PM being considered. The
32 values of the penetration factor for PM_{2.5} in residences have generally been estimated in the
33 range of 0.5 to 1.0 (Long et al. 2001; Suh et al. 1994, Koutrakis et al. 1992, Dockery and
34 Spengler 1981, Ozkaynak et al. 1996b), with California studies showing penetration factors
35 for PM_{2.5} and PM₁₀ close to 1.0 (Ozkaynak et al. 1996b; Thatcher and Layton 1995). More
36 recent field studies have found differences in penetration efficiencies among particles of
37 different sizes, with larger sizes showing reduced penetration (Abt et al. 2000; Vette et al.
38 2001; Long et al. 2001), especially under conditions of reduced air exchange. Laboratory
39 studies with simulated penetration and infiltration scenarios have generally supported and
40 complemented the field results, although they are limited to leakage measurements (Mosley
41 et al. 2001; Liu and Nazaroff 2001; Thornburg et al. 2001).

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

1 In the process of entering an indoor environment, particle concentrations may be removed by
2 various mechanisms, including deposition, transformation, decay, decomposition, and
3 adsorption. The cumulative effect of these processes is reflected in the particle deposition
4 (removal) rate. Typically, particles of larger aerodynamic diameter have higher deposition
5 rates (Frey 1989). Values for the particle deposition rate for California homes, estimated as
6 part of the PTEAM study, were 0.39 hr^{-1} for PM_{2.5} and 0.65 hr^{-1} for PM₁₀ (Ozkaynak et al.
7 1996b). Other investigators have found a wider range of deposition rates for particles of
8 different aerodynamic size, with the lowest deposition rates shown by particles in the 0.1 to
9 1.0 micron range (Thatcher and Layton 1995; Long et al. 2001; and others). Additionally, the
10 indoor furnishings and material surfaces can affect deposition, with rough “fleecy” materials
11 collecting particles more than smooth, slick surfaces.

12 **6.5.5 Indoor Concentrations in Public and Commercial Buildings**

13 Because people typically spend about 62% of their time in their residence (Jenkins et al.
14 1992), and children spend on average about 75% of their time at home, residences are the
15 most important locations for overall PM exposure for most people. However, significant time—
16 about 25% on average—is also spent in other buildings, such as at work and school (Jenkins
17 et al. 1992), so PM concentrations in these buildings are also important in estimating
18 exposure to PM.

19 PM concentrations in public and commercial buildings appear to often be lower than ambient
20 concentrations, but far fewer studies have been performed for public buildings than
21 residences. Reasons for lower indoor PM concentrations in public and commercial buildings
22 include the use of particle filters in larger, special use buildings; the fact that larger building
23 size (and use of inoperable windows) reduces the penetration efficiency for particle infiltration
24 from the outdoors; and because common residential indoor sources are typically absent.
25 However, as with residences, the presence of indoor sources in public and commercial
26 buildings can produce indoor concentrations that exceed concurrent ambient concentrations,
27 especially if smoking is allowed in the building. The largest public and commercial building
28 PM study to date was conducted in the Pacific Northwest for 38 commercial buildings (Turk et
29 al. 1987). Buildings where smoking was prohibited averaged $19 \mu\text{g}/\text{m}^3$ PM_{3.5} indoors, the
30 same as the outdoor level, while buildings where smoking was permitted averaged $70 \mu\text{g}/\text{m}^3$,
31 notably higher than the outdoor level. (PM_{3.5} was measured as respirable PM or “RSP”.)
32 Sheldon et al. (1988) measured PM in six buildings in the Eastern U.S., and found indoor PM
33 concentrations generally lower than outdoors where there was no smoking, but much higher
34 indoor concentrations where smoking was allowed (14 to $56 \mu\text{g}/\text{m}^3$ versus 13 to $17 \mu\text{g}/\text{m}^3$
35 outdoors).

36 Elevated PM concentrations can occur in other enclosed environments such as inside motor
37 vehicles, but few studies have been conducted to examine such exposures. The most
38 comprehensive study to date has been that of Rodes et al. (1998) conducted in Sacramento
39 and Los Angeles. Real-time fine particle count concentrations and black carbon
40 concentrations inside vehicles increased up to ten times the average roadway concentrations
41 when following certain diesel vehicles. However, average PM mass concentrations inside the
42 vehicle were similar to outdoor concentrations measured at the nearest ambient monitor,
43 while roadway PM concentrations were somewhat higher. Average in-vehicle PM₁₀
44 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
45 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
46 PM concentrations averaged 60 to 80% of those concentrations measured just outside the
47 vehicle, which reflected the elevated roadway concentrations. In summary, it appeared the
48 impact of traffic on PM exposures inside vehicles was small with regard to total mass,
49 although significant differences in traffic PM chemical composition and PM size distribution

1 are probably present compared to ambient PM. Using carpool lanes appeared to reduce in-
2 vehicle PM concentrations significantly, although carpool lanes were used in only two of the
3 29 two-hour runs.

4 **6.5.6 PM Exposures in Sensitive Subgroups**

5 Individuals with pre-existing respiratory disease, such as COPD and asthma, and pre-existing
6 cardiovascular disease can be more susceptible to adverse effects from exposure to
7 particulate pollutants. Until recently, personal exposures of such groups to particles had not
8 been measured. Only a few small, recent studies have been conducted to examine the PM_{2.5}
9 exposures of such groups.

10 Rojas-Bracho et al. (2000) and Linn et al. (1999) have reported on PM₁₀ and PM_{2.5}
11 exposures for individuals with COPD. Rojas-Bracho et al. found that mean personal PM₁₀
12 and PM_{2.5} concentrations were 67% and 52% above outdoor PM₁₀ and PM_{2.5}
13 concentrations, respectively, for 18 COPD patients in Boston. (PM₁₀ and PM_{2.5}
14 concentrations were 22 and 14 µg/m³ outdoors, 32 and 18 µg/m³ indoors, and 37 and 22
15 µg/m³ personal, respectively.) Personal-to-ambient concentration median longitudinal
16 correlations were moderate with better correlation observed for PM_{2.5} (R=0.61) than for
17 PM₁₀ (R=0.35) or for PM_{2.5-10} (R=0.35). The authors attribute this to the higher deposition
18 rate of PM_{2.5-10} than PM_{2.5}. The authors also found personal-to-outdoor concentration
19 ratios to be high (i.e., greater than 3) when air exchange rates were low (less than one
20 exchange per hour). Overall, this study found similar results to those of other studies for
21 healthy adults except PM concentrations were lower.

22 Linn et al. studied thirty COPD patients in Los Angeles and found that pooled personal-to-
23 ambient concentration correlations were quite low ($R^2 < 0.1$). Unlike other studies, this study
24 did not find personal concentrations to be significantly higher than indoors or outdoors (PM₁₀
25 and PM_{2.5} mean concentrations were 40 and 25 µg/m³ for outdoors, 33 and 24 µg/m³ for
26 indoors, and 35 and 24 µg/m³ for personal). Of the health measures studied (blood oxygen
27 saturation, blood pressure, lung function), only blood pressure showed any consistent
28 unfavorable longitudinal relationship with PM, and this was slightly stronger for the PM
29 measured at the ambient monitoring station than indoor or personal PM measurements.
30 Because no consistent relationship was found between personal PM concentrations and any
31 of the health effects, the authors concluded that the modest health effects associated with PM
32 were related to outdoor PM, although they caution that the study's small number of subjects
33 and short duration were major limitations.

34 **6.5.7 Summary**

35 Outdoor PM is usually the major contributor to indoor and personal PM exposure, especially
36 when few indoor sources are present. However, the relationships between indoor and outdoor
37 concentrations and personal and outdoor PM concentrations are complex, and correlations
38 are often low. People's proximity to sources of PM, such as indoor cooking and cigarette
39 smoke, typically results in higher personal exposure levels than indoor and outdoor levels
40 measured concurrently by stationary monitors. Indoor sources of PM such as cooking,
41 tobacco smoke, and cleaning activities such as vacuuming often contribute to elevated indoor
42 concentrations as well. Investigators have generally found somewhat greater correlations
43 between personal and outdoor PM concentrations for single individuals studied over several
44 days as compared to single day analyses for more individuals, and for elderly individuals with
45 more limited activities and few indoor sources. Correlations also tend to be greater for PM_{2.5}
46 than for PM₁₀, in part because of increased penetration and reduced deposition rates indoors
47 for smaller particles. However, there remains much uncertainty in the current understanding
48 of these relationships.

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1 Table 6-E-1. Recent Personal-Ambient Air Particulate Matter Exposure Studies

Reference	Location and population	No. of subjects	Study period	Age range	PM Size ^a	N ^b	Arithmetic mean concentration (SD); ($\mu\text{g}/\text{m}^3$)			Personal-Ambient correlation ^d	
							Personal	Indoor	Ambient	Value	Type
Probability-based studies											
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	50	01/97-12/97	25-55	PM2.5	44	24 (17)	NA ^f	19 (12)	0.07	P
	Subset with no ETS exposure	20	01/97-12/97	25-55	PM2.5	20	18 (13)	NA ^f	18 (7)	0.21	P
Not probability-based, California studies											
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
Not probability-based, recent United States studies											
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., 2000 ^{a,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: tvpes are Pooled (P) or median Longitudinal (L).

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

f-NA indicates information was not available

g-Spearman rank correlations