

2. BASIS FOR FIELD STUDY DESIGN

This section describes the central California study area, the magnitudes and locations of PM_{2.5} and PM₁₀ concentrations and their chemical components, emissions sources, meteorology that affects PM levels, and applicable transformation chemistry of the study area.

2.1 CRPAQS Study Area

Excessive PM concentrations result from a combination of emissions, transport, transformation, and accumulation of pollutants. Both primary and secondary particles cause high PM_{2.5} levels in central California, while nearly all of the coarse fraction derives from primary fugitive dust emissions. Primary particles are directly emitted by sources while secondary particles form from directly emitted gases by transformation in the atmosphere. Primary particles (mostly carbon and geological material), sulfur dioxide, nitrogen dioxide, ammonia, and organic gas emissions must be coupled with transport and transformation to understand the causes of elevated PM_{2.5}.

Central California is a complex region for air pollution, owing to its proximity to the Pacific Ocean, its diversity of climates, and its complex terrain. Figure 2.1-1 shows the overall study domain with major landmarks, mountains and passes. Figure 2.1-2 shows major political boundaries, including cities, counties, air quality planning districts, roads, Class 1 (pristine) areas, and military facilities. The Bay Area, the San Joaquin Valley (SJV), and the Mojave Desert are the three major regions in which particulate air pollution may be excessive. The central coast region has low PM₁₀ concentrations relative to previous NAAQS. The Sacramento area has experienced elevated PM concentrations during fall and winter similar to the situation in the SJV. The Bay Area and SJV, and possibly Sacramento, have the potential to exceed the annual PM_{2.5} standard. The Mojave Desert inherits poor visibility during summer and fall that is caused by PM_{2.5} generated in the other parts of central and southern California.

The Bay Area Air Quality Management District (BAAQMD) encompasses an area of more than 14,000 km² of which 1,450 km² are the San Francisco and San Pablo Bays, 300 km² are the Sacramento and San Joaquin river deltas, 9,750 km² are mountainous or rural, and 2,500 km² are urbanized. The Bay Area is bounded on the west by the Pacific Ocean, on the east by the Mt. Hamilton and Mt. Diablo ranges, on the south by the Santa Cruz Mountains, and on the north by the northern reaches of the Sonoma and Napa Valleys. The San Joaquin Valley lies to the east of the BAAQMD, and major airflows between the two air basins occur at the Sacramento delta, the Carquinez Strait, and Altamont Pass (elevation 304 m). The coastal mountains have nominal elevations of 500 m, although major peaks are much higher (Mt. Diablo, 1,173 m; Mt. Tamalpais, 783 m; Mt. Hamilton, 1,328 m). Bays and inland valleys punctuate the coastal mountains, including San Pablo Bay, San Francisco Bay, San Ramon Valley, Napa Valley, Sonoma Valley, and Livermore Valley.. Many of these valleys and the shorelines of the bays are densely populated. The Santa Clara, Bear, and Salinas Valleys lie to the south of the BAAQMD, containing lower population densities and larger amounts of agriculture.

The BAAQMD manages air quality in Alameda, Contra Costa, Marin, San Francisco, San Mateo, Santa Clara, and Napa counties, in the southern part of Sonoma county, and in the southwestern portion of Solano county. More than six million people, approximately 20% of California's population, reside within this jurisdiction. The Bay Area contains some of California's most densely-populated incorporated cities, including San Francisco (pop. ~724,000), San Jose (pop. ~782,000), Fremont (pop. ~173,000), Oakland (pop. ~372,000), and Berkeley (pop. ~103,000). In total, over 100 incorporated cities lie within the jurisdiction of the BAAQMD.

Major industries and areas of employment in the Bay Area include tourism, government/defense, electronics manufacturing, software development, agriculture (vineyards, orchards, livestock), petroleum-refining, power generation, and steel manufacturing. BAAQMD residences are often distant from employment locations, and more than 1,800 km of major controlled-access highways and bridges accommodate approximately 148 million vehicle miles traveled on a typical weekday. The Bay Area includes a diverse mixture of income levels, ethnic heritages, and lifestyles.

The San Joaquin Valley, administered by the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD), is much larger than the Bay Area but with a lower population. It encompasses nearly 64,000 km² and contains a population in excess of three million people, with a much lower density than that of the Bay Area. The majority of this population is centered in the large urban areas of Bakersfield (pop. ~175,000), Fresno (pop. ~355,000), Modesto (pop. ~165,000), and Stockton (pop. ~211,000). There are nearly 100 smaller communities in the region and many isolated residences surrounded by farmland.

The SJV is bordered on the west by the coastal mountain range, rising to 1,530 meters (m) above sea level (ASL), and on the east by the Sierra Nevada range with peaks exceeding 4,300 m ASL. These ranges converge at the Tehachapi Mountains in the southernmost end of the valley with mountain passes to the Los Angeles basin (Tejon Pass, 1,256 m ASL) and to the Mojave Desert (Tehachapi Pass, 1,225 m ASL, Walker Pass, 1,609 m ASL). Agriculture of all types is the major industry in the SJV. Oil and gas production, refining, waste incineration, electrical co-generation, transportation, commerce, local government and light manufacturing constitute the remainder of SJV the economy. Cotton, alfalfa, corn, safflower, grapes, and tomatoes are the major crops. Cattle feedlots, dairies, chickens, and turkeys constitute most of the animal husbandry in the region.

The Mojave Desert is located in southeastern California, north of the Los Angeles metropolitan area and west of California's San Joaquin Valley. It is bordered on the west by the Sierra Nevadas and Tehachapi Mountains and on the south by the San Gabriel and San Bernardino Mountains. The long and narrow Owens, Panamint, and Death Valleys lie to the north. The Mojave Desert is punctuated by a series of mountains and playas to the east, and reaches as far as Las Vegas, NV. The typical elevation of the desert is 500 to 1,000 m ASL.

The Mojave Desert occupies more than 60,000 km² and contains nearly all of San Bernardino county (excluding the city of San Bernardino), the portion of Kern county west of the Tehachapi Mountains, and the portion of Los Angeles county north of the San Gabriel Mountains. It is sparsely populated compared to the neighboring air basins, with

approximately 500,000 people. Most of these people live in suburbs of Los Angeles, including Apple Valley (pop. 48,000), Hesperia (pop. 50,000), Lancaster (pop. 97,000), Palmdale (pop. 69,000), and Victorville (pop. 40,000). Other cities of significance in the Mojave Desert have smaller populations, including Barstow (pop. 21,000), California City (pop. 6,000), Mojave (pop. 3,800), Ridgecrest (pop. 28,000), Rosamond (pop. 7,400), and Tehachapi (pop. 5,800). Several smaller communities are interspersed among these population centers.

The Mojave Desert's aridity, large flat valleys (many of which contain dry lake beds), low population densities, and isolation made it a good location for military facilities. The U.S. Department of Defense (DOD) operates Edwards and George Air Force Bases, the China Lake Naval Weapons Center, and the Fort Irwin Army National Training Center in the Mojave Desert. Nearly the entire area of the Mojave Desert and a lower portion of the Sierra Nevadas are designated as the R2508 airspace. Excluding Los Angeles commuters, the majority of employment is associated with military and aerospace activities. Recreation and leisure have been growing industries in recent years. A major mineral mining and processing facility is located in Trona, about 70 km east of Ridgecrest and several large cement facilities are located in the Barstow vicinity.

Figure 2.1-3 shows the major population centers in central California, while Table 2.1-1 summarizes populations for Metropolitan Statistical Areas (MSA) that are used to determine community exposure to PM_{2.5} (Watson et al., 1997). The San Francisco, San Jose, Stockton, Modesto, Fresno, and Bakersfield MSAs are required to have community-representative (CORE) monitoring sites that will assess compliance with PM_{2.5} standards.

Figure 2.1-4 shows land use within central California. There are substantial tracts of grazed and ungrazed forest and woodland along the Pacific coast and in the Sierra Nevadas. Cropland with grazing and irrigated cropland dominate land use in the San Joaquin Valley, while desert scrubland is the dominant land use east of Tehachapi Pass. Tanner et al. (1992) show the various vegetation classes determined from satellite imagery. The central portion of the SJV is intensively farmed; the periphery consists of open pasture into the foothills of the coastal ranges and the Sierra Nevadas. As elevations increase above 400 m, the vegetation progresses through chaparral to deciduous and coniferous trees.

Central California contains the state's major transportation routes, as shown in Figure 2.1-5. The western and central lengths of the SJV are traversed by Interstate 5 and State Route 99. U.S. Highway 101 is aligned with the south central coast, then through the Salinas Valley, through the Bay Area and further north. These are the major arteries for both local and long-distance passenger and commercial traffic. Major east-west routes include I 80 and SR 120, 152, 198, 46, and 58. Many smaller arteries, both paved and unpaved, cross the SJV on its east side, although there are few of these small roads on the western side. The major cities contain a mixture of expressways, surface connectors, and residential streets. Farmland throughout the region contains private lanes for the passage of off-road implements and large trucks that transport agricultural products to market.

2.2 PM_{2.5} Concentrations and Trends

PM_{2.5} concentrations in central California vary from year to year and season to season. Figure 2.2-1 shows annual average and maximum PM_{2.5} concentrations from ARB's dichotomous sampler network from 1991 through 1996 at the San Jose, Fresno, and Bakersfield sites. The data from this network is based on an every sixth day sampling frequency. There were substantial differences in annual average concentrations from year to year and from site to site. The 1994-1996 three year average places the San Jose site in compliance with the annual PM_{2.5} standard while the Fresno and Bakersfield sites exceed it by ~4 µg/m³. The average of 98th percentiles (the third highest value corresponds to the 98th percentile for the sixth-day sampling represented by these plots) did not exceed 65 µg/m³, although several values at Fresno and Bakersfield were in excess of 65 µg/m³. These extreme values have been relatively rare occurrences, as the 75th percentile is substantially lower than the highest values. The high values tend to influence the average, as seen by the large difference between arithmetic average and median concentrations in Figure 2.2-1. Statistics from Sacramento, Stockton, Modesto and Madera in Figure 2.2-2 show lower PM_{2.5} concentrations in recent years with annual averages that are only marginally in excess of 15 µg/m³.

Figure 2.2-3 shows that the highest seasonal average concentrations have occurred during the winter. These averages were lower during the fall, but still substantially higher than those for spring and summer. Highest 24-hour PM_{2.5} concentrations have been measured during both winter and fall. Spring and summer experienced low averages of 10 µg/m³ or less and low maximum concentrations, except for rare exceptions. Bringing these community exposure sites into attainment must address sources contributing to the elevated concentrations during winter and fall, and intensive field campaigns are oriented toward these periods.

The typical PM_{2.5} chemical composition in central California varies by season (Chow et al., 1993; 1996, Watson et al., 1997), and like most other areas consists of the following major components:

- **Organic Carbon:** Particulate organic carbon consists of hundreds, possibly thousands, of separate compounds (Rogge et al., 1993a). The mass concentration of organic carbon can be accurately measured, as can carbonate carbon (Chow et al., 1994), but only about ten percent of the specific organic compounds that it contains have been measured. Vehicle exhaust (Rogge et al., 1993b), residential and agricultural burning (Rogge et al., 1998), meat cooking (Rogge et al., 1991), fuel combustion (Rogge et al., 1997), road dust (Rogge et al., 1993c), and particle formation from heavy hydrocarbon gases (Pandis et al., 1992) are the most probable sources of PM_{2.5} in central California.
- **Elemental Carbon:** Elemental carbon is black, often called "soot." Elemental carbon contains pure, graphitic carbon, but it also contains high molecular weight, dark-colored, nonvolatile organic materials such as tar, biological material (e.g., coffee), and coke. Elemental carbon usually accompanies organic carbon in combustion emissions, with diesel exhaust, cold start exhaust, and poorly

maintained vehicle exhaust (Watson et al., 1994, 1998) being the largest contributors.

- **Sulfate:** Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), ammonium bisulfate (NH_4HSO_4), and sulfuric acid (H_2SO_4) are the most common sulfate compounds in $\text{PM}_{2.5}$, although non-neutralized forms were found only in the oilfields of western Kern county during the early 1980s (Jacob et al., 1983). These compounds are water-soluble and reside almost exclusively in the $\text{PM}_{2.5}$ size fraction. Sodium sulfate (Na_2SO_4) has been found in coastal areas where sulfuric acid has been neutralized by sodium chloride (NaCl) in sea salt. Although gypsum (Ca_2SO_4) and some other geological compounds contain sulfate, these are not easily dissolved in water and are more abundant in the coarse fraction than in $\text{PM}_{2.5}$; they are usually classified in the geological fraction.
- **Nitrate:** Ammonium nitrate (NH_4NO_3) is the most abundant nitrate compound. It is a large fraction of $\text{PM}_{2.5}$ during winter and a moderate fraction during fall. Sodium nitrate (NaNO_3) is found in the $\text{PM}_{2.5}$ and coarse fractions near sea coasts and salt playas. Small quantities of sodium nitrate can be found in summertime PM as far as Bakersfield owing to consistent downvalley transport (Chow et al., 1996). It has been observed only in the coastal regions of central California during other times of the year.
- **Ammonium:** Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium nitrate (NH_4NO_3) are the most common compounds containing ammonium from reactions between sulfuric acid, nitric acid, and ammonia gases. While most of the sulfur dioxide and oxides of nitrogen originate from fuel combustion in stationary and mobile sources, most of the ammonia derives from living beings, especially animal husbandry practiced in dairies and feedlots.
- **Geological Material:** Suspended dust consists mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides. Owing to eons of runoff from surrounding mountains, the mineral composition of central California soils is fairly homogeneous, with the exception of dry lake beds that have accumulated salt deposits. Industrial processes such as steel-making, smelting, and mining have distinct geological compositions, but these are not widespread in central California. A number of cement production and distribution facilities use alcaeous, siliceous, argillaceous, and ferriferous minerals that are not natural to the region, with limestone (CaCO_3) being the most abundant (Greer et al., 1992). Suspended geological material resides mostly in the coarse particle fraction (Houck et al, 1989,1990), and typically constitutes ~50% of PM_{10} , while contributing only 5 to 15% of $\text{PM}_{2.5}$ (Watson et al., 1995).
- **Sodium Chloride:** Salt is found in suspended particles near sea coasts, open playas, and after de-icing materials are applied in the Sierra Nevadas. Bulk sea water contains $57\pm 7\%$ chloride, $32\pm 4\%$ sodium, $8\pm 1\%$ sulfate, $1.1\pm 1\%$ soluble potassium, and $1.2\pm 0.2\%$ calcium (Pytkowicz and Kester, 1971). As noted above, sodium chloride is often neutralized by nitric or sulfuric acid in urban air where it is encountered as sodium nitrate or sodium sulfate.

2.3 Emissions and Source Contributions

Central California emission source categories include: 1) major point sources (e.g., power stations, incinerators, cement plants, and steam generators); 2) area sources (e.g., fires, wind blown dust, petroleum extraction operations, cooking, and residential fuel combustion); 3) mobile sources (e.g., cars, trucks, off-road heavy equipment, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling operations and ammonia emissions from livestock); and 5) biogenic sources (e.g., oxides of nitrogen from biological activity in soils and hydrocarbon emissions from plants).

Table 2.3-1 summarizes primary particle and precursor gas emissions from these source categories in each of the five air basins in central California and shows that mobile and area sources dominate nearly every source category in central California. Within these air basins, the SJV air basin emits the greatest amount of PM_{10} , contributing 34% of the annual central California PM_{10} inventory. The Southeast Desert (SED) air basin emits nearly this amount, contributing 31% to the annual central California PM_{10} inventory. The North Central Coast (NCC) air basin emits 5% of the annual PM_{10} in these air basins and contributes the least.

Table 2.3-1 gives the impression that fugitive dust is the largest PM contributor, constituting more than 76% of primary emissions. This is inconsistent with PM_{10} chemical compositions and receptor model source contribution estimates that attribute only 50% of PM_{10} to fugitive dust and only 5% to 15% of $PM_{2.5}$ to this source. Month-by-month fugitive dust emissions show these to be a minimum during winter and early spring when surfaces are moist. Dust emissions increase during late spring when ground surfaces are dry but frontal passages create windy conditions with patchy precipitation. They are moderate during summer when surface winds are sluggish but many agricultural fields are covered in vegetation. Dust emissions are largest between September and November when major harvests and land preparation activities take place under dry conditions. These trends follow the seasonal cycles in the geological contributions to $PM_{2.5}$ and PM_{10} (Chow et al., 1992; 1996). So-called “uninventoried” sources, such as landfills, equestrian centers, and leaf blowers are not specifically included in this inventory. Bounding estimates (Fitz et al., 1995) on these emissions show them to be negligible compared to the major categories of road dust, construction, agricultural activities, and wind erosion.

Table 2.3-1 shows that primary PM_{10} emissions from industrial sources are significant, accounting for 9% of the total annual PM_{10} emissions. This is larger than the fraction estimated by source apportionment studies. Oil is extracted, stored, and transported in the southern SJV, with major fields west of I-5 between McKittrick and Maricopa and northeast of Bakersfield. The majority of this oil is heavy crude that requires the injection of steam to liquefy it. While a portion of this extracted oil was burned in prior years to produce this steam, no residual oil is combusted in the SJV today.

PM emissions from motor vehicle exhaust, wood burning, and agricultural burning contribute 9% to the annual PM_{10} inventory. The Sacramento Valley and the San Joaquin Valley air basins contribute over 83% of the total vegetative burning for the five air basins. Burning contributions have been detected at urban and non-urban receptors throughout the

year, but they are most abundant during the wintertime holiday season at urban sites. Saturation studies show that the wood smoke contributions are more spatially variable than the motor vehicle exhaust contributions, with much higher contributions in residential neighborhoods than in commercial districts just a few kilometers away.

The San Francisco Bay air basin contains the highest mobile source emissions for NO_x and PM_{10} , constituting 32% of central California PM_{10} emissions. Mobile sources account for 70% of the total NO_x emitted in the central California air basins. The inventory summarized in Table 2.3-1 probably underestimates vehicle exhaust PM_{10} emissions; it is not explicit with respect to off-cycle emissions from cold starts and poorly maintained vehicles. A recent vehicle test and source apportionment study in northern Colorado (Watson et al., 1998) found high emitting vehicles and cold starts to emit many times the mass per mile that are estimated from current vehicle emissions models such as PART5. These were clearly identifiable through detailed organic speciation profiles. Similarly, the inventory does not adequately estimate meat cooking emissions that have been quantified as contributors in Los Angeles (Rogge et al., 1993), in Colorado (Watson et al., 1998), and during IMS-95. Table 2.3-2 lists several of the organic compounds that have been detected in the effluent of different sources and in ambient air.

Reiss et al (1996) show that diesel internal combustion engines once used to pump irrigation water in central California have been replaced largely by propane and electric pumps. According to the 1995 emissions inventory aircraft emissions are negligible representing only 1% of the total annual PM_{10} budget.

Table 2.3-3 further breaks down emissions within the SJV by county. Fresno county ranks as the highest emitter of primary PM_{10} with 27% of the total for the entire SJV. Kern county ranks second with 21% of valleywide emissions. The proportion of PM_{10} geological source emissions in the SJV is higher than for most other regions, constituting 84% of the total. Fresno and Kern Counties together contribute half of the geological source emissions. Vegetative burning is estimated at only 7% of primary PM_{10} emissions in the SJV, with the largest amount originating in Tulare county.

Figure 2.3-1 shows the locations of point source NO_x emitters and their magnitudes. These point sources are most densely located in the Bay Area, with many small emitters scattered throughout the SJV. Table 2.3-4 lists the top 100 point source emitters in terms of oxides of nitrogen. More than one-third of central California's point-source NO_x and more than 80% of primary point source $\text{PM}_{2.5}$ and SO_2 derive from the top 100. Bay Area refineries are the largest sulfur emitters, while oxides of nitrogen emissions are dominated by power generating stations, refineries, and oilfield steam generators.

Industrial stack heights are typically lower than 30 m agl in the SJV, with the exceptions being Libbey Owens Ford glass in Lathrop, Certaineed mineral wool manufacturing in Chowchilla, Delano Energy Co. power station in Delano, Madera Glass Co. bottle works in Madera, Kern Oil and Refining in Bakersfield, Modesto Energy Limited power station in Westley, Mendota Biomass power generators in Mendota, J.R. Simplot chemicals in Helm and Lathrop, and Rio Bravo power generation in Fresno. The tallest stacks are associated with Bay Area refineries and power generation. Figure 2.3-2 shows the

locations of point source SO₂ emitters and their magnitudes. These are fairly small and scattered throughout the SJV, with the exception of oil-industry clusters in Kern county. The largest and most dense population of these sources is clearly in the Bay Area.

Table 2.3-1 attributes most central California sulfur emissions to vehicle exhaust, especially that from diesel fuel and most probably diesel fuel used in off-road vehicles common to agricultural and construction activities. Sulfur dioxide and oxide of nitrogen emissions are most intense along the major roadways, as well as in population centers where many vehicle miles are logged each day. PM emissions are largest in the population centers and are minor at the point source locations. Vehicular sulfur emissions are expected to be lower in the future owing to lower-sulfur on-road diesel and gasoline formulations that went into effect in 1995. It is believed that higher sulfur fuels are used in off-road vehicles, specifically farm implements and construction equipment.

Figures 2.3-3 through 2.3-9 show the spatial distribution for potential NH₃ sources in central California. These figures are based on California Division of Water Resources (DWR) aerial photographic surveys. Only the counties of San Joaquin, Stanislaus, Merced, Madera, Fresno, Kings, Tulare and Kern are available in digital form. The data in these maps may not reflect current land use since some of the surveys date from 1987, although some are as recent as 1996. In these figures, the points represent individual ammonia emitters (livestock feedlots, dairies and poultry farms) and the dot diameters are proportional to each facility's area. Potential ammonia emissions locations differ substantially from those of the other sources that are concentrated in urban areas and along roadways. These livestock operations are commonly found in clusters with large numbers and sizes in Tulare, Fresno and Merced counties. Tulare county contains the largest aggregate area dedicated to concentrated animal husbandry. Based on 1993 DWR data, these potential ammonia emitters account for ~4.5% of Tulare county's total populated area.

Biogenic hydrocarbon emissions from crops and forests in and around the San Joaquin Valley (Tanner et al., 1992) may be more abundant than in other regions of central California. Oliver et al. (1984) estimated biogenic emissions of ROG in the SJV to be 300 tons/day, which was approximately 40% of anthropogenic ROG reported in the 1987 emissions inventory. Chinkin et al. (1990) estimated that 75% of ROG may originate from forested and agricultural areas in the SJV and surrounding mountains. These biogenic emissions will generally be higher in the summer than in the winter due to seasonal differences in temperature, incident solar intensity, and crop cover.

Field burning and wildfires are intermittent and local, and the annualized tons/day estimate do not reflect the degree to which these sources may have been contributors to ambient pollutant levels for the few days on which these activities took place.

2.4 Meteorology

Year-to-year climatic variations have a profound affect on both PM_{2.5} and PM₁₀ in central California. The majority of the PM₁₀ database was acquired between 1987 and 1992, a period of prolonged drought in the west. During this period, wintertime storms were infrequent, interspersed with up to 20 days of high pressure aloft that favored the

accumulation of particles below a shallow (200 to 500 m agl) mixed layer. Since 1993, Pacific storm fronts have moved through central California at two to seven day intervals, providing an effective particle ventilation and cleansing mechanism. During El Nino years, such as 1997-98, easterly trade winds decrease, warm water in the mid-Pacific moves north, and moisture that would normally arrive in east Asia bombards western North America (Trenberth and Hoar, 1996). During El Nino years there are few extended high pressure periods between storm fronts, and particle concentrations are low. CRPAQS field studies should not be conducted during El Nino periods. In the event that the winter of 2000/2001 will be during an El Nino, the winter field study will be delayed.

The abundance or dearth of water affects bare earth and agricultural practices. A wet winter engenders grasses and semi-arid shrubs on open grasslands and pasture that mitigate against dust suspension. During drought years these surfaces are large and often bare. Dry lake beds maintain a thin layer of water and particle-binding moisture well into the summer when water is abundant, but they create large surface with high erosion potential when they dry out.

Synoptic conditions change with season throughout the year. The Great Basin High, the Alberta Low, and Offshore Low Pressure (Lehrman et al., 1998) are the predominant regimes during winter. The Great Basin High pressure system results in the elevated temperatures aloft (850 mb) that trap air in the SJV and result in weak pressure gradients between the coast, the SJV, and the desert. The Alberta Low consists of low pressure east of the Rocky Mountains with a strong westerly flow. This condition can bring cold air from the north into the SJV, although it often stalls in northern California. Offshore low pressure systems move eastward through California and the Pacific Northwest, bringing abundant rain.

Spring often experiences small frontal passages with lower moisture content. These may result in high winds along the front. Summer meteorology is driven by heating over the desert that creates a thermal low pressure system and a large pressure gradient between the coast and the desert. Fall becomes more influenced by the Great Basin High, with prolonged periods of slow air movement and limited vertical mixing. Smith et al. (1996) found that wintertime 850 mb temperature was most often associated with the highest PM₁₀ concentrations in central California, and this is directly related to Great Basin High, and to a lesser extent to the Alberta Low synoptic conditions.

Smith et al. (1981a, 1981b, 1984, 1996) and Lehrman et al. (1998) describe the meteorological environments that persist during high PM₁₀ concentrations, as well as general aspects of flows, fogs, and mixing within central California. Mixing depths and ventilation are low in the morning during all seasons and remain low throughout the day during the winter. Relative humidities are highest in the winter, with low relative humidities in the summer and fall. For spring, summer, and fall, the typical winds are northwesterly, directed along the axis of the SJV from Stockton to Bakersfield. This is the predominant non-winter wind flow pattern both during the day and night, although it is more sluggish during fall.

Most air leaves the SJV over the Tehachapi Mountains southeast of Bakersfield and flows into the Mojave Desert during non-winter periods. Daytime upslope flow along the

Sierra and coastal mountains can transport SJV pollutants into these mountainous regions, but these flows are not a major ventilation mechanism for the SJV. Although pollutants from the edges of the valley floor may be transported up the mountains during the daytime upslope flow, they are partially returned to the SJV during nighttime drainage flows.

At night during the summer and fall, a high velocity stream frequently forms at approximately 360 m above ground level, with northwesterly winds of up to 15 m/s. In contrast to the daytime pattern, where upslope flows aid the transport of air over the Tehachapi Mountains, the nighttime stability inhibits transport over the mountains. Air transported by the nocturnal high velocity stream in the southern SJV is partially forced back northward along the eastern edge of the SJV. This results in a counterclockwise flow, known as the “Fresno Eddy” (Smith et al., 1981a, 1981b). A separate, but smaller, “Bakersfield Eddy” has also been identified. The Fresno Eddy aids mixing of pollutants within the valley, including some vertical transport of ground-level pollutants. Tracer studies reported by Smith et al. (1981a; 1981b) show transport from the San Francisco Bay area into the SJV. The transport from the SJV into the Mojave Desert has been documented by Reible et al. (1982) and Flocchini and Myrup (1984).

Winter flow patterns are characterized by stagnation periods interrupted by frontal passages. Most of the highest PM concentrations are found during stagnations of four to eight days duration. Although there is mixing within the SJV between ~50 m and ~300 m agl, the major means of ventilation is the gusty winds accompanying frontal or trough systems. The pressure gradient between the coast and desert areas, which drives the northwesterly winds, is much weaker during the winter when compared with other seasons. Smith et al. (1984) report a monthly average pressure gradient at 1500 PST between San Francisco and Las Vegas of 8.3 millibars (mb) during June and 1.1 mb during January 1975. These pressure gradients are less than 3 mb from November to February, and greater than 6 mb from April to July. Slightly lower pressure near the coast with respect to the Valley during stagnation may result in a moderate offshore flow between 50 and 300 m, but this has not been verified with detailed measurements.

Winter stagnation periods are accompanied by strong inversions, low visibility, and high relative humidities. Smith et al. (1996) found that wintertime 850 mb temperature was most often associated with the highest PM₁₀ concentrations in central California. Associations between elevated particle concentrations and relative humidity were more important at the southern end of the SJV than at the northern end. Smith et al. (1996) concluded that warm temperatures aloft are required to provide the stability that traps pollutants in shallow layers near the surface.

During winter nights and mornings, a shallow (30 to 50 m agl) radiation inversion forms, which only begins to couple to the valleywide mixed layer between 1000 and 1200 PST, and re-asserts itself after sunset at 1800 PST. Lehrman et al. (1998) show that vertical wind speeds are fairly consistent with height, 1 to 2 m/s, during this afternoon period. During the remainder of the day, however, winds are often <1 m/s in the radiation inversion while achieving speeds of 2 to 5 m/s within the deeper valleywide mixed layer. Pollutants transported aloft in the afternoon can spread substantially throughout the SJV, and possibly even between air basins, in flows aloft during night and early morning. Figure 2.4-1 illustrates

this concept and shows several vertical profiles of wind speed over Fresno during January 3, 1996. The effects of coupling between the surface and valleywide layer can be seen in the 1600 PST profile with light winds up from the surface to 500 m. During the other sounding periods there appears to be a decoupling between the shallow surface layer and the valleywide layer. Winds aloft are much more vigorous than those at the surface.

These flows aloft and afternoon mixing are consistent with diurnal variations in IMS-95 particle chemistry (Chow et al., 1998). Primary emittants represented by elemental carbon were often highest during nighttime and morning hours in the cities, and lowest at the non-urban sites. Several afternoon samples showed a decrease in urban elemental carbon levels, but a slight increase in non-urban elemental carbon concentrations. This is consistent with the major sources of elemental carbon being urban emissions that accumulate in the shallow surface layer, then mix aloft in the afternoon. Once aloft, these particles are effectively separated from the surface by the re-formation of a surface layer after sunset. They can also transport throughout the valley and mix to the surface at non-urban sites during afternoon of subsequent days.

This mechanism may also explain how non-urban ammonia joins with urban oxides of nitrogen to produce uniform ammonium nitrate concentrations throughout central California. Both of these precursor gases mix upward within the valleywide layer during the afternoon to locations where insolation is higher and where reactive species such as ozone can be mixed in from above the valleywide layer. The nitric acid and ammonia circulate throughout the region via the higher wind speeds aloft, mixing to the surface the next day and manifesting themselves as an afternoon increase in ammonium nitrate concentrations at both urban and non-urban sites. These vertical and horizontal mixing hypotheses constitute will be tested during the winter campaign.

Extensive and persistent low clouds and fogs are common in the SJV, sometimes occur in the Bay Area, but are rare in the Desert. Within the SJV, fogs near the surface in urban areas disperse owing to the heat generated by the city, but they can be intense and hug the ground outside of and between the cities. These fogs are highly variable in location and intensity. Visibility may be near zero in the northern SJV, while blue sky is visible in the southern SJV at the same time. Measurements that indicate the location, intensity, and duration of fogs are sparse and often unreliable. The valleywide mixed layer containing these fogs also shows substantial variability in depth with location and time of day.

Fogs serve as both reactors for creating particles and as vehicles for particle removal. During heavy fogs, particles and precursor gases are scavenged as fog droplets grow to sizes that settle rapidly to the surface. The extent and intensity of these fogs is so poorly characterized, however, that it is not yet possible to determine where and when particle formation overtakes particle deposition, thereby adding to the $PM_{2.5}$ concentration loading.

2.5 Atmospheric Transformations

Ammonium nitrate and ammonium sulfate are the best documented secondary particles found at urban and non-urban sites throughout central California during winter. These particles can form when precursor gas molecules are attracted to and adhere to existing

particles and when precursors oxidize and combine with other gases that are more stable in the particulate than in the gaseous phase.

Sulfur dioxide gas changes to particulate sulfate through gas- and aqueous-phase transformation pathways. In the gas-phase pathway, sunlight induces photochemical reactions creating oxidizing species that react with a wide variety of atmospheric constituents in a way which adds oxygen atoms to their chemical structures. The gas-phase transformation rate appears to be controlled more by the presence or absence of the hydroxyl radical and its competing reactions of other gases than by the sulfur dioxide concentrations.

In the presence of fogs or clouds, sulfur dioxide dissolves in droplets where it experiences aqueous reactions that are much faster than gas-phase reactions. When ozone and hydrogen peroxide are dissolved in the droplet, the sulfur dioxide is quickly oxidized to sulfuric acid. Central California fogs are highly buffered (Collett et al., 1998) and it appears that the aqueous ozone reaction dominates this transformation. When ammonia is also dissolved in the droplet, the sulfuric acid is neutralized to ammonium sulfate. As relative humidity decreases below 100% (i.e., the fog or cloud evaporates), the sulfate particle is present as a small droplet that includes a portion of liquid water. As the relative humidity further decreases below 70%, the droplet evaporates and a small, solid sulfate particle remains. The reactions within the fog droplet are very fast, and the rate is controlled by the solubility of the precursor gases. Aqueous transformation rates of sulfur dioxide to sulfate are 10 to 100 times as fast as gas-phase rates.

Nitrogen oxide converts to nitrogen dioxide, primarily by reaction with ozone. Nitrogen dioxide can: 1) change back to nitrogen oxide in the presence of ultraviolet radiation; 2) change to short-lived species which take place in other chemical reactions; 3) form organic nitrates; or 4) oxidize to form nitric acid. The major pathway to nitric acid is reaction with the same hydroxyl radicals that transform sulfur dioxide to sulfuric acid. Nitric acid deposits from the atmosphere fairly rapidly but, in the presence of ammonia, it is neutralized to particulate ammonium nitrate. Chow and Egami (1997) show that SJV ammonia concentrations are large during winter. Conversion rates for nitrogen dioxide to nitric acid, ranging from less than 1%/hr to 90%/hr, are typically five to ten times the conversion rates for sulfate formation. Though they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours, in contrast to the gas-phase sulfate chemistry that is most active during daylight hours.

Most nitrogen during the winter of 1995 and 1996 was in the gas rather than particle phase (Kumar et al., 1998). Urban areas had more nitrogen as fresh NO and rural areas had more nitrogen as NO₂, HNO₃, and NH₃. A small portion of the available NO_x is converted to nitric acid and nitrate during a typical episode during winter. Similar to ozone, this conversion may be limited by available hydrocarbons or by available NO_x, depending on where and when the conversion occurs.

While ammonium sulfate is a fairly stable compound, ammonium nitrate is not. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. Figure 2.5-1 shows how the fraction of nitrate in the particle phase changes with temperature, relative humidity, and the amount of excess ammonia in the atmosphere.

These curves were generated from the SCAPE-2 equilibrium model as described in the caption to Figure 2.5-2. Atmospheric particle nitrate can occur in atmospheric aerosol particles as solid ammonium nitrate or as ionized ammonium nitrate in aerosol particles containing water.

In both the solid and ionized forms, ammonium nitrate is in equilibrium with gas phase nitric acid and ammonia. In the SCAPE-2 model, the total sulfate concentration was set to $5 \mu\text{g}/\text{m}^3$ of equivalent H_2SO_4 , and the total nitrate concentration was set to $20 \mu\text{g}/\text{m}^3$ of equivalent HNO_3 . The total ammonia concentration was varied to simulate different ammonium enrichment regimes, and this is indicated in the legends as the molar ratio of total available ammonia to total nitrate plus twice the of sulfate (to account for the two ammonium molecules in $(\text{NH}_4)_2\text{SO}_4$). When this “ion ratio” is unity, there is exactly enough ammonium ion available to neutralize all available nitric and sulfuric acid.

For fixed relative humidity, increasing temperature decreases the particle nitrate fraction. This is a consequence of the direct relation between the equilibrium constants and temperature. As temperature increases, the equilibrium constants increase, which means higher gas phase pressures can be supported, thereby reducing the particle nitrate fraction. For fixed humidity, decreasing temperature increases the particle nitrate fraction. As temperatures approach 0°C , the curves approach limiting values—particle fractions of one for ion ratios greater than or equal to one, and particle fractions determined by the amount of available ammonia for ion ratios less than one. For the higher temperatures, increasing relative humidity increases the particle nitrate fraction. This is a consequence of liquid water present for the 60% and 80% relative humidity cases. When there is sufficient ammonia present with 30% relative humidity, more than 90% of the nitrate is in the particle phase for temperatures less than 20°C . More than half of the particle nitrate is gone at temperatures above 30°C , and all of it disappears at temperatures above 40°C .

These curves explain why Chow and Egami (1997) found little volatilized nitrate during winter, in contrast to large amounts of volatilized nitrate during summer (Chow et al., 1996) in the SJV. The low wintertime temperatures, high wintertime humidities, and abundance of ammonia kept the nitrate in the 90% to 100% part of these curves during the sampling periods. The high temperature conditions during summer first favored the gas phase for nitric acid and tended to shift equilibrium of samples already taken as temperatures rose throughout the day.

Atmospheric water is another important component of suspended particulate matter. The presence of ionic species (such as sulfate and nitrate compounds) enhances the liquid water uptake of suspended particles, as shown in Figure 2.5-2. The sharp rise in liquid water content at relative humidities between 55% and 75% is known as deliquescence. Precise humidities at which soluble particles take on liquid water depends on the chemical mixture and temperature, as explained in the caption to Figure 2.5-2. Particles containing these compounds grow into the droplet mode as they take on liquid water, so the same concentration of sulfate or nitrate makes a much larger contribution to light extinction when humidities are high ($>70\%$) than when they are low ($<30\%$). Excess liquid water is also measured as part of the $\text{PM}_{2.5}$ mass when sampled by continuous monitors or when filters have not been equilibrated at relative humidities less than 30% prior to weighing.

Some of the organic carbon in suspended particles is also of secondary origin. Secondary organic compounds in particulate matter include aliphatic acids, alcohols, aromatic acids, nitro-aromatics, carbonyls, esters, phenols, and aliphatic nitrates (Grosjean and Seinfeld, 1989; Grosjean, 1992, Pandis et al., 1992, 1993; Seinfeld and Pandis, 1998). Although secondary organic aerosol was thought to be minimal during winter in central California, recent analyses (Strader et al, 1998) demonstrate that it could be as much as 20% of 24-hour organic carbon in some samples. This occurs because low wintertime temperatures lower the saturation vapor pressure for semi-volatile organic compounds and due to the long residence time of secondary precursor laden air parcels. This effect is probably minor during winter and fall when photochemical reactions are not dominant.

The exact precursors of secondary organics are not well understood, but they are believed to consist of heavy hydrocarbons with more than seven carbon atoms. Odum et al (1997) identify aromatics as the major group of commonly measured ROG that affect both ozone and secondary aerosol formation. Strader et al (1998) identified aromatics as the major species group influencing secondary organic aerosol formation during clear sky conditions without fog. Their modeling efforts conclude that aromatics produce up to 80% of the secondary organic aerosol for the clear sky high photochemical scenario.

Meng et al. (1997) demonstrate that changes in organic gas emissions that reduce ozone concentrations may inadvertently increase PM_{2.5} concentrations, and vice versa. Several organic compounds have also been identified as toxic substances and apportioned to sources with receptor models (e.g., Edgerton and Czuczwa, 1989; Harley et al., 1994). Though not of importance to tropospheric pollution, halocarbons used as refrigerants, degreasers, and fire suppressants participate in the reduction of stratospheric ozone and may increase global warming (Lovelock et al., 1973). Halocarbons have also been used in receptor models to determine contributions to other pollutants from distant sources (Bastable et al., 1990; Hisham and Grosjean, 1991; Miller et al., 1990; Schorran et al., 1987; White et al., 1990).

The characterization of organic compounds in particles and precursor gases plays a crucial role in the CRPAQS. Organic compound concentrations will be used to directly determine primary source contributions using receptor models. They will also be used as input to chemical mechanisms in air quality models and to evaluate model outputs. Several terms are used inconsistently but interchangeably to describe different fractions of atmospheric organic material, thus creating substantial confusion among scientists and regulators. The following terms are defined as they are used throughout this plan:

- **C_x**: Molecules containing x carbon atoms (e.g. C₇ means the molecule contains seven carbon atoms). This notation is useful since many sampling and analysis techniques respond to different numbers of carbon atoms rather than to specific compounds.
- **Organic carbon**: Gases and particles containing combinations of carbon and hydrogen atoms. Organic compounds found in ambient air may also be associated with other elements and compounds, particularly oxygen, nitrogen,

sulfur, halogens, and metals. Various operational definitions based on measurement method are applied to different subsets of organic compounds.

- **Inorganic carbon:** Carbon dioxide and carbon monoxide are the most abundant inorganic gases found in the atmosphere, while amorphous graphite is the most common particulate component. Particulate elemental carbon is operationally defined by optical and combustion methods (Chow et al., 1993), and it contains heavy organic material as well as inorganic carbon.
- **Hydrocarbons:** Organic compounds that consist only of carbon and hydrogen atoms.
- **Reactive organic gases (ROG):** Organic gases with potential to react (<30 day half-life) with the hydroxyl radical and other chemicals, resulting in ozone and secondary organic aerosol. The most reactive chemicals are not necessarily the largest contributors to undesirable end-products, however, as this depends on the magnitude of their emissions as well as on their reactivity (Carter, 1990; Carter and Lurmann, 1991).
- **Total Organic Gases (TOG):** Organic gases with and without high hydroxyl reactivity. TOG typically includes ROG plus methane and halocarbons.
- **Non-methane hydrocarbons (NMHC, also termed light hydrocarbons):** C₂ through C₁₂ (light) hydrocarbons collected in stainless steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14 (U.S. EPA, 1991). NMHC excludes carbonyls, halocarbons, carbon dioxide, and carbon monoxide even though some of these may be quantified by the same method. NMHC is most often used to quantify ozone precursors.
- **Halocarbons:** NMHC with chlorine, fluorine, and bromine compounds attached, quantified from canisters by gas chromatography with electron capture detection (GC-ECD). Methylchloride, methylchloroform, methylbromide, and various refrigerants (Freon-12, Freon-22, SUVA) are most commonly measured (Khalil et al., 1985; Rasmussen et al., 1980; Wang et al., 1997). These compounds have long lifetimes and are not reactive enough to cause major changes in tropospheric ozone and secondary organic aerosol. Halocarbons have been implicated in the long-term depletion of stratospheric ozone.
- **Heavy hydrocarbons:** C₈ through C₂₀ hydrocarbons collected on TENAX absorbing substrates and analyzed by thermal desorption and gas chromatography (Zielinska and Fung, 1994; Zielinska and Fujita, 1994; Zielinska et al., 1996). These are sometimes termed “semi-volatile” compounds because the >C₁₅ compounds are often found as both gases and particles (Hampton et al., 1982, 1983). Most of the total hydrocarbon mass is measured in the gas phase.

- **Carbonyls:** Aldehydes, the most common being formaldehyde, acetone, and acetylaldehyde (Carlier et al., 1986). Carbonyls are operationally defined as C₁ through C₇ oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C₁₈ cartridges and analyzed by high performance liquid chromatography with UV detection (HPLC/UV) (Zielinska and Fujita, 1994).
- **Non-Methane Organic Gases (NMOG):** NMHC plus carbonyls.
- **Semi-Volatile Organic Compounds (SVOC):** Particles and gases collected on filters backed with polyurethane foam (PUF) or absorbing resins, extracted in a variety of solvents, and analyzed by gas chromatography/mass spectrometry. This class includes polycyclic aromatic hydrocarbons, hopanes, steranes, guayacols, and syringols. These are heavy (>C₂₀) non-polar compounds that are gases or particles depending on ambient equilibrium conditions. The heavy hydrocarbons are often classified as SVOCs, but they are given a separate identity here for precision and clarity.
- **Volatile organic compounds (VOC):** NMHC plus heavy hydrocarbons plus carbonyls plus halocarbons, typically <C₂₀. VOC has been imprecisely used to describe most of the other categories defined above.

These different fractions are relevant to both chemical source models that contain secondary organic aerosol formation mechanisms and to receptor models that attribute ambient concentrations to their sources. Both the gas and particle phases are of use for these models.

Since precursor gases are not always emitted by the same sources and undergo complicated chemical reactions in the atmosphere, it is not always the case that reductions in their emissions will result in proportional reductions in the ambient concentrations of their particulate end products. Sulfur dioxide to particulate sulfate and nitrogen oxide to particulate nitrate reactions compete with each other for available hydroxyl radicals and ammonia. Ammonia reacts preferentially with sulfuric acid to form ammonium bisulfate and ammonium sulfate, and the amount of ammonium nitrate formed is only significant when the total ammonia exceeds the sulfate by a factor of two or more on a mole basis (Seinfeld and Pandis, 1998). This implies that reducing sulfur dioxide emissions might actually result in increased ammonium nitrate concentrations that exceed the reductions in ammonium sulfate where the availability of ammonia is limited. Sulfate concentrations are sufficiently low, and ammonia levels are sufficiently large, that this is unlikely in central California.

In central California during winter, however, low temperatures, high humidities, and an abundance of free ammonia, cause sulfate to be completely neutralized as ammonium sulfate and all available nitrate is present as particulate ammonium nitrate. There is no ammonia limitation (Chow and Egami, 1997; Blanchard et al., 1997), and more than 50% reductions in ammonia would be required before moderate reductions in ammonium nitrate particle concentrations would be observed (Kumar et al., 1998). Sulfate levels are much

lower than nitrate levels, and even the complete elimination of sulfate would not free sufficient ammonia to shift the ammonium nitrate equilibrium.

During the fall, however, higher ammonium nitrate concentrations are often found at non-urban areas under higher temperatures and lower relative humidities. This may occur because higher non-urban ammonia concentrations shift the equilibrium toward the particle phase, similar to the condition found for Rubidoux, CA (Chow et al., 1992) that lies directly downwind of large dairy farms in the South Coast Air Basin.

**Table 2.1-1.
Populations and Areas for Central California Metropolitan Statistical Areas**

State	Metropolitan Area	TYPE	Counties	1990 Population	1995 Est. Population	1995 pop density (km ⁻²)	Area (km ²)
CA	Bakersfield, CA	MSA	Kern County	543,477	617,528	29.3	21086.7
CA	Chico-Paradise, CA	MSA	Butte County	182,120	192,880	45.4	4246.6
CA	Fresno, CA	MSA	Fresno County Madera County	755,580	844,293	40.2	20983.3
CA	Riverside-San Bernardino, CA	PMSA	Riverside County San Bernardino County	2,588,793	2,949,387	41.8	70629.2
CA	Ventura, CA	PMSA	Ventura County	669,016	710,018	148.5	4781.0
CA	Merced, CA	MSA	Merced County	178,403	194,407	38.9	4995.8
CA	Modesto, CA	MSA	Stanislaus County	370,522	410,870	106.1	3870.9
CA	Sacramento, CA	PMSA	El Dorado County Placer County Sacramento County	1,340,010	1,456,955	137.8	10571.3
CA	Yolo, CA	PMSA	Yolo County	141,092	147,769	56.4	2622.2
CA	Salinas, CA	MSA	Monterey County	355,660	348,841	40.5	8603.8
CA	Oakland, CA	PMSA	Alameda County Contra Costa County	2,082,914	2,195,411	581.5	3775.7
CA	Sacramento-Yolo, CA	CMSA	El Dorado County Placer County Sacramento County Yolo County	1,481,220	1,604,724	121.1	13250.4
CA	San Francisco, CA	PMSA	Marin County San Francisco County San Mateo County	1,603,678	1,645,815	625.7	2630.4
CA	San Francisco-Oakland-San Jose, CA	CMSA	Alameda County Contra Costa County Marin County San Francisco County San Mateo County Santa Clara County Santa Cruz County Sonoma County Napa County Solano County	6,249,881	6,539,602	341.1	19173.7
CA	San Jose, CA	PMSA	Santa Clara County	1,497,577	1,565,253	468.0	3344.3
CA	Santa Cruz-Watsonville, CA	PMSA	Santa Cruz County	229,734	236,669	205.0	1154.6
CA	Santa Rosa, CA	PMSA	Sonoma County	388,222	414,569	101.6	4082.4
CA	Vallejo-Fairfield-Napa, CA	PMSA	Napa County Solano County	451,186	481,885	117.6	4097.5
CA	San Luis Obispo-Atascadero-Paso Robles, CA	MSA	San Luis Obispo County	217,162	226,071	26.4	8558.6
CA	Santa Barbara-Santa Maria-Lompoc, CA	MSA	Santa Barbara County	369,608	381,401	53.8	7092.6
CA	Stockton-Lodi, CA	MSA	San Joaquin County	480,628	523,969	144.6	3624.5
CA	Visalia-Tulare-Porterville, CA	MSA	Tulare County	311,921	346,843	27.8	12495.0

**Table 2.3-1.
1995 Annual Emissions in Central California Air Basins (Metric tons/day).**

Basin	Type	MOBILE				AREA				STATIONARY				NATURAL				TOTAL			
		PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG
SFB	Geol					92	0		9	7	1	0	6					99	1	0	15
	GasMV	5	259	18	272													5	259	18	272
	DieselMV	6	134	4	24	0	0	0	8									6	134	4	33
	VegBrn					1	1	0	1					0	0	0	0	1	1	0	1
	Industrial								59	8	35	42	94					8	35	42	153
	NatGas					18	18	1	8	2	57	5	2					20	75	6	10
	Aircraft	3	14	0	13													3	14	0	13
	SFB Total	14	406	22	309	111	19	1	85	17	93	47	103	0	0	0	0	142	519	70	497
SVJ	Geol					328			132	3	1	0	5					331	1	0	137
	GasMV	2	168	3	169													2	168	3	169
	DieselMV	7	130	4	24	0	0	0	5									7	130	4	30
	VegBrn					22	5	0	15					8	1		4	30	5	0	19
	Industrial								30	15	69	11	108				0	15	69	11	138
	NatGas					11	7	0	5	5	103	9	4					16	110	9	8
	Aircraft	4	5	1	14													4	5	1	14
	SVJ Total	13	302	7	207	361	12	0	188	24	172	20	116	8	1		4	406	487	27	514
SED	Geol					265			22	9	31	6	1					274	31	6	23
	GasMV	1	77	2	76													1	77	2	76
	DieselMV	5	98	5	11	0	0	0	1									5	98	5	12
	VegBrn					5	0	0	4					2	0		1	6	0	0	5
	Industrial					0			12	75	5	0	10					75	5	0	22
	NatGas					3	4	0	1	3	67	4	4					5	71	4	5
	Aircraft	3	5	1	6													3	5	1	6
	SED Total	8	180	7	93	272	4	0	39	87	103	10	15	2	0		1	369	286	17	148
SV	Geol					154			23	4	2	0	2					158	2	0	24
	GasMV	2	115	2	137													2	115	2	137
	DieselMV	5	91	6	16	0	0	0	5									5	91	6	22
	VegBrn					22	0	0	15					7	1		3	29	1	0	18
	Industrial					0			24	6	5	1	44				0	6	5	1	67
	NatGas					16	6	0	7	1	16	0	0					17	23	0	7
	Aircraft	0	2	0	2													0	2	0	2
	SV Total	7	208	8	155	192	6	0	74	11	23	1	45	7	1	0	3	218	238	9	278
NCC	Geol					46			13	2	3	1	2					48	3	1	15
	GasMV	0	27	0	29													0	27	0	29
	DieselMV	1	23	1	4	0	0	0	2									1	23	1	5
	VegBrn					2	0	0	1					3	0		1	5	0	0	2
	Industrial								7	0	0	0	11				0	0	0	0	18
	NatGas					4	2	0	2	0	19	0	0					4	21	0	2
	Aircraft	0	0	0	0													0	0	0	0
	NCC Total	1	50	1	33	52	2	0	24	2	22	1	13	3	0		1	57	73	2	71
Total for All Basins	Geol					885			199	24	37	7	15					910	37	7	214
	GasMV	9	646	24	683													9	646	24	683
	DieselMV	24	475	19	80				22									24	475	19	102
	VegBrn					51	5	0	36					20	2		8	71	7	0	44
	Industrial								132	105	113	54	267				0	105	113	54	398
	NatGas					52	37	1	23	11	262	18	9					63	299	19	32
	Aircraft	9	24	2	34													9	24	2	34
Grand Total	43	1146	45	797	988	43	1	411	141	413	79	291	20	2	8	1191	1603	125	1508		

Table 2.3-2
Examples of Organic Compounds Found in Different Emission Sources and in Ambient Air

<u>Species</u>	<u>Predominant Sources</u>	<u>Particle-Gas Phase Distribution</u>
PAH, for example		
naphthalene	Motor vehicles, wood smoke	Gas Phase
methylnaphthalenes	Motor vehicles, wood smoke	Gas Phase
dimethylnaphthalenes	Motor vehicles, wood smoke	Gas Phase
biphenyl	Motor vehicles, wood smoke	Gas Phase
acenaphthylene	Motor vehicles, wood smoke	Gas Phase
acenaphthene	Motor vehicles, wood smoke	Gas Phase
fluorene	Motor vehicles, wood smoke	Gas Phase
phenanthrene	Motor vehicles, wood smoke	Particle-Gas Phase
anthracene	Motor vehicles, wood smoke	Particle-Gas Phase
fluoranthene	Motor vehicles, wood smoke	Particle-Gas Phase
pyrene	Motor vehicles, wood smoke	Particle-Gas Phase
retene	Wood smoke -softwood	Particle-Gas Phase
benzo[b]naphtho[2,1]thiophene	Motor vehicles	Particle Phase
benz[a]anthracene	Motor vehicles, wood smoke	Particle Phase
chrysene	Motor vehicles, wood smoke	Particle Phase
benzo[b+j+k]fluoranthene	Motor vehicles, wood smoke	Particle Phase
benzo[e]pyrene	Motor vehicles, wood smoke	Particle Phase
benzo[a]pyrene	Motor vehicles, wood smoke	Particle Phase
indene[123-cd]pyrene	Motor vehicles, wood smoke	Particle Phase
dibenzo[ah+ac]anthracene	Motor vehicles, wood smoke	Particle Phase
benzo[ghi]perylene	Motor vehicles, wood smoke	Particle Phase
coronene	Motor vehicles, wood smoke	Particle Phase
Hopanes and Sterenes		
Cholestanes	Motor vehicles	Particle Phase
Trisnorhopanes	Motor vehicles	Particle Phase
Norhopanes	Motor vehicles	Particle Phase
Hopanes	Motor vehicles	Particle Phase
Guaiacols, for example		
4-methylguaiacol	Wood smoke	Gas Phase
4-allylguaiacol	Wood smoke	Particle-Gas Phase
isouegenol	Wood smoke	Particle-Gas Phase
Acetovanillone	Wood smoke	Particle Phase
Syringols, for example		
Syringol	Wood smoke, mostly hardwood	Particle-Gas Phase
4-methylsyringol	Wood smoke, mostly hardwood	Particle-Gas Phase
Syringaldehyde	Wood smoke, mostly hardwood	Particle Phase
Lactons, for example		
Caprolactone	Meat cooking	Gas Phase
Decanolactone	Meat cooking	Particle-Gas Phase
Undecanoic-G-Lactone	Meat cooking	Particle-Gas Phase
Sterols, for example		
Cholesterol	Meat cooking	Particle Phase
Sitosterol	Meat cooking, wood smoke	Particle Phase

**Table 2.3-3.
1995 Annual Emissions in Central California (Metric tons/day).**

County	Type	MOBILE				AREA				STATIONARY				NATURAL				TOTAL			
		PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG	PM ₁₀	NO _x	SO ₂	ROG
San Joaquin	Geol					32			9	1	0	0	0					33	0	0	9
	GasMV	0	27	0	29													0	27	0	29
	DieselMV	1	20	0	2	0	0	0	1									1	20	0	3
	VegBrn					3	1	0	2					0	0	0	0	3	1	0	2
	Industrial								5	2	4	2	9					2	4	2	15
	NatGas					2	1	0	1	0	12	1	0					2	13	1	1
	Aircraft	0	0	0	0													0	0	0	0
	San Joaquin Total	1	47	0	31	36	2	0	18	3	15	3	9	0	0	0	0	40	64	3	58
Stanislaus	Geol					28			23	0			1					28	0	0	24
	GasMV	0	19	0	19													0	19	0	19
	DieselMV	0	14	0	2	0	0	0	1									0	14	0	3
	VegBrn					3	0		2					0	0	0	0	3	0	0	2
	Industrial								5	2	1	1	5					2	1	1	9
	NatGas					2	1	0	1	0	7	1	0					2	8	1	1
	Aircraft	0	0	0	1													0	0	0	1
	Stanislaus Total	0	33	0	22	33	1	0	31	2	8	2	5	0	0	0	0	34	42	2	58
Merced	Geol					36			11	0	0	0	0					36	0	0	11
	GasMV	0	15	0	11													0	15	0	11
	DieselMV	1	15	0	2	0	0	0	0									1	15	0	2
	VegBrn					3	0		2					0	0	0	0	3	0	0	2
	Industrial								2	1	3	0	2					1	3	0	4
	NatGas					1	0	0	0	0	4	1	1					1	4	1	1
	Aircraft	3	2	1	5				0									3	2	1	5
	Merced Total	4	33	1	17	40	0	0	15	1	6	1	3	0	0	0	0	44	39	2	34
Madera	Geol					17			5	0	1	0	0					17	1	0	5
	GasMV	0	6	0	7													0	6	0	7
	DieselMV	0	7	0	1	0	0	0	0									0	7	0	1
	VegBrn					1	0	0	1					1	0	0	0	2	0	0	1
	Industrial								1	0	6	0	2					0	6	0	3
	NatGas					1	0	0	1	0	4	0	0					1	4	0	1
	Aircraft	0	0	0	0													0	0	0	0
	Madera Total	0	14	0	8	19	0	0	7	0	11	0	2	1	0	0	0	20	24	0	17
Fresno	Geol					98			24	1	0	0	4					99	0	0	27
	GasMV	0	38	0	43													0	38	0	43
	DieselMV	1	24	0	5	0	0	0	2									1	24	0	6
	VegBrn					4	1	0	3					2	0	1	1	5	1	0	4
	Industrial								7	3	18	4	19			0	0	3	18	4	26
	NatGas					3	2	0	1	1	15	4	0					4	16	4	1
	Aircraft	0	1	0	1													0	1	0	1
	Fresno Total	1	64	0	48	104	3	0	36	5	33	7	23	2	0	1	1	112	99	7	108
Kings	Geol					30			15	0			0					30	0	0	15
	GasMV	0	5	0	5													0	5	0	5
	DieselMV	0	5	0	0	0	0	0	0									0	5	0	0
	VegBrn					2	0		2					0		0	0	2	0	0	2
	Industrial								1	1	1	0	2					0	1	1	0
	NatGas					0	0	0	0	0	9	0	0					0	9	0	0
	Aircraft	0	1	0	3													0	1	0	3
	Kings Total	0	12	0	7	32	0	0	18	1	10	0	2	0		0	0	33	22	0	27
Kern	Geol					70			25	3	14	3	0					73	14	3	25
	GasMV	0	40	0	39													0	40	0	39
	DieselMV	2	32	0	4	0	0	0	1									2	32	0	5
	VegBrn					2	1		2					2	0	1	1	4	1	0	3
	Industrial								6	4	34	5	64			0	0	4	34	5	70
	NatGas					2	2	0	1	3	49	2	2					5	51	2	3
	Aircraft	3	3	0	6													3	3	0	6
	Kern Total	5	74	0	49	73	3	0	35	9	97	9	65	2	0	1	1	89	174	9	151
Tulare	Geol					37			19	0	0	0	0					37	0	0	19
	GasMV	0	19	0	20													0	19	0	20
	DieselMV	0	16	0	4	0	0	0	1									0	16	0	5
	VegBrn					5	1		4					3	0	1	1	8	1	0	5
	Industrial								3	2	0	0	5					2	0	0	7
	NatGas					1	1	0	1	0	5	0	1					1	5	0	2
	Aircraft	0	0	0	1													0	0	0	1
	Tulare Total	0	35	0	24	44	2	0	27	2	5	0	5	3	0	1	1	48	42	0	58
All Types	Geol					348			131	5	15	3	5					353	15	3	135
	GasMV	0	171	0	172													0	171	0	172
	DieselMV	5	134	0	18	0	0	0	5									5	134	0	24
	VegBrn					22	4	0	16					7	0	3	29	29	4	0	19
	Industrial								30	14	67	11	106			0	0	14	67	11	136
	NatGas					11	6	0	5	4	103	8	4					15	110	8	9
	Aircraft	5	6	1	16													5	6	1	16
	Natural																	0	0	0	0
Grand Total	10	311	1	207	381	10	0	188	22	185	22	114	7	0	3	3	420	506	23	512	

**Table 2.3-4
Top 100 NO_x Emitters in Central California.**

Facility	Activity	City	Emission Rate (Metric tons per year)			
			NO _x	PM _{2.5}	ROG	SO _x
SHELL MARTINEZ REFINING COMPAN	Petroleum refining	MARTINEZ	4034	390	1336	2278
P G & E	Electric services	MOSS LANDING	3669	95	53	128
RIVERSIDE CEMENT COMPANY	Cement, hydraulic	ORO GRANDE	3443	188	115	478
TOSCO CORP AVON REFINERY	Petroleum refining	MARTINEZ	2867	115	2737	4420
EXXON CORPORATION	Petroleum refining	BENICIA	2793	176	737	5521
SOUTHWESTERN PORTLAND CEMENT C	Cement, hydraulic	VICTORVILLE	2702	112	45	71
NORTH AMERICAN CHEMICAL	Industrial inorganic chemicals, nec	TRONA	2107	2734	135	94
CAL PORTLAND CEMENT CO.	Cement, hydraulic	MOJAVE	2037	52	3	223
SYCAMORE COGENERATION	Electric services	OILDALE	1917	62		4
PACIFIC GAS & ELECTRIC CO PIT	Electric and other services combined	PITTSBURG	1743	65	16	10
PG&E HINKLEY COMPRESSOR STA	Natural gas transmission	HINKLEY	1641	5	98	0
KAISER CEMENT CORPORATION	Cement, hydraulic	CUPERTINO	1536	50	12	421
UNOCAL CORPORATION	Petroleum refining	RODEO	1525	47	542	544
CALRESOURCES LLC	Crude petroleum and natural gas	FRESNO COUNTY	1510	159	69	33
CALAVERAS CEMENT CO	Cement, hydraulic	MONOLITH	1417	48		259
NATIONAL CEMENT CO	Cement, hydraulic	LEBEC	1383	143	3	6
UNION OIL COMPANY OF CA	Crude petroleum and natural gas	COALINGA	1382	5	53	
MITSUBISHI CEMENT	Cement, hydraulic	LUCERNE VALLEY	1330	316	13	859
CHEVRON U.S.A. INC.	Crude petroleum and natural gas	KERN CENTRAL HEAVY	1273	66	240	25
CHEVRON INC	Petroleum refining	RICHMOND	1254	61	2222	327
KERN RIVER COGEN	Electric services	OILDALE	1148	41		3
SOUTHERN CALIFORNIA GAS CO	Natural gas transmission	BAKERSFIELD AREA	1116	10	21	0
GUARDIAN INDUSTRIES CORP.	Flat glass	KINGSBURG	1059	8	1	519
COOLWATER GENERATING STATION	Electric services	DAGGETT	971	70	197	30
LONE STAR INDUST CEMENT PLANT	Cement, hydraulic	DAVENPORT	861	108	5	237
PPG IND INC	Flat glass	FSNO	822	32	8	100
OWENS-BROCKWAY GLASS CONTAINER	Glass containers	OAKLAND	780	54	2	116
PACIFIC GAS AND ELECTRIC CO A	Electric and other services combined	ANTIOCH	761	16	4	4
ANCHOR GLASS CONTAINER CORPORA	Glass containers	HAYWARD	741	37	1	169
DOW CHEMICAL COMPANY	Alkalies and chlorine	PITTSBURG	717	83	37	1
NAVAL PETROLEUM RESERVE NO. 1	Crude petroleum and natural gas	TUPMAN	713	19	712	0
OWENS ILLINOIS	Glass containers	TRACY	712	80	2	261
PACIFIC GAS & ELECTRIC CO HUN	Electric and other services combined	SAN FRANCISCO	666	15	10	8
LIBBEY OWENS FORD	Flat glass	LATHROP	649	67	7	100
P G & E-MORRO BAY	Electric services	MORRO BAY	621	77	10	705
PACIFIC GAS & ELECTRIC CO POT	Electric and other services combined	SAN FRANCISCO	586	14	4	31

**Table 2.3-4 (continued)
Top 100 NO_x Emitters in Central California.**

Facility	Activity	City	Emission Rate (Metric tons per year)			
			NO _x	PM _{2.5}	ROG	SO _x
UNION CHEMICALS	Petroleum and coal products, nec	RODEO	512	83		1393
MOBIL OIL CORP	Crude petroleum and natural gas	SAN ARDO	508	53	104	116
TEXACO REFINING AND MARKETING	Petroleum refining	BAKERSFIELD	488	50	839	128
SANTA FE ENERGY RESOURCES INC	Crude petroleum and natural gas		480	47	20	37
MADERA GLASS COMPANY	Glass containers	MADERA	448	59	2	144
SIERRA PACIFIC INDUSTRIES	Sawmills & planing mills, general	STANDARD	424	202	32	50
US ARMY NATIONAL TRAINING CTR.	National security	FORT IRWIN	393	29255	111	25
CHEVRON - WARREN GP	Natural gas liquids	LOST HILLS	392	2	28	
AFG INDUSTRIES INC	Flat glass	VICTORVILLE	390	2	2	23
JEFFERSON SMURFIT CORPORATION	Paperboard mills	SANTA CLARA	360	12	58	1
PACIFIC REFINING COMPANY	Petroleum refining	HERCULES	350	11	320	263
MARTINEZ COGEN LIMITED PARTNER	Electric and other services combined	MARTINEZ	338	14	1	9
ORCUTT HILL IC ENGINES	Crude petroleum and natural gas	ORCUTT HILL FIELD	320	0	48	10
GALLO GLASS CO	Glass containers	MODESTO	296	205	2	246
SAN JOSE/SANTA CLARA WATER POL	Sewerage systems	SAN JOSE	294	12	50	9
PACIFIC GAS & ELECTRIC CO	Natural gas transmission	CONCORD	288	0	1	
OWENS CORNING	Mineral wool	SANTA CLARA	281	7	8	2
GEORGIA PACIFIC	Sawmills & planing mills, general	MARTELL	275	312	80	2
TEXACO E & P (DENVER)	Natural gas liquids		275	3	112	0
LAIDLAW GAS RECOVERY SYSTEMS	Refuse systems	SAN JOSE	273	10	5	1
CALIFORNIA & HAWAIIAN SUGAR CO	Cane sugar refining	CROCKETT	250	45	11	1
ACE COGENERATION	Electric services	TRONA	248	7	0	278
LFC POWER SYSTEMS GREENLEAF #1	Electric services	YUBA CITY	242	8	1	0
HOLLY SUGAR CORP	Beet sugar	TRACY	219	5	0	3
LOUISIANA PACIFIC CORPORATION	Pulp mills	OROVILLE	217	136	51	
CARDINAL COGEN A JOINT VENTURE	Electric and other services combined	PALO ALTO	215	22	4	1
PACIFIC-ULTRAPOWER CHINESE STA	Sawmills & planing mills, general	JAMESTOWN	213	46	55	30
CHEVRON USA INC.	Drilling oil and gas wells		212		6	
PROCTER & GAMBLE	Soap and other detergents	SACRAMENTO	206	39	134	1
GILROY ENERGY COMPANY	Turbines and turbine generator sets	GILROY	200	6	1	1
BEALE AIR FORCE BASE	National security	MARYSVILLE	197	14	62	2
TORCH OPERATING COMPANY	Crude petroleum and natural gas		196	7	1	7
RIO BRAVO POSO	Crude petroleum and natural gas	BAKERSFIELD	196	1	1	63
CAT CANYON IC ENGINES	Crude petroleum and natural gas	CAT CANYON FIELD	183	0	106	
OILDALE COGENERATION	Electric services	BAKERSFIELD	181	21	2	1
TEXACO WEST (DENVER)	Crude petroleum and natural gas	MCKITTRICK	181	9	6	90

**Table 2.3-4 (continued)
Top 100 NO_x Emitters in Central California.**

Facility	Activity	City	Emission Rate (Metric tons per year)			
			NO _x	PM _{2.5}	ROG	SO _x
CERTAINTTEED CORP.	Mineral wool	CHOWCHILLA	177	63	18	1
DELANO ENERGY CO. INC.	Electric services	DELANO	171	35		0
O L S ENERGY - BERKELEY	Electric services	BERKELEY	170	13	2	1
EAST BAY MUNICIPAL UTILITY DIS	Sewerage systems	OAKLAND	156	14	15	17
MARE ISLAND/SSPORTS	Steam and air-conditioning supply	VALLEJO	155	4	8	1
WESTFIELD GINNING CO.	Cotton ginning	FIVE POINTS	151	1		
CALIFORNIA ENERGY COMPANY INC.	Steam and air-conditioning supply	COSO	150	6		43
KERN OIL & REFINING COMPANY	Petroleum refining	BAKERSFIELD	149	18	115	421
DEL MONTE CORP	Canned fruits and vegetables	MODESTO	148	1	1	0
MT POSO COGENERATION CO.	Crude petroleum and natural gas	BAKERSFIELD	148	3	0	49
JACKSON VALLEY ENERGY PARTNERS	Petroleum and coal products, nec	IONE	147	57	133	187
GAYLORD CONTAINER CORPORATION	Paperboard mills	ANTIOCH	140	18	11	1
EXXON COMPANY USA	Crude petroleum and natural gas		140		18	
MASONITE HARDBRD DIV	Wood products, nec	UKIAH	131	139	112	92
MOBIL EXPL'N & PROD'G U.S. INC	Crude petroleum and natural gas		127		14	
CELITE CORPORATION	Minerals, ground or treated	LOMPOC	125	25	8	402
HUNT-WESSON FDS	Canned fruits and vegetables	OAKDALE	125	3	1	0
SAN JOAQUIN REFINERY	Petroleum refining	BAKERSFIELD	116	27	55	316
STANISLAUS FOOD PRODUCTS CO	Canned fruits and vegetables	MODESTO	115	2	0	0
ENRON OIL & GAS CO	Crude petroleum and natural gas		114		12	
NATIONAL REFRAC&MNRL-NATIVIDAD	Lime	SALINAS	110	12	2	51
SPRECKLES SUGAR	Beet sugar	FSNO	105	3	0	63
SAN FRANCISCO THERMAL L P	Electric and other services combined	SAN FRANCISCO	102	2	3	0
ENERGY FACTORS EFFR	Electric services	MARYSVILLE	98	29	3	31
RIO-BRAVO	Electric services	LINCOLN	97	24	4	19
MARTELL COGENERATION PLANT	Electric services	MARTELL	94	46	24	26
SANTA FE MINERALS INC.	Crude petroleum and natural gas	LIVE OAK	94		3	
DELTA DIABLO SANITATION DISTRI	Sewerage systems	ANTIOCH	92	0	13	

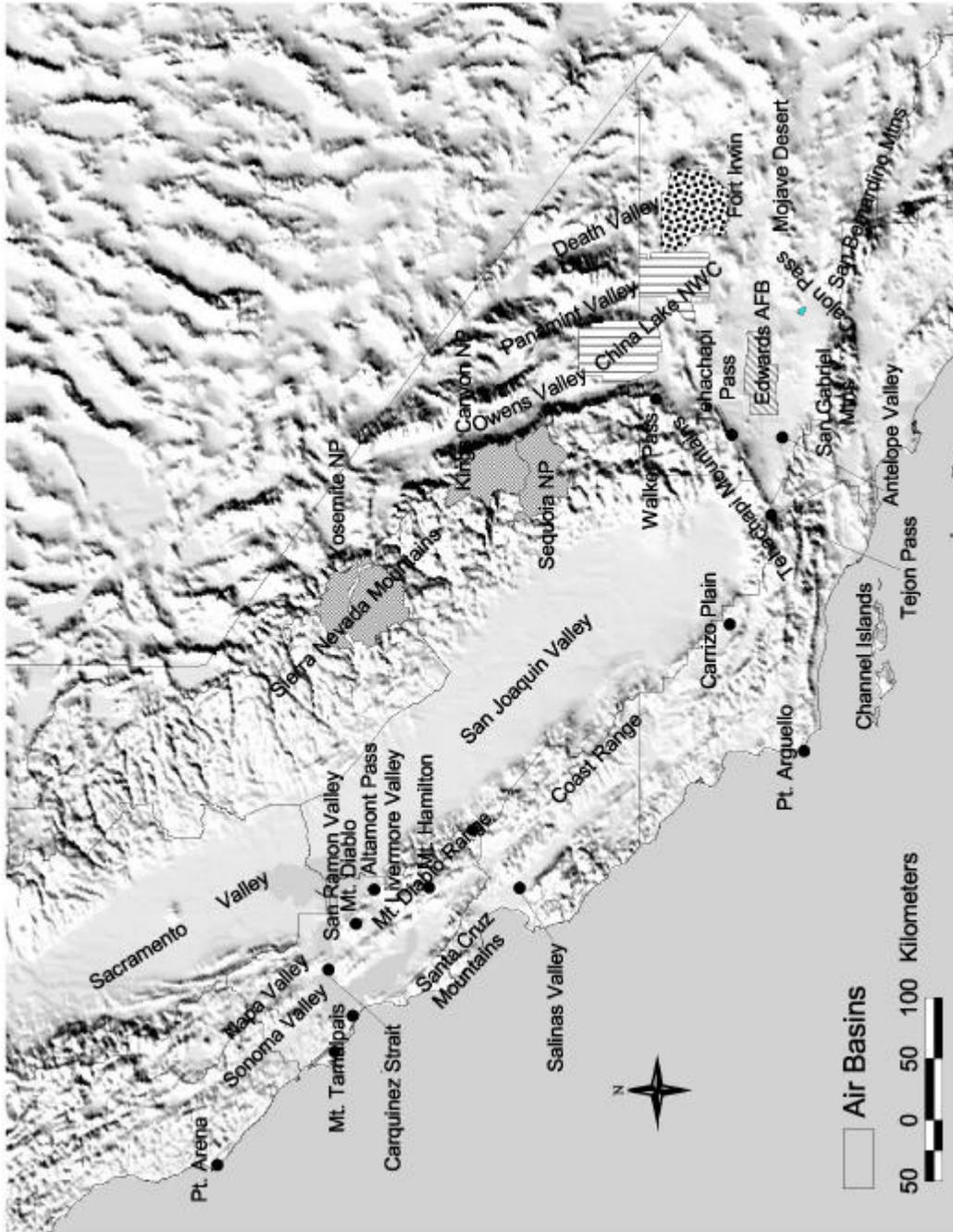


Figure 2.1-1. Overall study domain with major landmarks, mountains and passes.

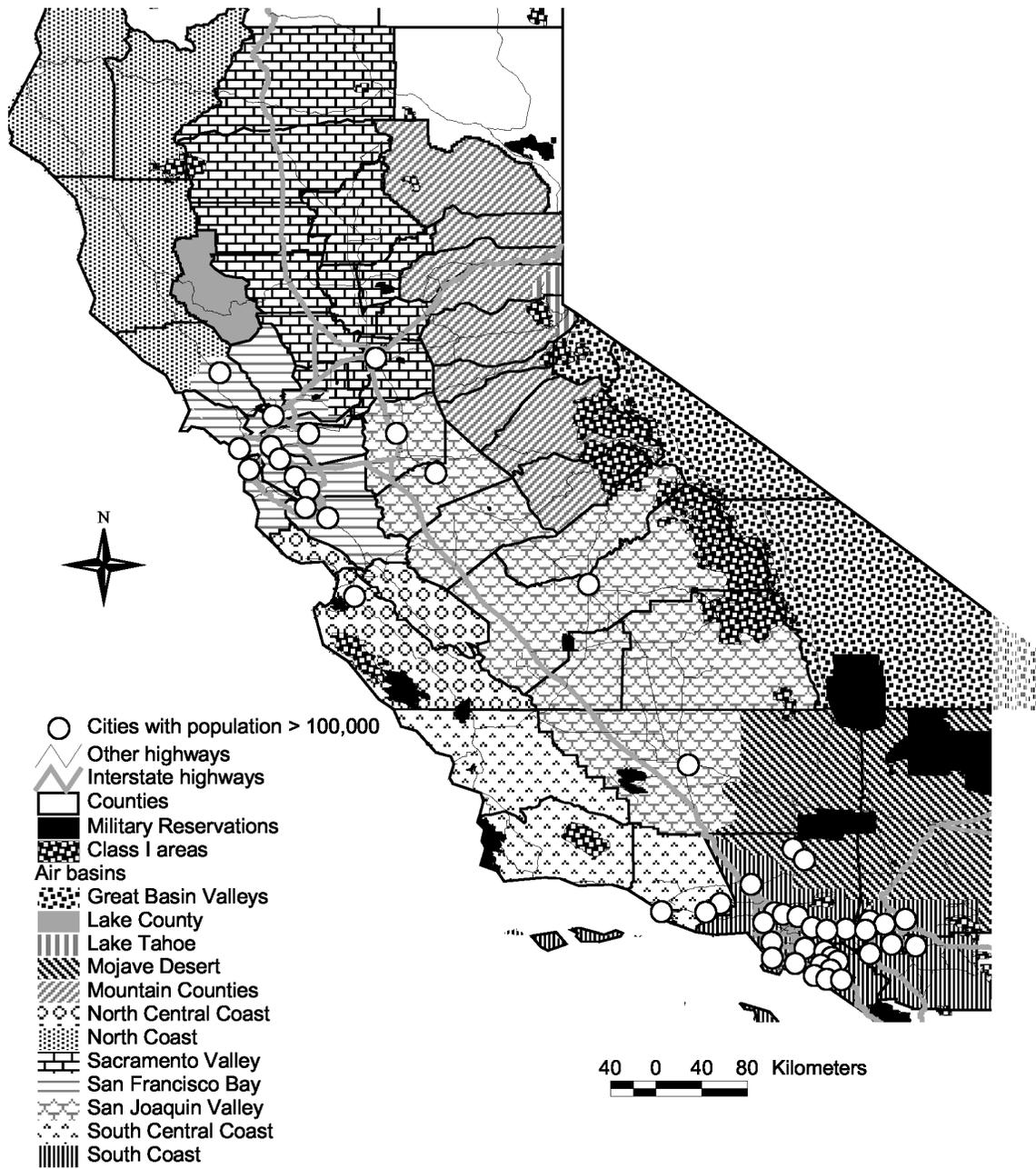


Figure 2.1-2. Major political boundaries and air basins within central California.

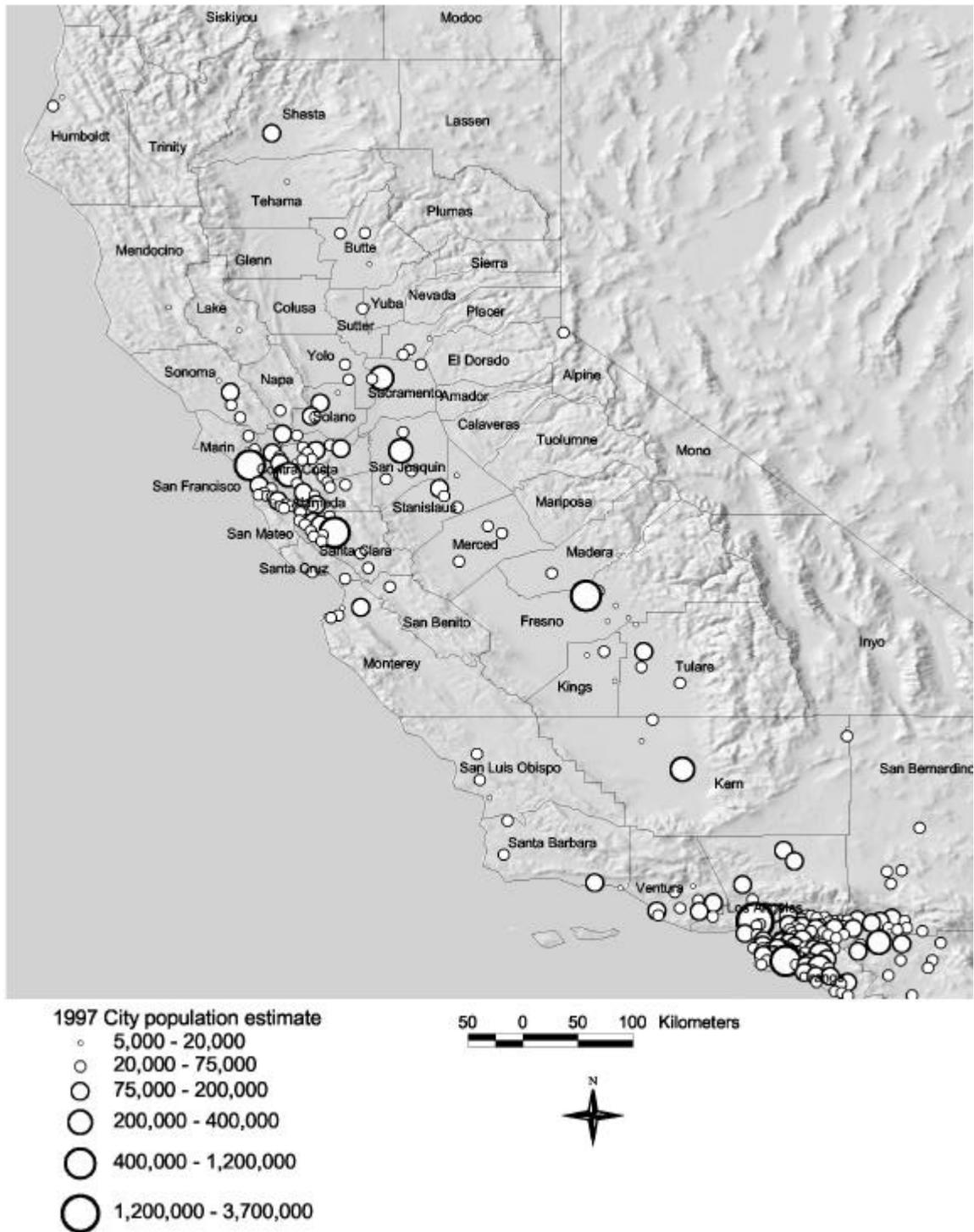


Figure 2.1-3. Major population centers within central California.

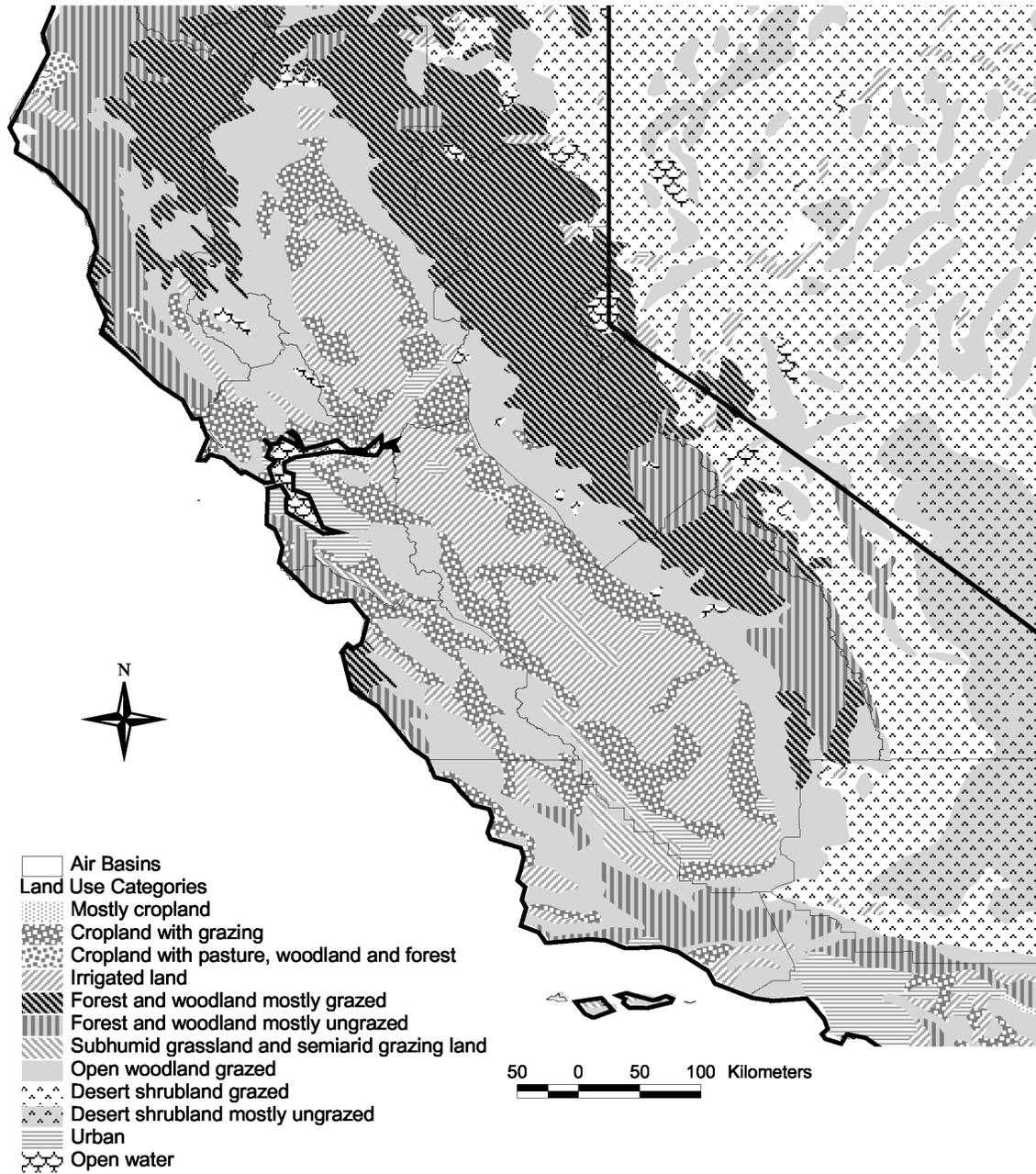


Figure 2.1-4. Land use within central California from the U.S. Geological Survey.

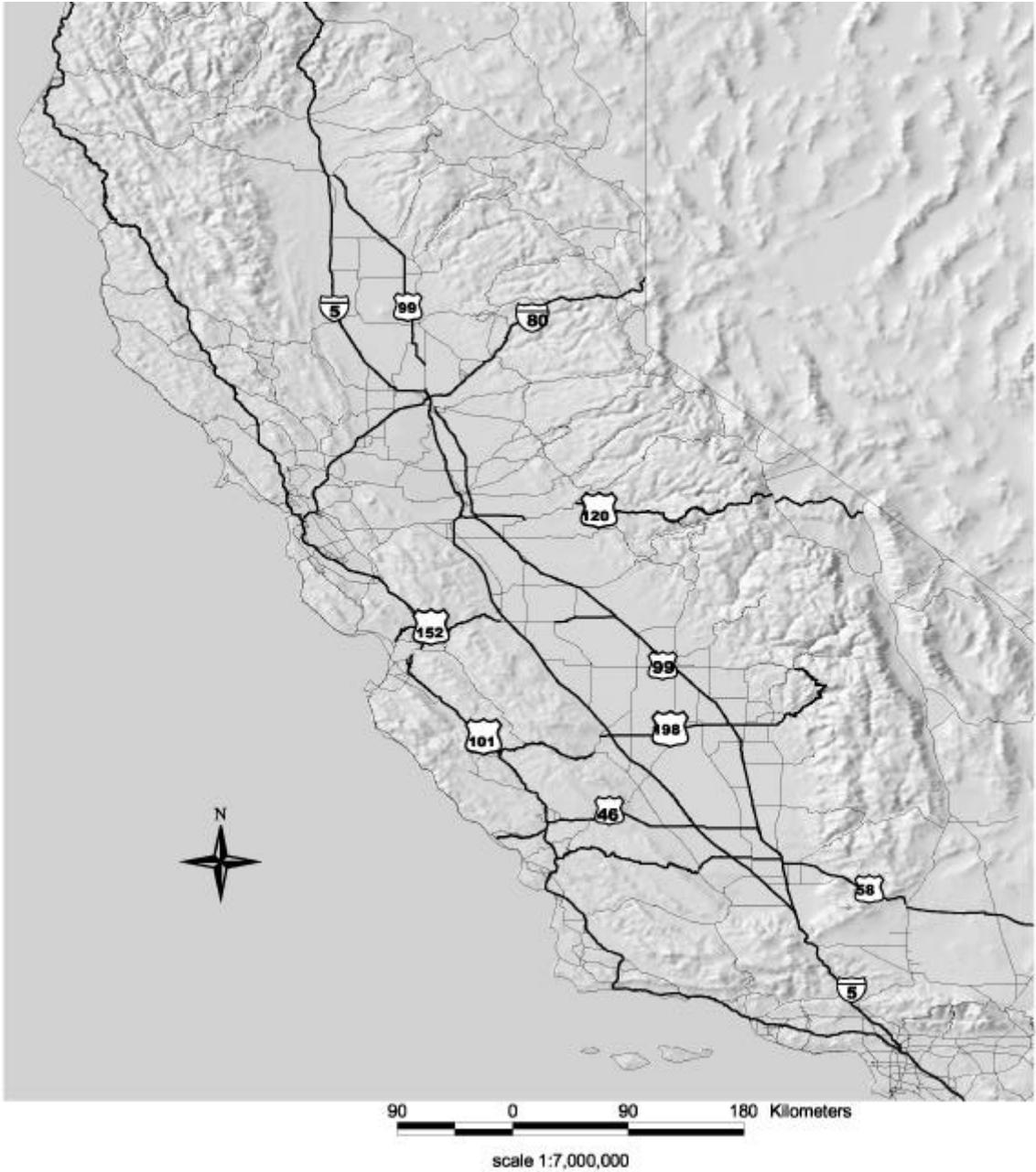


Figure 2.1-5. Major highway routes in central California.

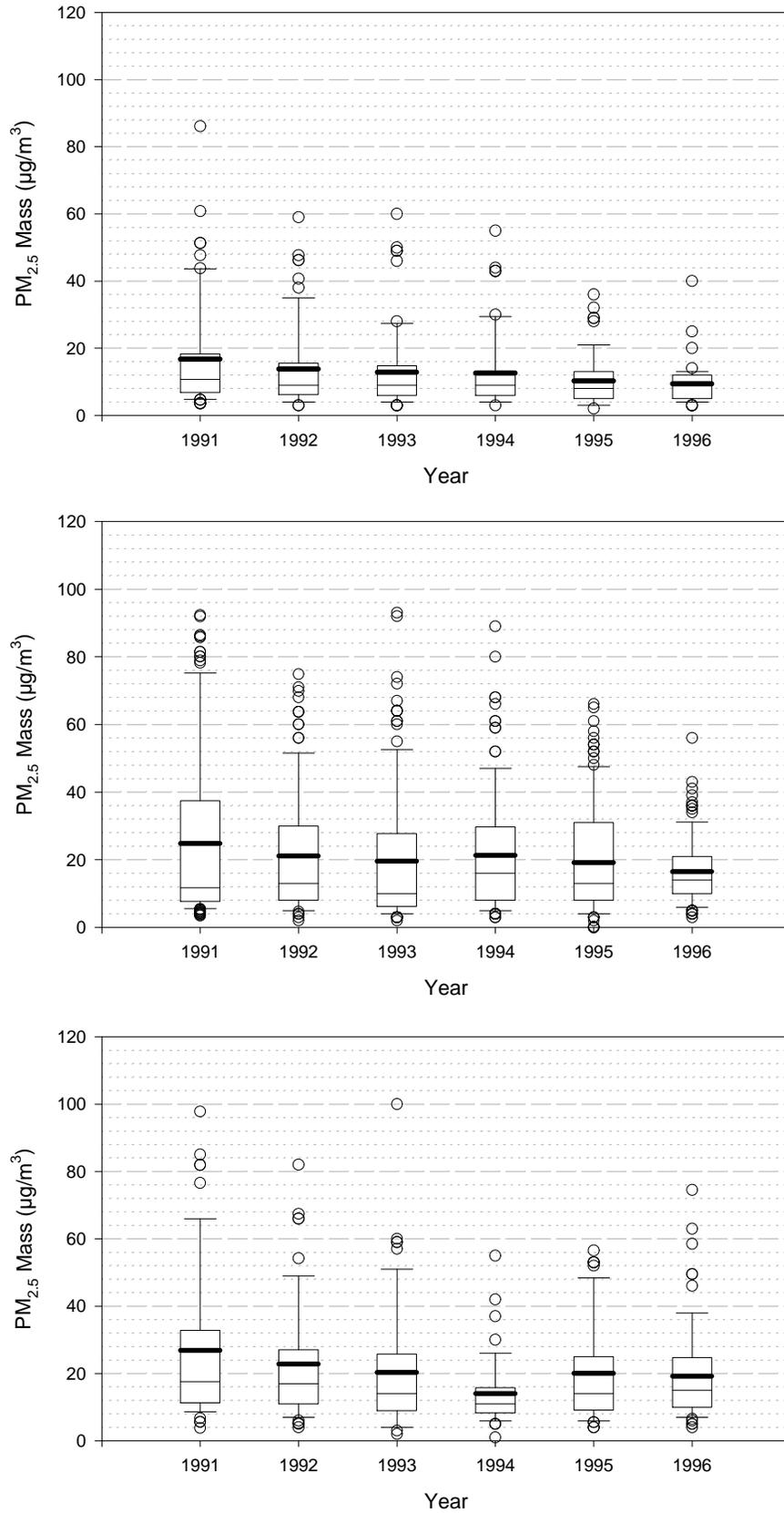


Figure 2.2-1. Annual average and maximum PM_{2.5} from 1991 to 1996 at San Jose (top), Fresno (middle) and Bakersfield (bottom) for sixth-day dichotomous sampling. Circles =extreme values, dark bar=arithmetic average, light bar=median, ends of box=25th &75th percentiles, whiskers=5th and 95th percentiles.

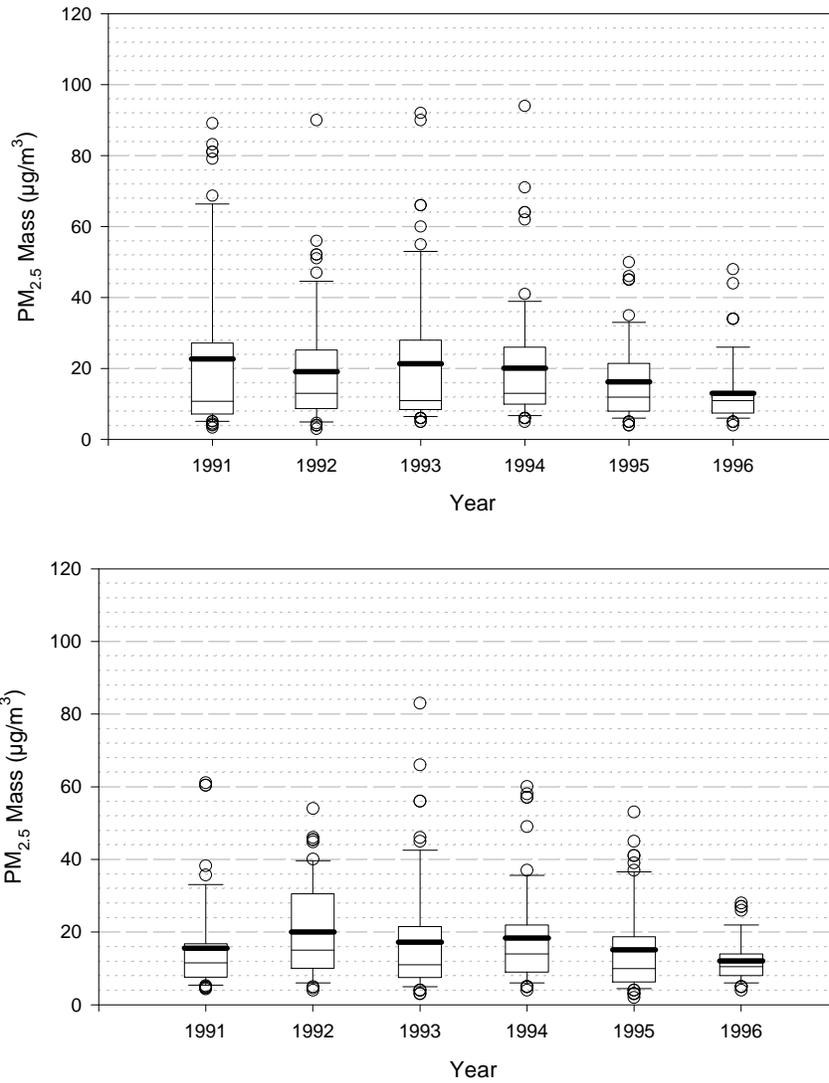


Figure 2.2-2. Annual average and maximum PM_{2.5} from 1991 to 1996 at Stockton (top), Modesto (middle) and Madera (bottom) for dichotomous samples. Circles =extreme values, dark bar=arithmetic average, light bar=median, ends of box=25th & 75th percentiles, whiskers=5th and 95th percentiles.

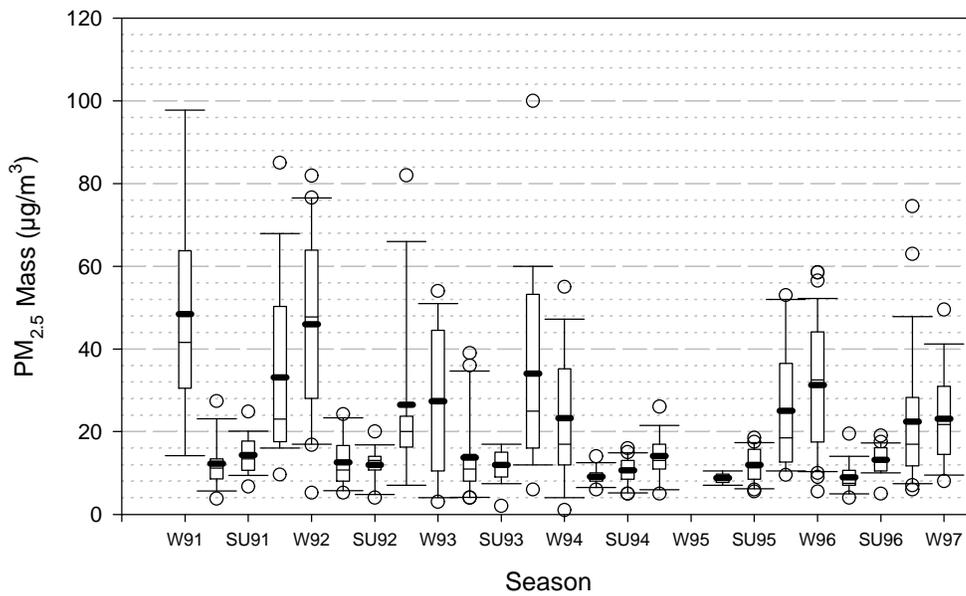
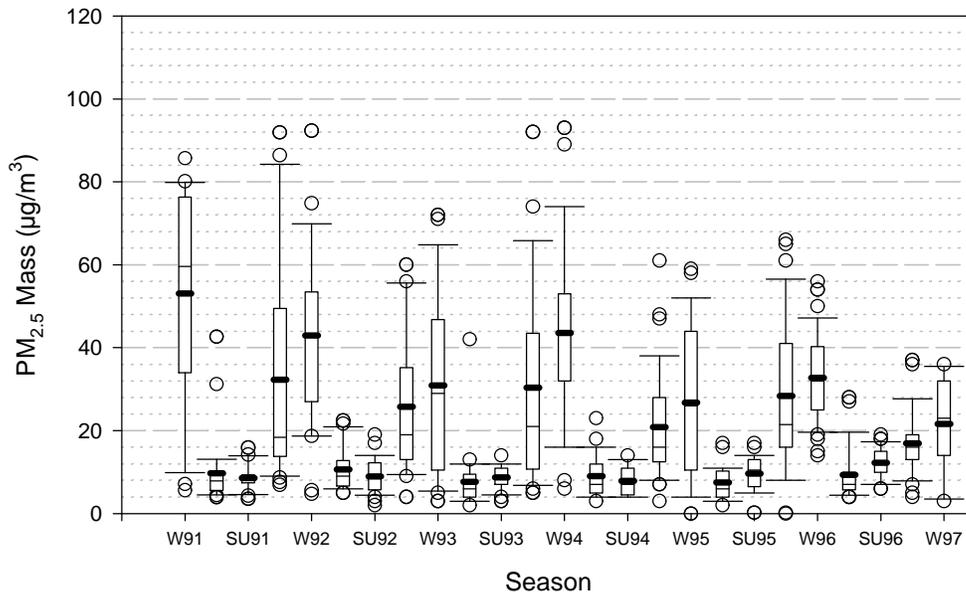


Figure 2.2-3. Seasonal summaries of $PM_{2.5}$ from 1991 to 1996 at Fresno (top), and Bakersfield (bottom) for dichotomous samples taken every sixth day. Circles = extreme values, dark bar = arithmetic average, light bar = median, ends of box = 25th & 75th percentiles, whiskers = 5th and 95th percentiles.

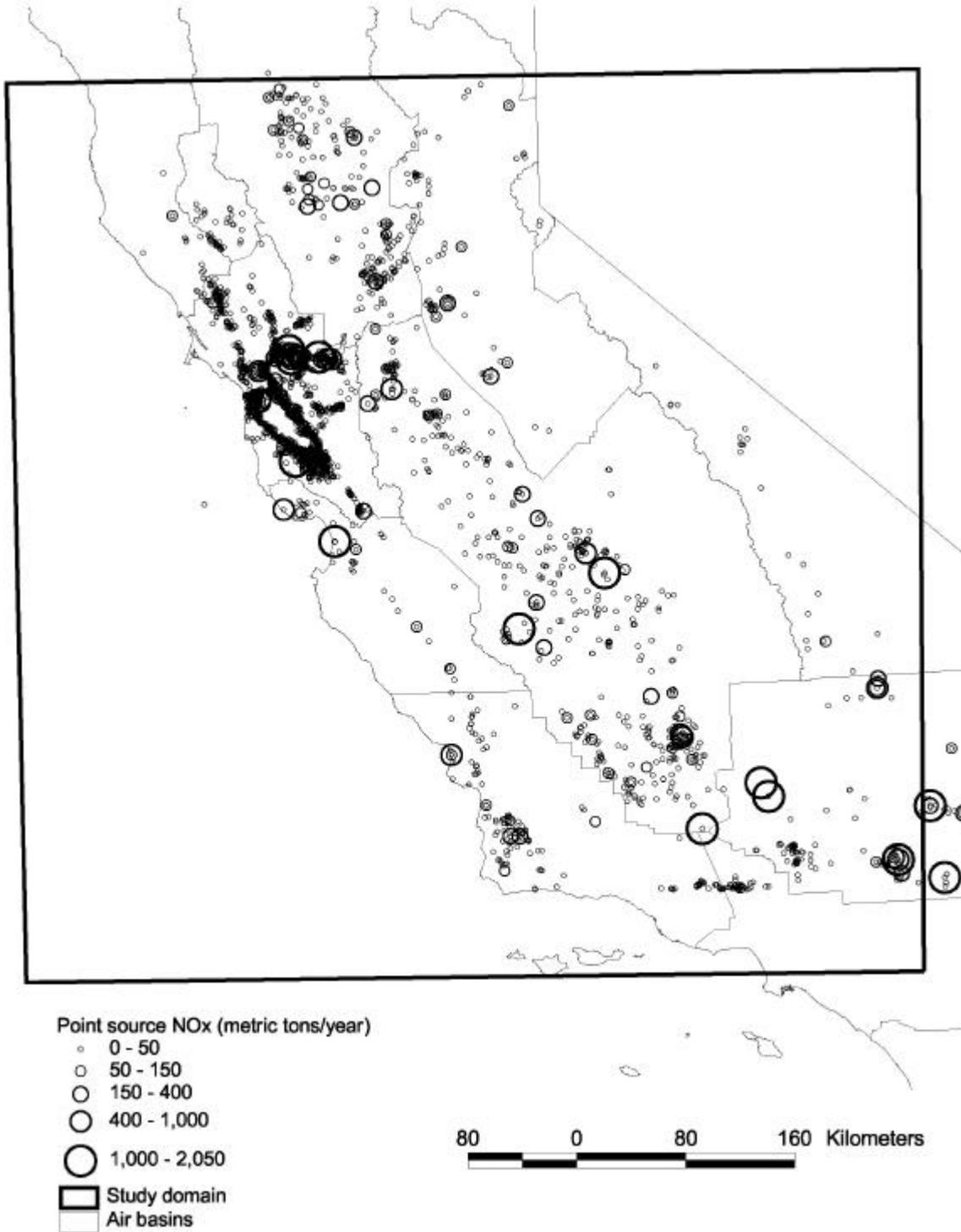


Figure 2.3-1. Locations and magnitudes of point source emissions. Diameter of symbol is proportional to NO_x emission rate.

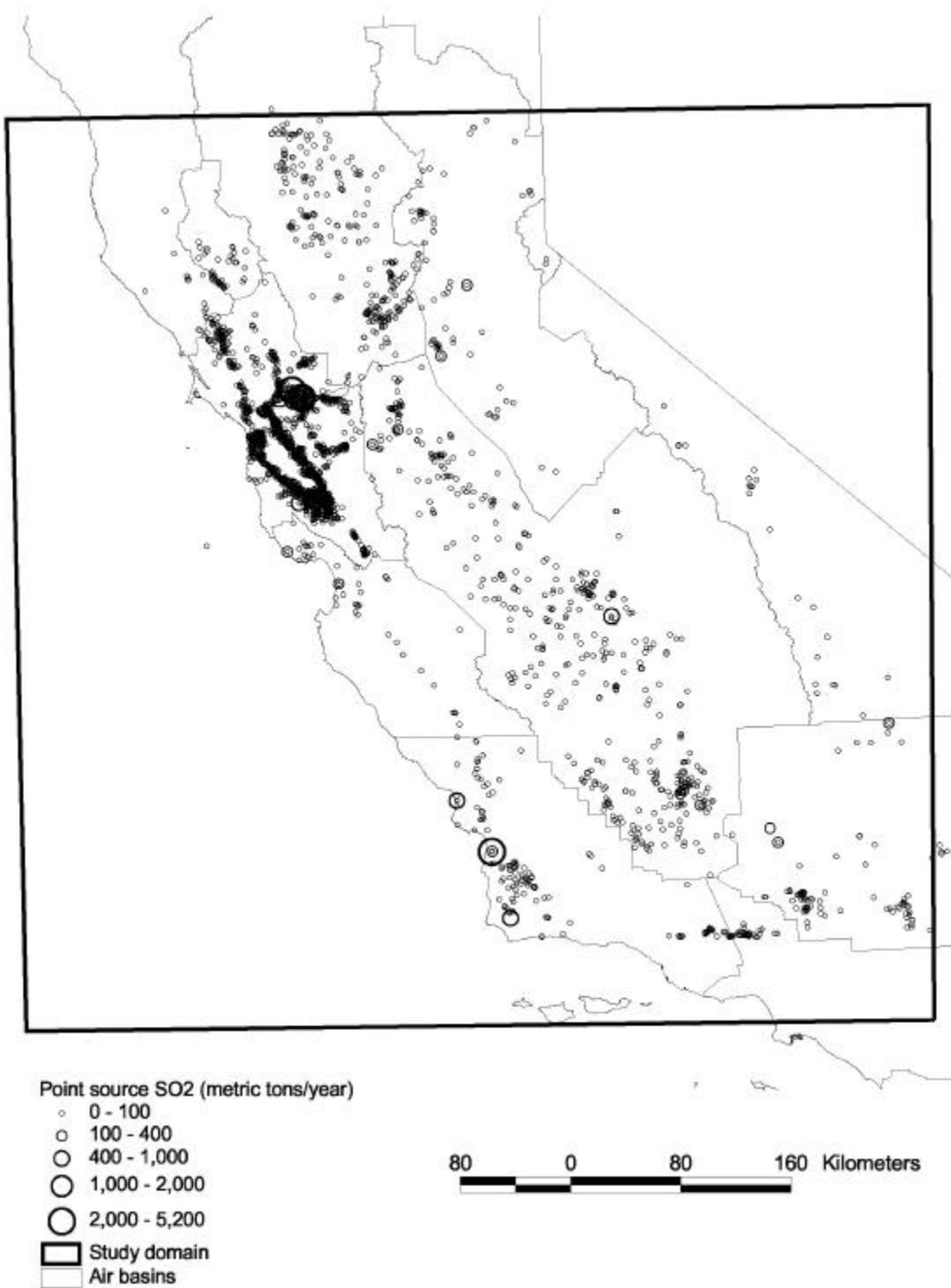


Figure 2.3-2. Locations and magnitudes of SO₂ point source emissions. Diameter of symbol is proportional to SO₂ emission rate.

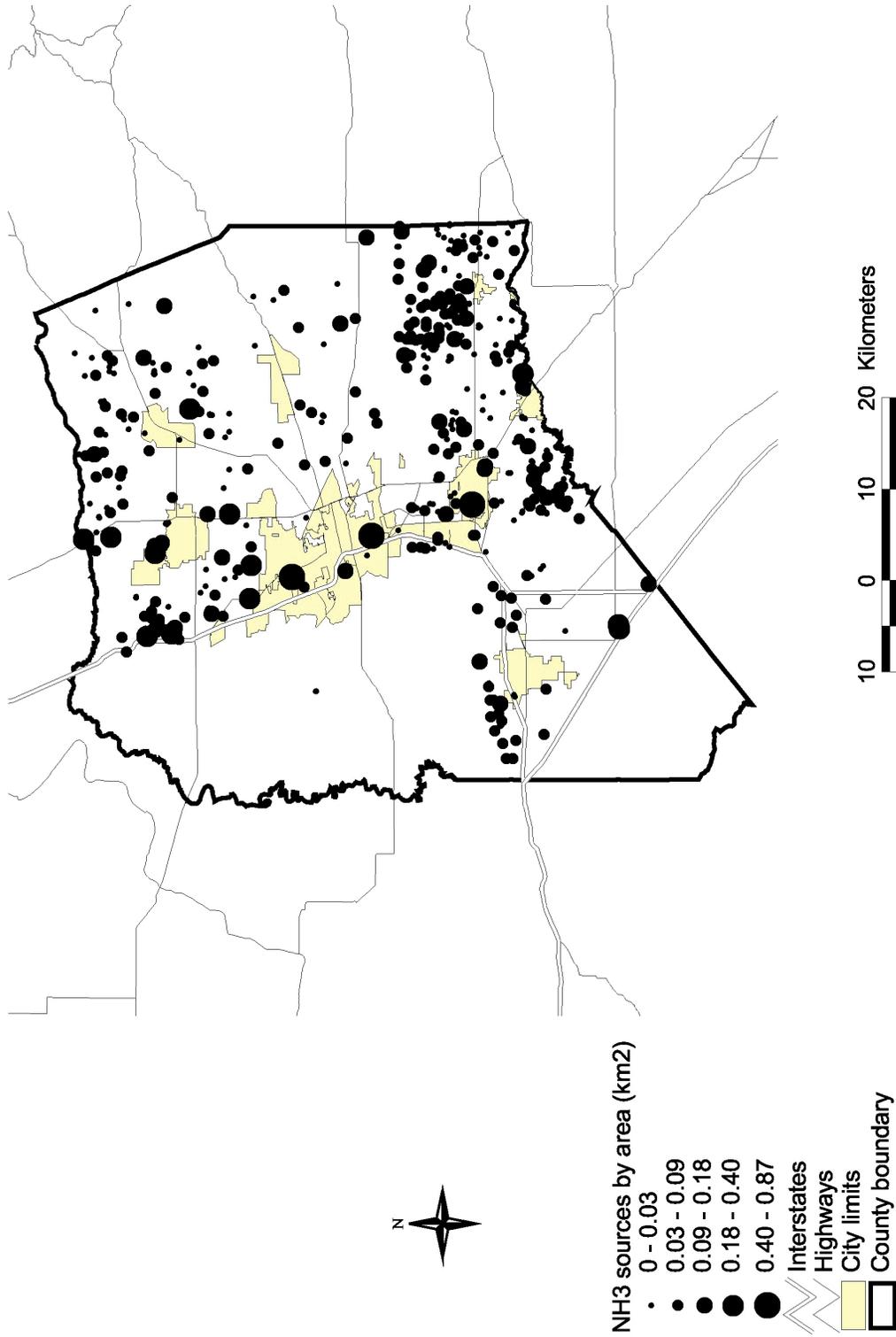


Figure 2.3-3. Locations and sizes of feedlots and dairies in San Joaquin County.

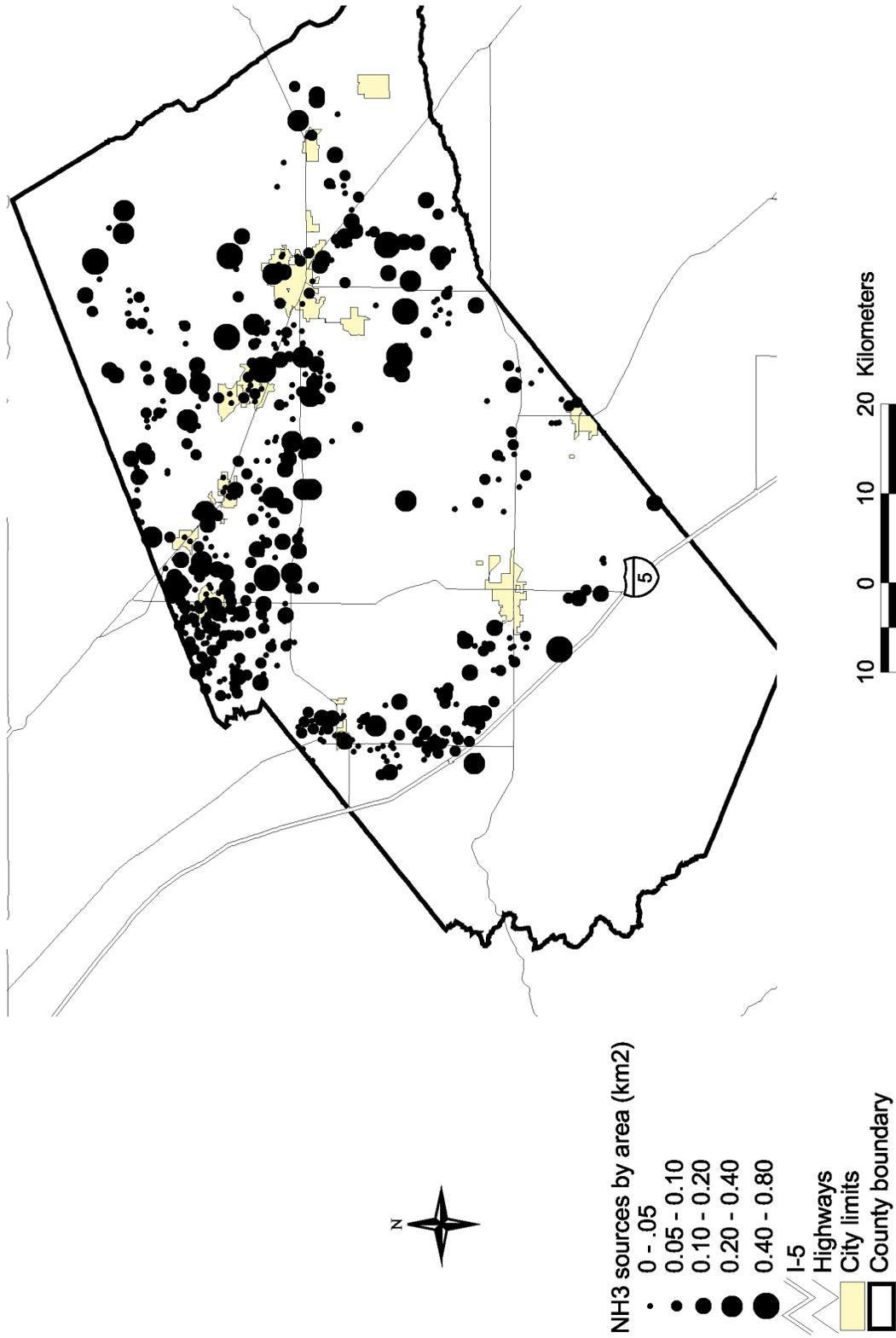


Figure 2.3-4. Locations and sizes of feedlots and dairies in Merced County.

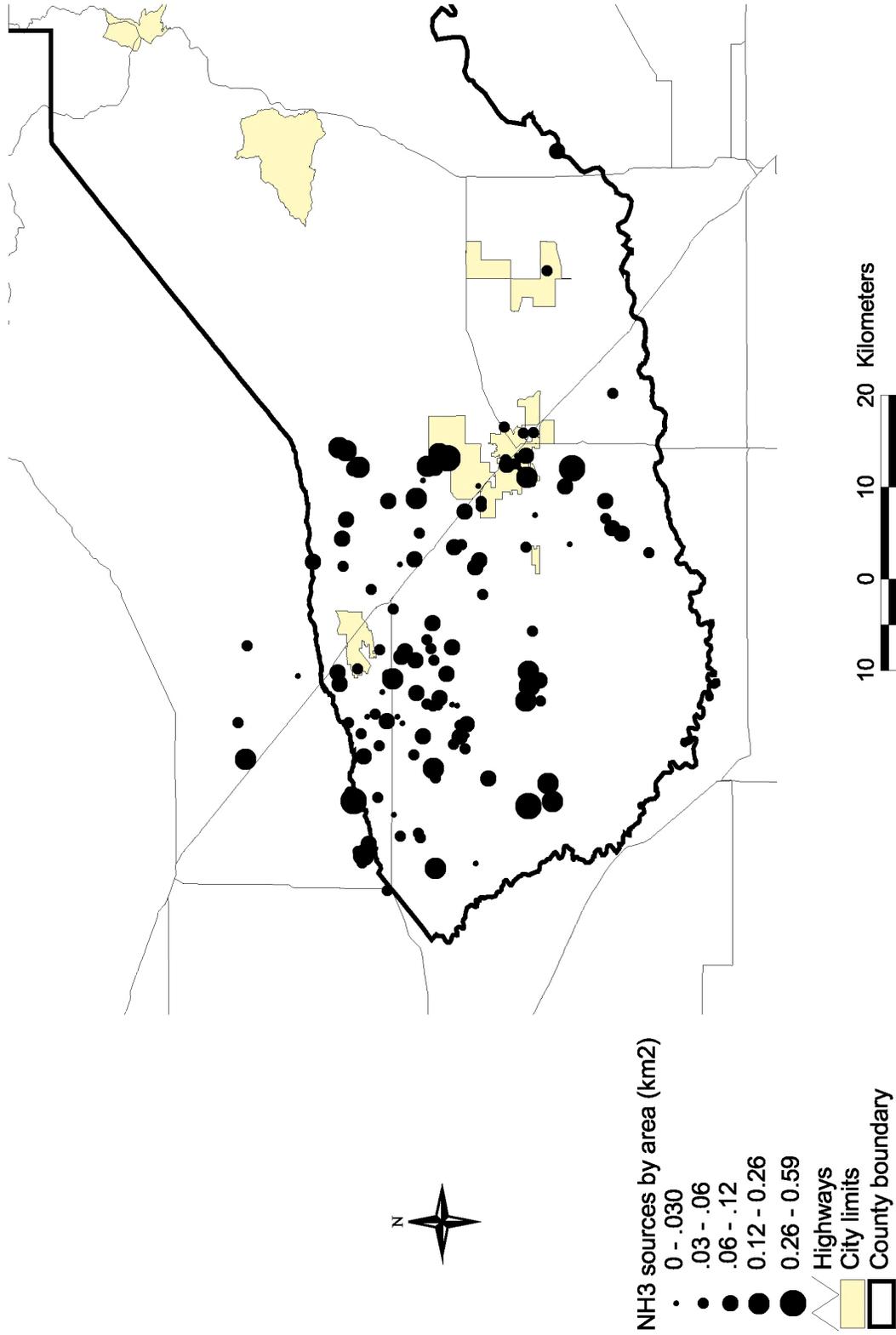


Figure 2.3-5. Locations and sizes of feedlots and dairies in Madera County.

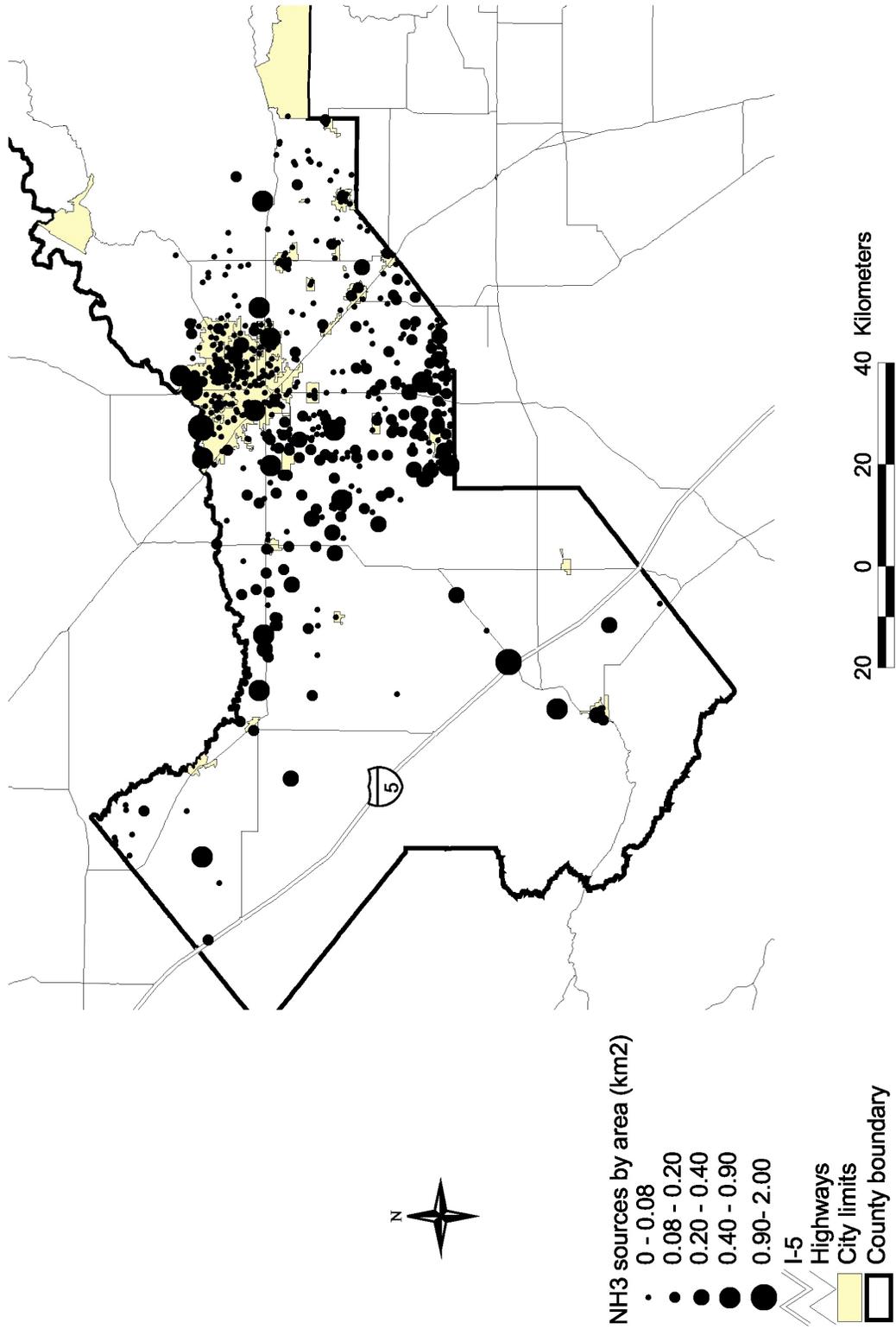


Figure 2.3-6. Locations and sizes of feedlots and dairies in Fresno County.

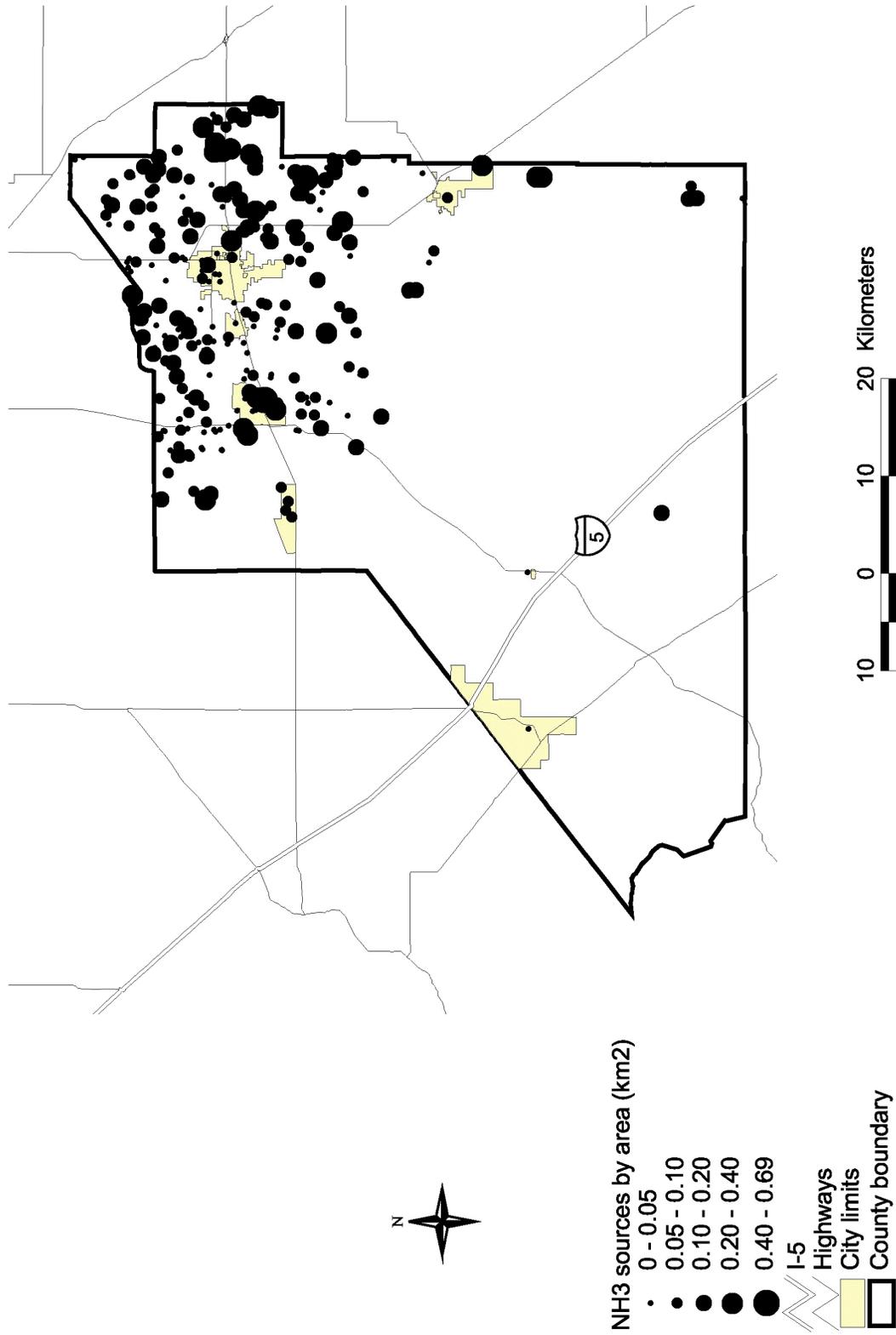


Figure 2.3-7. Locations and sizes of feedlots and dairies in Kings County.

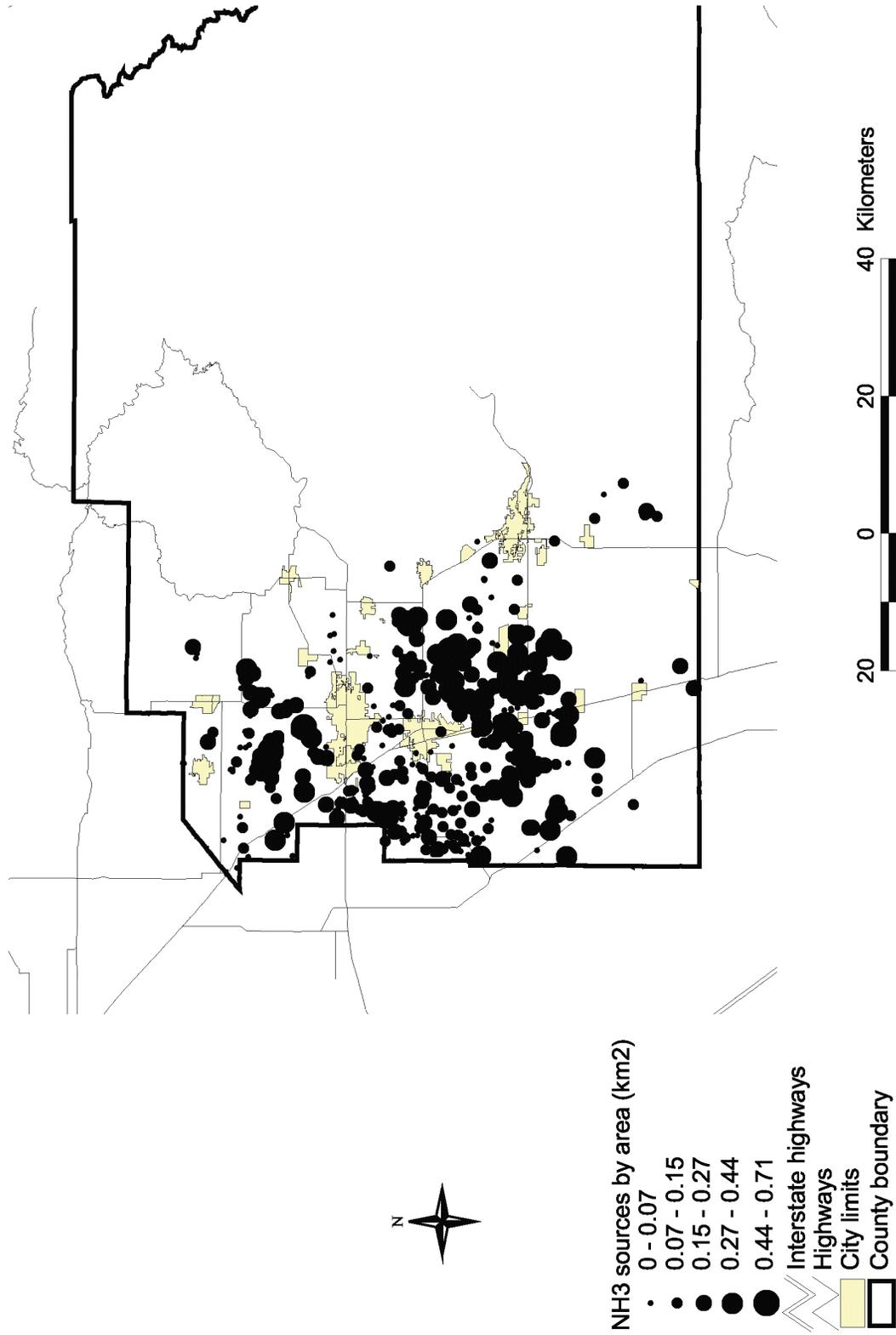


Figure 2.3-8. Locations and sizes of feedlots and dairies in Tulare County.

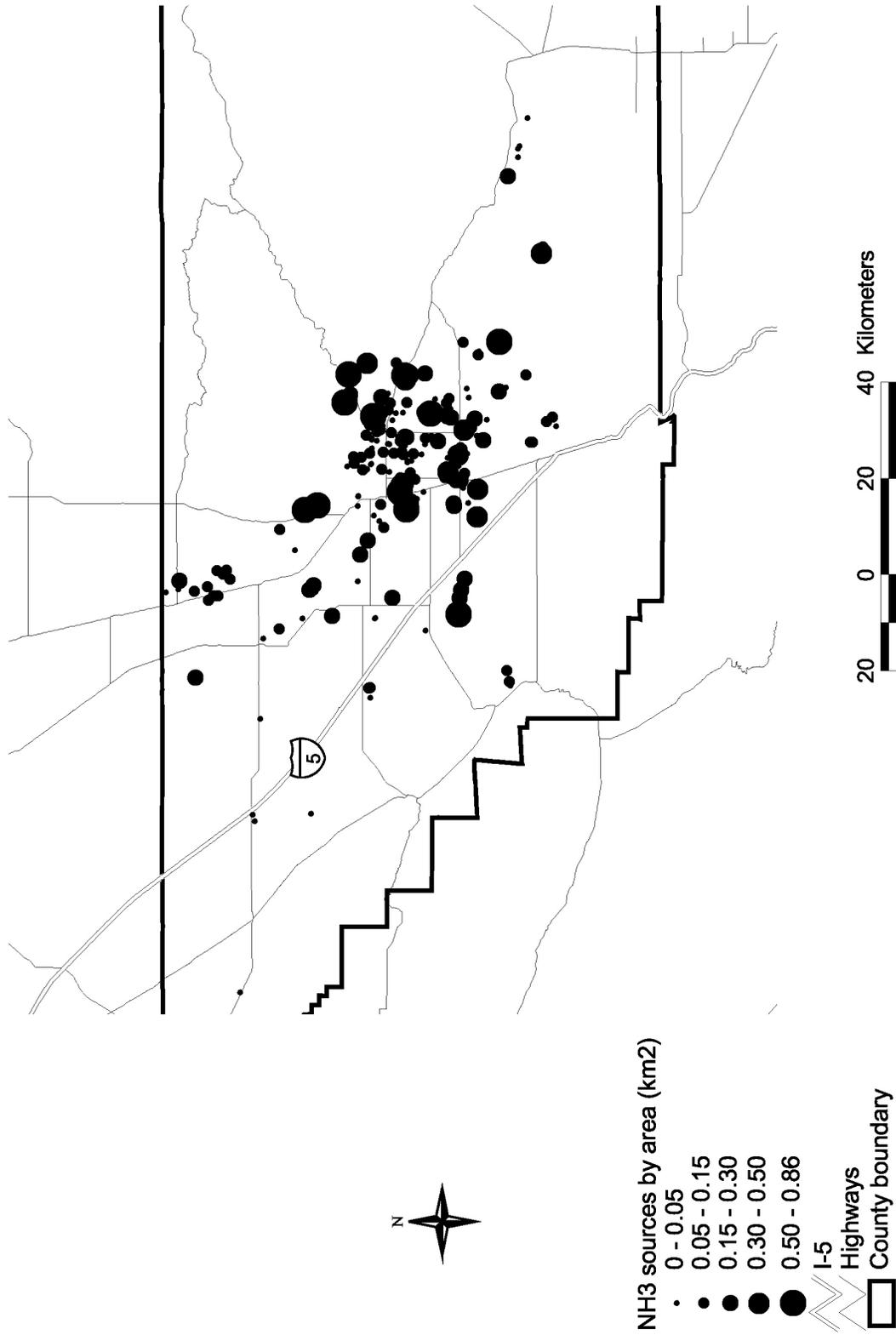


Figure 2.3-9. Locations and sizes of feedlots and dairies in Kern County.

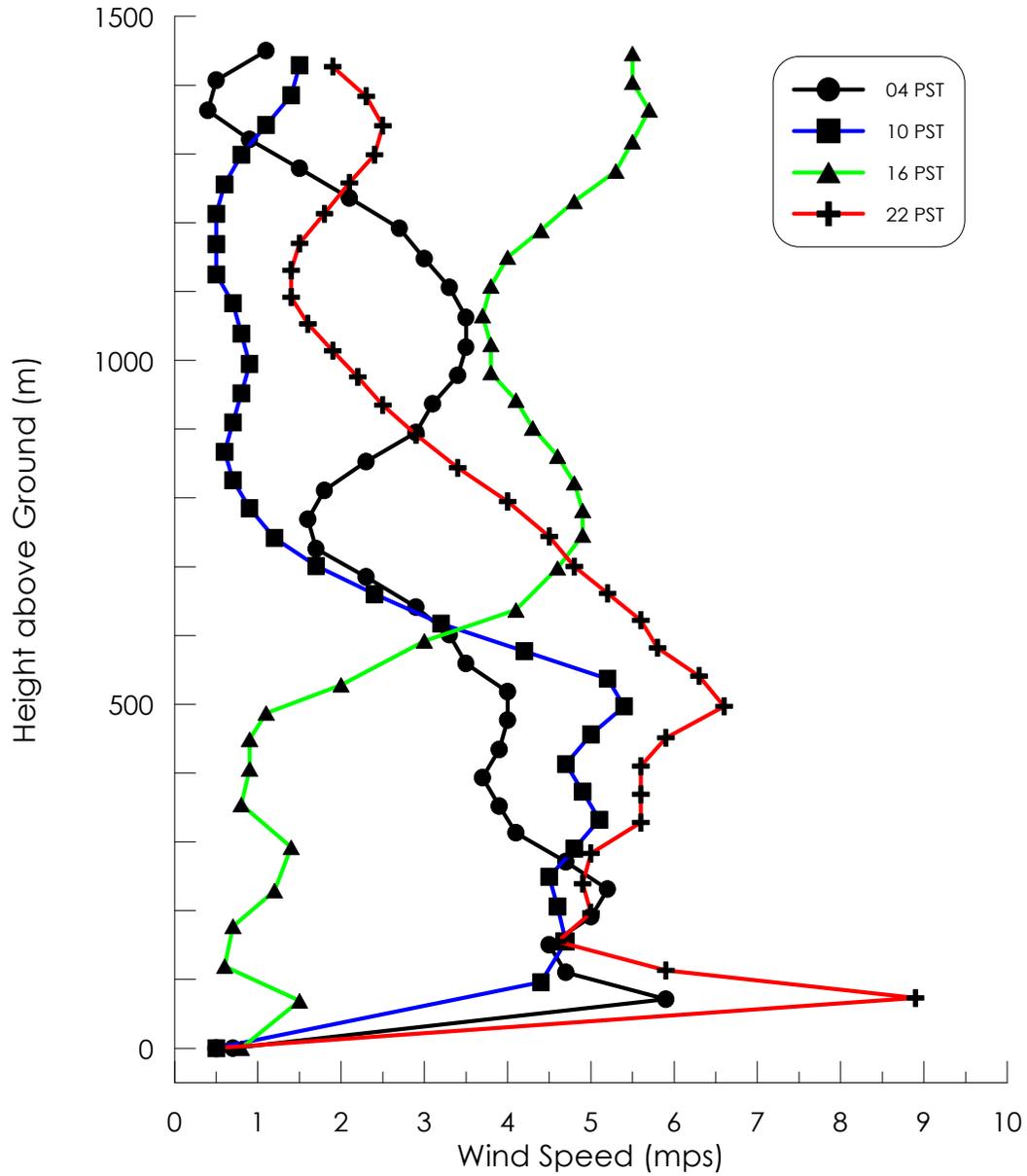


Figure 2.4-1. Wind speed vertical profiles at Fresno on January 3, 1996. Notice that most wind speeds aloft are much faster than wind speeds at the surface. Measurements are from rawinsonde releases during IMS-95.

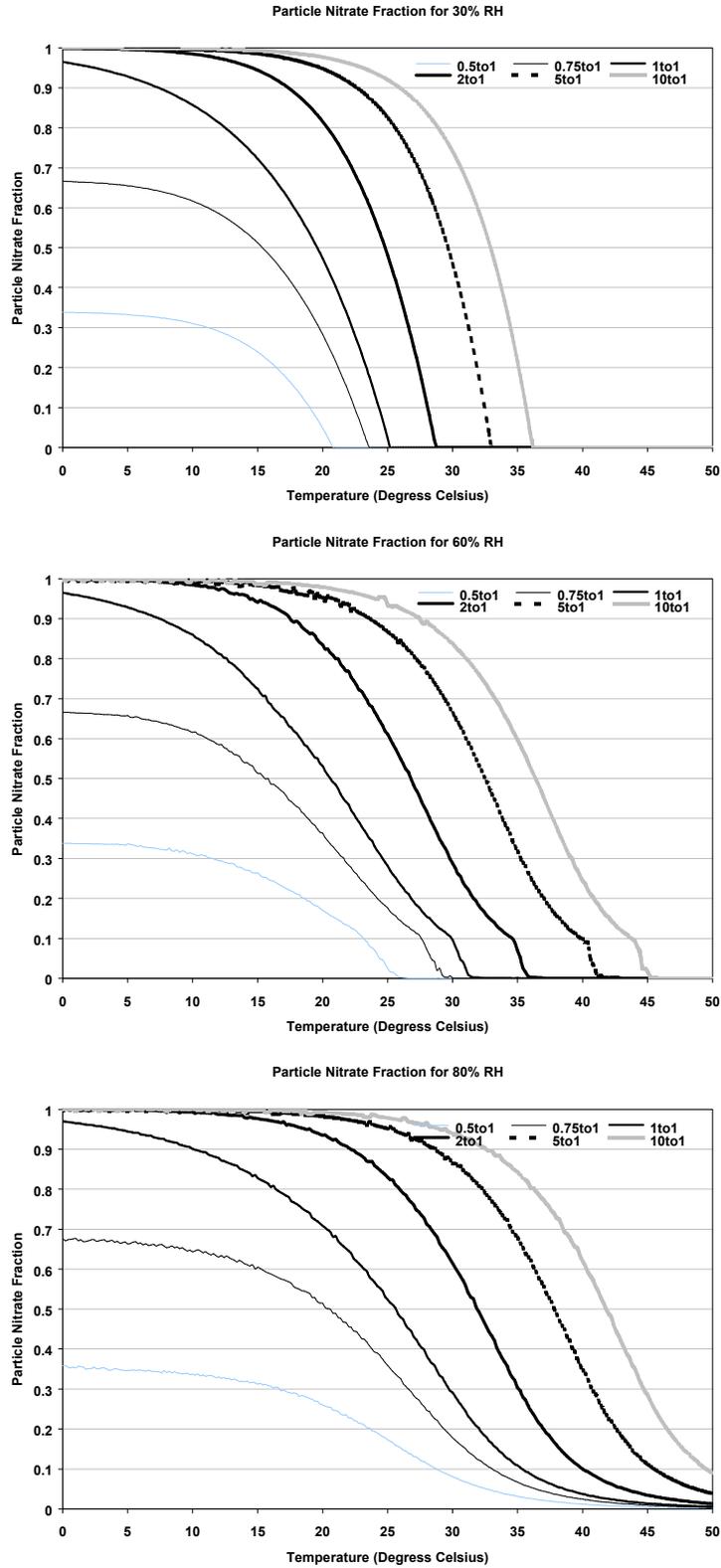


Figure 2.5-1. Fraction of total nitrate as particulate ammonium nitrate at different temperatures for various relative humidities and ammonia/nitrate molar ratios.

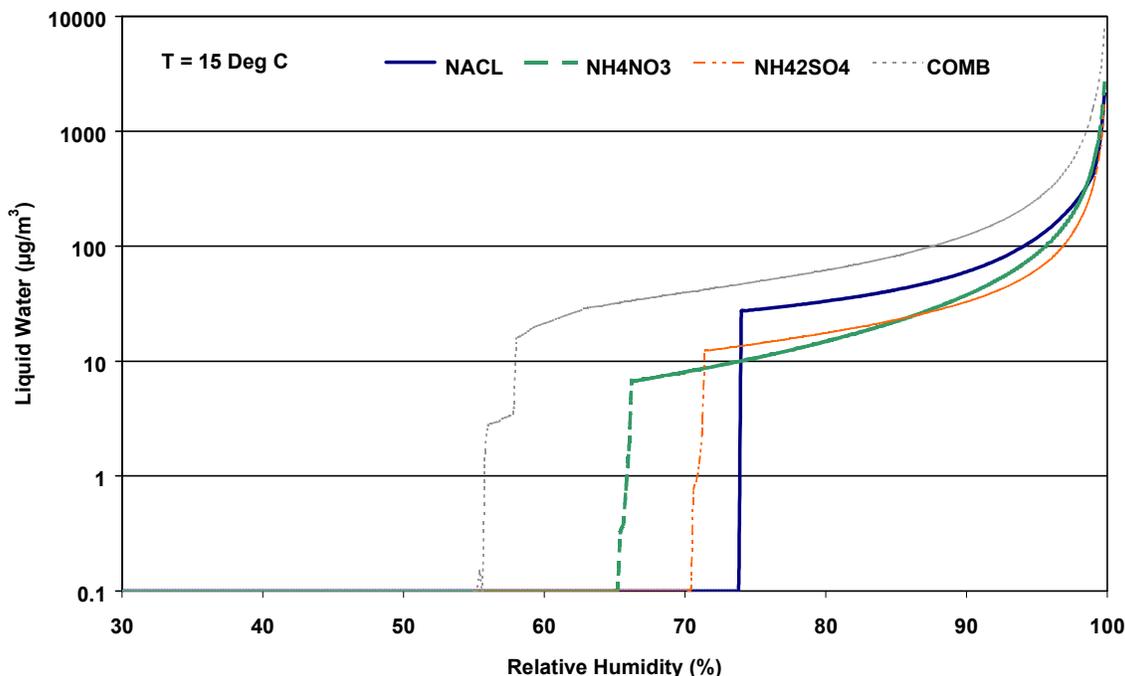


Figure 2.5-2. Changes in liquid water content of sodium chloride, ammonium nitrate, ammonium sulfate, and a combination of compounds at different relative humidities. These curves were generated from the SCAPE aerosol equilibrium model (Kim et al., 1993a; 1993b; Kim and Seinfeld, 1995; Meng et al., 1995). The NaCl case is for $3.83 \mu\text{g}/\text{m}^3$ of sodium ion and $6.24 \mu\text{g}/\text{m}^3$ of gas phase HCl. The NH_4NO_3 case is for $10 \mu\text{g}/\text{m}^3$ of gas phase HNO_3 and $10 \mu\text{g}/\text{m}^3$ of gas phase H_2SO_4 . At a temperature of 15 degrees Celsius, solid NH_4NO_3 is present for the lower relative humidities. SCAPE shows a deliquescence relative humidity of 66.2%, within 4% of the measured value of 62% for 25 degrees Celsius (Pruppacher and Klett, 1978). The $(\text{NH}_4)_2\text{SO}_4$ case is for $10 \mu\text{g}/\text{m}^3$ of gas phase NH_3 and $10 \mu\text{g}/\text{m}^3$ of H_2SO_4 ; there is sufficient ammonia to neutralize the available sulfate, and the gas-phase constituents are in equilibrium with solid-phase ammonium sulfate for the lower relative humidities. The deliquescence point of around 80% is expected (Tang et al., 1978). The COMB case consists of $10 \mu\text{g}/\text{m}^3$ of equivalent HNO_3 and H_2SO_4 , $20 \mu\text{g}/\text{m}^3$ of equivalent NH_3 , $3.83 \mu\text{g}/\text{m}^3$ of sodium ion and $6.24 \mu\text{g}/\text{m}^3$ of equivalent HCl. SCAPE yields solid-phase sodium sulfate, ammonium sulfate, ammonium chloride, and ammonium nitrate for the lower humidities, with a deliquescence relative humidity for the mixture of approximately 57%. This is in agreement with the fact that the deliquescence point for a mixture lies below the minimum deliquescence points for the individual salts (Wexler and Seinfeld, 1991; Kim and Seinfeld, 1995), and is in agreement with a deliquescence relative humidity of 56% found by Tang (1980) for a mixture of 45% by weight NH_4NO_3 and 55% by weight $(\text{NH}_4)_2\text{SO}_4$.

3. CONCEPTUAL MODELS, QUESTIONS, AND DATA NEEDS

This section integrates the results of previous PM studies in central California and elsewhere. It updates conceptual models that explain the mechanisms thought to cause elevated PM_{2.5} and PM₁₀ levels. The conceptual model for winter has changed substantially from previous versions as a result of new knowledge gained in the 1995 Integrated Monitoring Study (IMS95). This section re-casts and supplies answers to questions posed as part of the CRPAQS data analysis plan. Finally, it describes modeling approaches applicable to source apportionment and control strategy evaluation and the inputs required of those models.

3.1 Conceptual Models

As shown in Section 2, PM_{2.5} concentrations are high throughout the region during winter, and on a more localized basis during fall. PM₁₀ exceedances dominated by coarse, rather than PM_{2.5}, particles have been found during all seasons but not consistently throughout the central California region. The conceptual models for high PM_{2.5} occurrences are: 1) winter secondary aerosol formation in fog with primary source superposition; and 2) fall secondary formation without fog and primary source superposition. The conceptual models for high PM₁₀ concentrations that are dominated by coarse particles are: 1) low winds with nearby manmade dust sources; and 2) high wind dust suspension. These four conceptual models are not yet proven. They are consistent with results from prior field studies, analysis of existing data, and current knowledge of emissions, meteorology, and transformation. These four conceptual models serve as a basis for developing mathematical simulations and designing the field studies.

3.1.1 Winter Secondary Formation (fog) and Primary Source Superposition

The highest PM₁₀ and PM_{2.5} concentrations occur between mid-November and mid-February when several source contributions are superimposed on each other. Secondary ammonium nitrate is the largest component, often constituting more than 50% of PM_{2.5} in urban areas and even more in non-urban areas. Organic and elemental carbon are the next largest component, constituting 25% to 50% of PM_{2.5} in urban areas, but a much smaller fraction in non-urban areas. Ammonium sulfate and suspended dust constitute the rest of PM_{2.5}. Average ammonium sulfate levels are similar, at ~3 µg/m³, from the Bay Area to Bakersfield at present, although maximum sulfate concentrations are higher in Kern County than at sites further north. Measurements prior to 1993 showed twice as much average sulfate in Kern County as at other sites, and these increments were attributed to crude oil combustion in oilfield steam generators. The spatially uniform average sulfate concentrations show that using natural gas instead of crude oil has had a measurable and beneficial result. These changes are also evidenced by much lower vanadium and nickel concentrations that characterized crude oil combustion contributions in the past (Chow et al., 1992; White and Macias, 1991).

During winter, nitric acid constitutes 10% to 20% of total nitrate, with particulate ammonium nitrate constituting the particle phase. Ammonia concentrations are variable but always in excess of that needed to neutralize most of the available sulfuric and nitric acid.

Ammonium nitrate and ammonium sulfate concentrations are similar throughout the Bay Area and the San Joaquin Valley, and these concentrations are highly correlated on a day-to-day basis. Organic and elemental carbon and geological material are dissimilar, even within urban areas and especially when measurement sites are close to sources.

Oxides of nitrogen that are precursors to particle nitrate come from ground-level sources, mostly mobile. Ten to twenty percent of nitrogen oxide is emitted from elevated sources that may loft plumes above the top of the surface layer during nights and mornings, but not during the afternoon. Most of the tall stack NO_x remains within the valleywide layer. Some of these stationary sources also emit sulfur dioxide, but most sulfur emissions derive from combustion of diesel fuel and gasoline. Large numbers of diesel tractor trailers traverse highways SR 59, SR 99, and I-5, many of which have residual fuel purchased in neighboring states and not subject to California's fuel formulations. Construction with off-road equipment continues in the winter, as does some off-road agricultural activity, but it is not as intense as during non-winter months.

Gasoline-powered passenger vehicles and light trucks span a broad range of age and maintenance conditions. A few percent of the fleet are poorly maintained and have high particle emissions rates, only some of which are visible. Even well-maintained vehicles emit larger amounts of $\text{PM}_{2.5}$ during power enrichment cycles. Cold winter nights elevate emissions from morning cold starts as latent oil is cleared from engine chambers and a cold catalyst passes unburned and incompletely combusted gasoline. Diesels are the main source of heavy hydrocarbons that may turn into particles, but the quantities of these heavy hydrocarbons in cold start, visible emitters, and woodburning are unknown.

Ammonia is emitted everywhere, but it is highest near large concentrations of animal waste, such as that found at feedlots and dairies. Wastewater treatment plants are only moderate ammonia emitters, and ammonia near chicken coops, turkey coops, and in urban areas is similar to regional concentrations. Agricultural burning is uncommon as are forest fires, but residential wood burning is popular during the holiday season.

After a recent frontal passage, a Great Basin high pressure system sets in. Satellite photos show that another storm is not due for a week or more. The ground is wet, humidities are high and a low bank of stratus clouds extends from Sacramento to Bakersfield in the SJV. The days are sunny and clear in the desert, near the mountains, and along the coast with some patchy morning fog in the Bay area and Livermore Valley.

The cold and damp weather is alleviated by a warm fire in the fireplace or wood stove in urban residential areas. This activity is enhanced several fold on Thanksgiving weekend and from a few days before Christmas until after New Years. Surface wind speeds are low, all day long within the SJV, often <1 m/s, and directions are variable throughout the day and from site to site. Cold starts in the cities during morning rush hours inject a larger quantity of primary particles, highly enriched in organic and elemental carbon, into the shallow radiation layer than during any other part of the day. These are accompanied by higher nitrogen oxides and light and heavy hydrocarbon emissions. Sulfur emissions are consistent throughout the day and are directly proportional to the sulfur content of the combusted fuels.

Primary particle and precursor gas concentrations are added to whatever has accumulated from previous days.

By early morning, the sun breaks through the stratus cloud layer and heats the surface to an extent that the surface-based radiation layer rises into the valleywide mixed layer. This mixing is very rapid after 1000 PST and is complete before 1400 PST. The accumulated primary particles and precursor gases in this layer mix aloft, reducing surface concentrations in the cities. Analogously in non-urban areas, ammonia from feedlots, dairies, and wastewater treatment plants that accumulated during night and morning mix aloft and their surface concentrations are also diluted.

Afternoon solar radiation engenders photochemical reactions. Nitric acid and ozone are formed as hydroxyl radicals are produced within the valleywide layer. The stratus cloud formation and evaporation at the top of the valleywide layer also mixes ozone and other oxidants from the clear sky above down into the valleywide layer, as well as venting some of the pollutants that mixed aloft. This venting is small compared to the influx from the surface. Nitric acid, ozone, and secondary aerosol are formed aloft during the afternoon. This formation is not as rapid as during summer. With low wind speeds and a shallow valleywide layer, however, their concentrations increase each day. The patchy stratus clouds contain small water droplets that absorb the available gases, including the produced and entrained ozone and sulfur dioxide, and rapid conversions to sulfate occur in the droplets. Available ammonia is scavenged first by the resulting sulfuric acid, leaving an excess of nitric acid aloft.

After sunset, the radiation inversion again sets in, effectively separating the pollutants aloft from those being accumulated at the surface. Wind speeds aloft pick up, but directions are variable throughout central California. The “upwind” or “downwind” location of a receptor is not well-defined or consistent, as it is during the summer. During some occasions, slightly negative pressure gradients between the Pacific Coast and the SJV may result in offshore flows through the Carquinez straits; the distance from which pollutants emitted in the central to southern part of the SJV could arrive at the Bay Area is unknown.

Although upper air transport directions are inconsistent, wind speeds are sufficient to mix ammonia from the non-urban feedlots and dairies with the nitric acid formed during the afternoon and by nighttime reactions in cloud droplets. Ammonium nitrate particles form and remain in the particulate phase owing to the low temperatures, high humidities, and abundance of ammonia. On the following day, this cycle repeats itself. Secondary ammonium nitrate, ammonium sulfate, organic carbon, and aged primary emissions from the day before mix to the surface in urban and non-urban areas. $PM_{2.5}$ remains from the day before and is augmented by fresh accumulations during the night and morning. The afternoon dilution of this mixture is counteracted by the down mixing reacted gases and primary emissions from previous days. By the fourth or fifth day of an episode, $PM_{2.5}$ has achieved levels that contribute substantially to the annual average and has the highest potential to cause exceedances of the 24-hour standards.

Attenuating this buildup is the day-to-day afternoon dilution and spreading of urban emissions throughout the SJV. In non-urban areas, especially in the rural central and

northern SJV where surfaces are intensely irrigated, surface fogs form that scavenge particles near the surface and remove them by deposition. Although additional sulfate formation in droplets nearly balances deposition losses, ammonium nitrate concentrations show a net decrease. Surface fogs are infrequent and highly variable in the warmer cities, however, and deposition losses are lower than in the countryside. Bakersfield experiences fewer and less intense fogs than does Fresno, owing to its drier land surfaces, so ammonium nitrate concentrations may be slightly higher. Bakersfield is also in closer proximity to the few remaining point sources of sulfur dioxide, and when aqueous-phase transformation conditions are right, ammonium sulfate levels are higher in that city than in other parts of the SJV. This is not a common occurrence, however, as evidenced by maximum 24-hour sulfate concentrations being only slightly higher than in other parts of the SJV.

At last, a fresh Pacific storm front arrives, breaking up the valleywide mixed layer, scavenging particles with rain, and ventilating the San Joaquin Valley atmosphere up and over the Sierra Nevadas or into the Mojave Desert. These storm tracks are variable, however, and this cleansing may affect the northern or southern SJV without affecting other parts of the Valley.

This process repeats itself several times throughout the winter season, and the buildup to highest levels depends on the number of days between storms, with a minimum of four days before a buildup would be classified as an “episode.” No single source type contribution causes the PM_{2.5} standards to be exceeded. It is the combination of the primary and precursor source emissions, the persistence of the valleywide layer, and the formation processes for secondary aerosol that all occur simultaneously to yield the highest PM_{2.5} concentrations.

3.1.2 Fall Secondary Formation (no fog) and Primary Source Superposition

Although secondary particle contributions are highest during winter, having been found to exceed 100 µg/m³ of PM₁₀ in the past, they attain 20 to 40 µg/m³ levels from late September through early November when there are no fogs, the air is relatively dry, and temperatures are moderate. While PM₁₀ concentrations are driven by PM_{2.5} concentrations in winter, and solving the wintertime PM_{2.5} problem will also address the wintertime PM₁₀ problem, both PM_{2.5} and PM₁₀ standards could be exceeded during the fall. These exceedances would not be as regional as the wintertime concentrations as the valleywide mixed layer is much deeper and there is still a well-defined, albeit weak, along-axis flow that eventually ventilates particle accumulations into the Mojave Desert. The central SJV is most likely to experience PM_{2.5} and PM₁₀ exceedances under this situation.

Agricultural burning, harvesting, and planting are very active during this period, but residential wood combustion is not. Temperatures are moderate rather than hot or cold. Photochemical activity produces substantial amounts of nitric acid, owing to clear skies and sunlight that is present for several hours longer than during December. There are no fogs and the ground is dry. The principal ammonia sources are the same as during winter, dominated by feedlots, dairies, and water treatment plants in non-urban areas. Additional ammonia is released after fertilizer application and from natural soil emissions.

During clear sky stagnation, the thermal low over the Mojave Desert has weakened owing to a Great Basin high pressure system, and downvalley flows weaken. There are few calms, however, and primary particles and precursor gases generated in the cities move slowly downvalley, diluting and depositing as they travel. Cotton, the most abundant crop in the SJV, as well as other crops are harvested during fall and land is prepared for new planting. Numerous agricultural activities suspend dust from fields. Most of this dust drops from the atmosphere within less than 100 m from the emissions point, but a small amount from each emitter remains suspended, adding to the overall atmospheric burden.

Off-road vehicle emissions are larger, as farm implements ply fields and construction crews rush to finish projects before the winter rains. Large tractor trailers ply rural unpaved roads and paved roads with unpaved shoulders at high speeds as they rush to carry their payloads to processing facilities and return for the next load. In addition to diesel exhaust, these trucks generate dust emissions from the roads and shoulders and carry dust onto paved streets in urban areas where it is further ground down and suspended by normal urban traffic. Harvesting continues for twenty-four hours a day, so there is no let up in these dust and vehicle emissions.

Temperatures and relative humidities are marginal for favoring the particle phase of ammonium nitrate. The ammonia concentration is more influential on ammonium nitrate levels during fall than during the stagnation with fog situation. As nitric acid forms in a reactive plume downwind of major roadways and urban centers it passes across large dairy and feedlot ammonia emissions that shift equilibrium to the particulate ammonium nitrate phase. These particles, with deposition velocities one fifth to one tenth that of nitric acid, have longer residence times and can travel further downwind than the precursor gases. As afternoon winds abate and temperatures lessen, particulate nitrate during night and morning makes substantial contributions to the 24-hour average. Light and variable nighttime and morning winds may carry these particles back to their city of origin or to downwind cities.

3.1.3 Low Wind Local Source

When surface wind speeds are consistently sluggish ($< \sim 4$ m/s), a high PM_{10} concentration is sometimes measured at a single receptor in an urban or non-urban area. This is usually caused by a localized emitter in that area for which concentrations are substantially diluted after brief transport. The 1990 $435 \mu\text{g}/\text{m}^3$ PM_{10} concentration recorded at Kettleman City, which was subsequently associated with a storage pile movement, is an example of this situation.

The low wind local source situation is usually encountered at a population-oriented monitoring site owing to a nearby, and temporary, activity that ejects large amounts of dust into the atmosphere. The low wind local source condition may exist for $PM_{2.5}$ residential wood burning or cooking, but $PM_{2.5}$ community-oriented siting criteria (see Section 8) should minimize this effect. In urban areas this is often associated with roadwork, construction, or material storage near the monitoring site. In non-urban areas, nearby sources include tilled fields, unpaved roads, and agricultural burning. Primary emissions dominate the cause of the excessive PM. This situation has been found most often during non-winter months when dust suspension is not suppressed by moisture and construction and agricultural

activities are more intense. Intermittent emissions information is often unavailable for these episodes, and they can only be interpreted after the fact by anecdotal observation or analysis of particle chemistry.

Since wind speeds are below the dust suspension threshold, a suspension mechanism is needed. This is primarily vehicle movement and the contact of tires with the dust surface. This contact decreases the particle size due to grinding of the dust by tires, and it adds a portion of the ground up tires to the dust. The wake induced by vehicle passage also adds to the suspension and increases the vertical mixing of the dust. During construction, dust is blown from haul trucks as they move dirt from one part of a site to another part. The contact of farm implements with surfaces also decreases particle sizes and injects dust into the atmosphere.

Middle- and neighborhood-scale studies show that the zone of influence of a local source is small, not more than 100 m. Community-representative monitoring sites should not experience this type of situation except under identifiable circumstances of a rarely implemented nearby activity. If the nearby activity becomes routine, then the site's zone of representation is small and it can no longer be classified as community-oriented. Owing to the coarse nature of nearby suspended dust, this situation will effect PM_{10} as well as $PM_{2.5}$ concentrations. As noted in Section 1, the statistical forms of both the $PM_{2.5}$ and PM_{10} standards lessens the importance of an infrequent maximum occurrence at a single site such as that represented by this conceptual model.

3.1.4 High Wind Dust Suspension

High winds over disturbed surfaces can raise dust into the air and transport it over long distances. Prior to passage of a frontal system, wind speeds exceed suspension thresholds (>5 m/s). After years of drought, land is dry, and many fields are fallow owing to lack of water. Winds cause particles to saltate, thereby breaking larger particles into smaller particles. These particles are mixed throughout the mixed layer owing to substantial vertical components of the wind. The highest PM concentrations are observed at measurement locations closest to the disturbed land, but the deep mixing layers and turbulent updrafts can keep dust particles suspended for transport over long distances. Concentration distributions shift toward the $PM_{2.5}$ size fraction with distance from the source as larger particles deposit owing to gravitational settling.

The geological component at several sites increases, although not always to an extent that the 24-hour PM_{10} or $PM_{2.5}$ standards are exceeded. Owing to the longer transport distances, much of this dust deposits onto paved roads, where it can be resuspended by vehicles.

This and the prior conceptual model are highly influenced by the analysis of PM_{10} measurements taken during the drought years of 1986 through 1992. More recent years have experienced normal or above normal precipitation, resulting in higher soil moisture content and increased vegetative cover. Both of these decrease the erodibility of soil by wind. Erodibility is poorly understood in central California.

3.2 Questions and Answers

The following questions have guided CRPAQS analysis of long-term historical data and data from IMS95.

3.2.1 How well do PM measurement systems quantify mass concentrations, particle sizes, and chemical components?

- What is the comparability and equivalence among collocated sampling methods, what are the biases of one instrument with respect to others, and how can these biases be minimized?
 - Collocated filter-based samplers can provide mass measurements within 0.5 to 5 $\mu\text{g}/\text{m}^3$. Equivalence is better for $\text{PM}_{2.5}$ than for PM_{10} measurements, probably owing to more precise mass measurements on smaller filters and lower breakthrough from smaller particles. There are still some notable outliers.
 - Heated TEOM PM_{10} mass measurements are equivalent to collocated filter measurements during summer when geological material and carbon are the major components, but they are ~50% of filter-based measurements during winter when volatile species are present.
 - $\text{PM}_{2.5}$ is predictable from collocated light scattering measurements, even during high humidities, when accurate relative humidity measurements >70% are available. $\text{PM}_{2.5}$ is predictable from light scattering measurements if a heated nephelometer is used such as ARB's method V.
 - MOUDI samples for RH >80% are inaccurate owing to condensation and deposition in the impactor.
 - The aethalometer provides a high time resolution measurement of light absorption. Although the measurements are precise and repeatable, the method lacks primary standards to accurately relate its results to light absorption and black carbon. Its readings can be correlated with collocated filter measurements.
 - The Minivol saturation samplers are capable of acquiring data comparable to fixed, higher flow rate samplers. There are some large discrepancies that are probably operational rather than inherent limitations of the measurement device. The PM_{10} and $\text{PM}_{2.5}$ inlets that are commonly used have not been characterized.
 - Continuous ammonia monitors adapted from nitric oxide analyzers have not been shown to be comparable to filter measurements.
 - Continuous (10 minute) nitrate particle measurements are feasible and are comparable to filter measurements.
- How do changes in sampler inlet characteristics affect PM_{10} and $\text{PM}_{2.5}$ mass concentrations?
 - Changes in PM_{10} inlet cutpoints of one micron, which have been demonstrated for different inlet designs and amount of deposited material, can cause 20% differences in collocated measurements. Samplers with $\text{PM}_{2.5}$ inlets typically

yield collocated mass concentrations within $\pm 10\%$ of each other. Mass differences for samplers with differences between different $PM_{2.5}$ inlets are minimal.

- How much ammonium nitrate is lost in the sampling and analysis process?
 - More than 50% of ammonium nitrate is lost during summer and spring sampling. Less than 10% is lost during winter sampling when filters are handled and stored at reduced temperatures. Backup filters without denuders provide an adequate estimate of nitric acid during winter.
 - Discrepancies were found during IMS-95 between backup filter ammonia on Minivol and SGS filters.
- How much organic carbon is lost from samples due to volatilization and how much organic carbon is really due to adsorption of vapors on filters?
 - Volatilized organic carbon has not been quantified. However, measured mass is reproduced, or sometimes overestimated, by summing chemical components. Losses would need to be the same on Teflon and quartz filter for this to occur.
 - Organic carbon on backup filters behind Teflon filters is 10% to 20% of front filter carbon during winter and up to 50% of front filter carbon in summer. The absolute organic carbon concentration on backup filters is highest during summer. The causes of this backup filter carbon are unknown.
- What combinations of instrumentation and analysis are most practical for research and long-term compliance monitoring?
 - The $PM_{2.5}$ Federal Reference Method (FRM), sequential filter sampler with Teflon/quartz filters, Minivol, TEOM, aethalometer, beta attenuation monitor, organic/elemental carbon analyzer, and nephelometer are practical for application in long-term networks with 24-hour filter samplers. The Minivol and some versions of the nephelometer are small, inexpensive, and battery powered. They can be inexpensively deployed and operated at a large number of sites for 24-hour sampling periods.
 - Continuous in-situ measurement of 55 light hydrocarbons with continuous gas chromatographs is feasible and practical, but it is costly.
 - Diurnal resolution with filter samples is feasible, but not practical, for many sites in long-term networks owing to costs, labor, and logistics. Even in short-term episodic networks, five hundred filter packs/day, the amount processed during IMS95, stresses existing research capabilities.
 - Continuous in situ measurements of particulate nitrate, particulate sulfate, nitric acid, and individual particles are feasible, but not practical for long-term networks. These can be applied at up to five locations during episodes.
 - Substrate and canister measurements for light and heavy hydrocarbons and organic particles are feasible, but not practical, for long-term networks. These can be applied at up to five locations during episodes.

- Continuous in situ ammonia measurement methods exist, but they have not been proven feasible.
- Continuous in situ elemental or speciated organic measurements are not feasible or practical. Samples must be acquired on substrates for later laboratory analysis.

3.2.2 What are the temporal and spatial requirements for research and compliance monitoring networks?

- How well do existing PM monitoring sites represent human exposures and maximum source impacts?
 - Most central city sites in central California are well placed for urban-scale representation. Bakersfield (California Street) and Fresno (First Street) are well-located for representing exposures in those communities. On average neighborhood-scale contributions are <15% of urban- and regional-scale contributions. These sites measure lower concentrations, by $\sim 10 \mu\text{g}/\text{m}^3$, with respect to some nearby neighborhoods, especially ones that burn wood during winter.
- How should monitors be sited and what should they measure to corroborate emissions rate measurements for large PM contributors?
 - For 24-hour samples, source-oriented monitors need to be located right next to, and nominally downwind, of an emitter to detect differences in its contributions. High-time resolution (minutes) monitors detect nearby source contributions as pulses that correspond to wind direction. Most nearby primary emissions are undetectable at distances more than 50 to 100 m from the emitter in a 24-hour sample.
 - Primary emissions, e.g. dust, organic carbon, elemental carbon, and ammonia, are most variable and most affected by proximity to the source and are quantified at source-oriented sites.
 - During fall, a large ammonia source may change ammonium nitrate equilibrium toward the particle. Nitric acid upwind and downwind of such a site should be measured in this situation.
- What are monitoring siting characteristics needed to represent neighborhood, urban, and regional PM concentrations and to evaluate transport between source and receptor areas? What differences in characteristics exist for primary and secondary contributions?
 - Sporadic observations of nearby activities, even when made everyday, are not a reliable predictor of high or low concentrations or of measurable increments in 24-hour PM concentrations.
 - Most PM episodes occur under sluggish surface transport. During winter, regional mixing appears to occur aloft with coupling to the surface in the afternoon. Diurnal resolution is needed, as well as sampler placement in non-

urban and urban areas, to detect the effects of wintertime transport. During fall, more sites are needed at different distances between non-urban and urban, and between urban and non-urban, to estimate gradients and distances. These scales are not regional, however, but sub-regional.

- Ammonium nitrate and ammonium sulfate concentrations are more uniform in space and time than elemental and carbon concentrations.
- How frequent must measurements be acquired and with what duration to represent changes in mass and chemical concentrations throughout the day? How should temporal resolution be balanced with spatial resolution?
 - Temporal resolution can be translated into spatial resolution. The duration of pollution pulses arriving at a receptor is indicative of their sources, and also can be correlated with their directions when wind speeds exceed thresholds. Pulses of 5-min or less are attributable to individual, nearby emitters. Pulses of one hour duration are attributable to neighborhoods. Pulses of three or four hours duration are urban to regional scale. Non-urban measurements must be compared with urban measurements to separate urban from non-urban contributions.
 - Twenty-four hour average primary carbon and dust are most variable within urban areas and depend on proximity to sources, especially roadways.
- How well do existing meteorological measurements represent the following phenomena: 1) transport and dispersion under low wind speed/stagnation conditions; 2) frequency, spatial extent, and intensity of fogs; 3) temperatures at 850 mbar; 4) downvalley and cross-valley flows; 5) mixed layer depths, vertical distributions of winds, temperature, and relative humidity; 6) wind gusts above suspension thresholds; and 7) extent of the three-dimensional coverage of fogs. What changes are needed in long-term and short-term meteorological monitoring? How well do existing measurements characterize the presence of fog and/or stratus clouds?
 - The existing network detects wind speeds to 1 m/s, but it is not accurate below this threshold. One-hour averaging times do not capture the variable wind velocities or gusts that may affect net transport. Sonic anemometers do not provide more accurate measurements of air movement than low-threshold wind vanes.
 - Existing relative humidity sensors are not accurate enough at RH to detect fogs. Automated NWS ASOS measurements detect fog well, as do ambient temperature nephelometers, but their placement is not dense enough to evaluate the times and locations of fogs. The CALTRANS road fog network has not been evaluated.
 - Temperatures at 850 mb are represented by the Oakland airport sounding. These temperatures are predictable from soundings in the SJV.
 - Downvalley and crossvalley flows are quantifiable at the surface with existing measurements when they occur. Flows aloft, especially at night and early morning, are not detectable with the current surface network, although the surface

wind measurements are similar in direction and magnitude to winds within the valleywide layer between 1100 and 1700 PST during winter.

- Mixed layer depths are highly variable throughout central California during winter and cannot be quantified with the existing network.
- Wind gusts are not quantified by the existing network.
- What are the most probable monitoring periods and averaging times for describing phenomena associated with each conceptual model?
 - The stagnation with fog model can occur from mid-November through mid-March. Highest $PM_{2.5}$ levels are usually found from the beginning of December through mid-February. The period of mid-December through mid-January experiences the largest contributions from residential wood burning. Highest $PM_{2.5}$ concentrations occur during Great Basin high pressure systems of at least four days duration between storms. These conditions are reliably predictable. In urban areas, concentrations are relatively constant at night, build up over several hours during the morning, with rapid changes during the period of ~1000 to 1900 PST when vertical mixing occurs. $PM_{2.5}$ levels also increase after sunset when samples are near residential wood burning emitters. A moderate fraction of primary contributions in urban areas results from many short-duration pulses of contributions from nearby sources over periods of a few minutes to hours.
 - The clear sky stagnation model most frequently occurs during fall, from mid-September through mid-January. The diurnal cycle is unmeasured, but it is believed to be less pronounced than that of the winter owing to a deeper surface layer that does not persist late into the morning, less neighborhood-scale burning and fewer cold starts.
 - The low wind local source condition requires an extended source of similar activity for community-representative sites. Individual emitters do not normally have a large influence beyond ~100 m from their point of origin. Fall in the central SJV represents the most likely time and place where this condition occurs.
 - The high wind dust suspension condition can occur anytime, anywhere. It is less likely in recent years during which there is abundant vegetative cover.

3.2.3 What are the temporal, spatial, chemical, particle size and variations in central California?

- How does the frequency and location of excessive PM concentrations vary from year-to-year?
 - Maximum and annual average PM_{10} are much higher during drought years. These years experience longer periods of high pressure between wintertime storms that allow primary and secondary contributions to build up. More surface moisture and vegetation during other parts of the year suppress dust. PM_{10} levels are now much lower than they were during the 87-92 drought.

- At what locations and during what seasons are state and federal PM standards exceeded?
 - The annual PM_{2.5} standard is most likely to be exceeded in the Fresno and Bakersfield urban areas. It is also expected that Corcoran may still exceed the 24-hour PM₁₀ standard. Higher average concentrations during winter and fall offset lower concentrations during spring and summer.
 - The annual PM₁₀ standard can be exceeded at urban and non-urban sites. High PM₁₀ concentrations that are not driven by PM_{2.5} (e.g., winter) are rare enough that they are not likely to exceed the 3-year 99th percentile 24-hour standard.
- How do the highest PM values affect the annual average concentrations? Will reducing the highest concentrations also significantly reduce the annual average?
 - The few highest PM values do not drive the annual average for PM_{2.5} or for PM₁₀. Numerous concentrations occur during winter and fall, however, that are more than twice the annual average values (i.e., >30 µg/m³ for PM_{2.5} and >100 µg/m³ for PM₁₀).
- When do elevated ozone concentrations correspond to excessive PM_{2.5} concentrations, and what fraction of the PM_{2.5} corresponds to photochemical end-products?
 - Ozone concentrations that exceed standards do not correspond to PM_{2.5} concentrations that exceed standards. There have been some corresponding exceedances of the PM₁₀ standard, but these are not consistent nor are they associated with secondary pollutants that derive from ozone formation. While secondary nitrate and secondary organic aerosol are formed along with ozone, high temperatures keep most of the nitrate in the gas phase and favorable transport and dilution (relative to winter and fall) mitigate against the buildup of secondary organic aerosol.
- What are the continuous particle size distributions of different chemical components and what causes them to vary in space and time?
 - Summer and winter size distribution measurements show little variation. Sulfate, nitrate, and carbon distributions peak in the range of 0.3-0.5 µm during both summer and winter, with a narrow elemental carbon distribution during summer in the 0.1-0.2 µm range. Nearly all of the elemental concentrations are found in sizes >1.0 µm. McDade et. al (1998) and Kumar et. al. (1998) show that there were several samples with significant amounts of coarse carbon. Urban/rural and fog/nonfog differences size distributions are not adequately characterized and size resolved chemical measurements are limited to the southern San Joaquin Valley.
- How much of PM₁₀ is composed of PM_{2.5} and how does this relationship change by measurement site and season? How accurately can PM_{2.5} concentrations be deduced from PM₁₀ measurements? What are the major chemical components of

PM₁₀ and PM_{2.5} and how do these differ by site, season, time of day, and emission activity? How important is the crustal component in PM_{2.5}?

- On average, about 50% of PM₁₀ is in the PM_{2.5} size fraction at all sites. For winter, however, PM_{2.5} is 70% to 80% of PM₁₀, and during fall PM_{2.5} is 50% to 60% of PM₁₀.
- PM₁₀ and PM_{2.5} are highly correlated during different seasons, but their regression slopes are not consistent. There are some significant outliers from predictive relationship, especially outside of winter.
- During nonwinter months, the highest concentrations of PM₁₀ are dominated by crustal material and have little spatial homogeneity. The PM_{2.5} fraction is dominated by nitrate, sulfate, ammonium, organic carbon and elemental carbon which account for 75% to 80% of the PM_{2.5} mass. Average PM_{2.5} ammonium and sulfate concentrations are similar among the urban and nonurban sites. The PM_{2.5} geological components of aluminum, silicon, iron, and titanium are about 10% of their corresponding values in the PM₁₀ fraction, while the majority of the remaining components are in the PM_{2.5} size fraction. The spatial homogeneity of PM₁₀ and PM_{2.5} mass concentrations is similar, and is most homogeneous between the two major cities, Fresno and Bakersfield. Crustal contributions are not evenly distributed in the PM₁₀ fraction but are more homogeneously distributed in the PM_{2.5} fraction. Secondary nitrate is more homogeneously distributed throughout the SJV than are other components of PM_{2.5} that are related to primary emissions.
- Geological material in the PM_{2.5} fraction is highly correlated with geological material in the PM₁₀ size fraction. Geological PM_{2.5} is in the smaller size fraction of the coarse mode rather than in the upper size range of the accumulation mode. On average 2% to 9% of PM_{2.5} mass is contributed by this coarse mode aerosol. For individual samples, the geological PM_{2.5} can approach 50% of the PM_{2.5} mass. This extreme usually occurs when PM_{2.5} concentrations are relatively low, however, and at non-urban sites.

3.2.4 What meteorological characteristics are associated with elevated PM₁₀ and PM_{2.5} concentrations?

- What meteorological conditions are associated with previously observed PM₁₀ standard exceedences? Which variables are most important for each situation?
- Morning and evening 850 mb temperatures from the Oakland sounding are the most reliable meteorological indicator of winter and fall PM exceedences. This is associated with persistent high pressure systems. Low or negative pressure gradients between Oakland and Reno or Las Vegas are also highly associated with the high pressure system.
- Wind speeds at existing stations exceeding 8 m/s are necessary, but not sufficient, indicators to predict windblown dust emissions. Wind gusts can raise dust in areas without monitors, or they can be of short enough duration that gusts are averaged into less intense winds during an hour.

- The presence or absence of fog is not a reliable indicator of excessive PM. Intense fog attenuates PM levels by increasing deposition rates. Fogs form as a by-product of the limited mixing caused by high pressure after storms have deposited substantial surface moisture. They co-occur with, rather than serve as the major causes of, secondary nitrate formation. Higher sulfate concentrations are likely to be found than would occur without the fog, but sulfate concentrations are low ($\sim 2 \mu\text{g}/\text{m}^3$ during winter). Fogs appear to attenuate nitrate levels.
- What are the transport pathways within and between air basins in central California? When is transport between air basins associated with elevated PM concentrations?
 - Transport during summer is typically downvalley, extending from the Bay Area into the Mojave Desert within a single day. This transport constitutes part of the contribution (along with transport from the South Coast Air Basin) to visibility degradation in the Mojave Desert.
 - Well-defined transport between air basins is associated with the lowest PM concentrations, owing to dispersion and dilution during transport.
 - Weak offshore flows aloft may transport pollutants from the SJV to the Bay Area under high pressure systems during winter.
- What are vertical variations in horizontal wind velocities and how do they affect transport and mixing?
 - Vertical changes in wind speed and direction are most important during winter with respect to PM. Afternoon mixing of surface emissions within the valleywide layer, where wind speeds are consistently higher than at the surface during non-afternoon periods, appears to be the major mechanism for distributing primary emissions throughout the region and for mixing emissions from urban and non-urban sources.
- How does the mixed layer depth change through the day and night and what are the effects of these changes on PM concentrations?
 - During winter, pollutants accumulate in a 30 m to 50 m deep mixed layer from ~ 1800 PST to ~ 1000 PST. $\text{PM}_{2.5}$ builds up in urban areas from primary emissions, but this buildup is not observed in non-urban areas during this period. During afternoon, pollutants mix aloft and diluted and reacted pollutants from previous days mix to the surface in both urban and non-urban areas. Smith et. al. (1996) found that during stagnant winter conditions the maximum mixing heights are on the order of 400 m agl.

3.2.5 What are the spatial, temporal, size, emission rate, and chemical characteristics of specific emissions sources? What characteristics allow contributions from these sources to be distinguished from each other? What are the specific source contributions to the highest PM₁₀ and PM_{2.5} concentrations?

- How well characterized are mass emission rates for each source category and major pollutant?
 - Sulfur dioxide emissions rates are well characterized in space and time for mobile, area, and industrial sources. While total NO_x emissions from mobile sources are probably well characterized, spatial and temporal variations are not.
 - Primary particle emissions rates are poorly characterized in space and time for diesel exhaust, cold-start exhaust, high emitting vehicle exhaust, and hot-stabilized vehicle exhaust.
 - Primary particle emission rates are poorly characterized in space and time for residential woodburning, forest wildfires, prescribed forest burns, and agricultural burning.
 - Primary particle emissions rates are poorly characterized in space and time for road dust, construction, and windblown dust. They are moderately well characterized for agricultural dust.
 - Cooking emissions rates are undetermined.
 - Ammonia emissions rates are inadequately determined.
- To what extent can fugitive dust emission rates be estimated?
 - Fugitive dust emissions rates appear to be overestimated in the winter with respect to their relative abundance in receptor samples. This overestimation can be due to: 1) non-representative emissions factors; 2) inaccurate activity estimates; or 3) inaccurate representation of “effective emissions” of transportable material that deposits near the point of emission.
 - While the potential or susceptibility for fugitive dust emissions can be estimated and ranked, based on available or obtainable soil surface property and land use measurements, precise emissions estimates will probably always be inaccurate owing to variable and constant changes in the variables that affect suspension.
- How do emissions rates change from year-to year, month to month, day-to-day, and throughout the day?
 - Sulfur emissions in the southern SJV have been reduced by half owing to the elimination of crude oil combustion, and this is reflected in the ambient sulfate, vanadium, and nickel concentrations.
 - Lead emissions have been reduced by >99% and this is reflected in the ambient lead measurements.

- Wildfires, prescribed burning and windblown dust are the most variable year-to-year emissions. These emissions may vary by factors of two or more from year to year. Prolonged drought results in higher emissions from these sources.
- Residential wood combustion emissions peak during winter, agricultural dust emissions peak during fall, forest fire emissions peak during late summer and fall, and agricultural burning emissions peak during spring.
- Where are the ammonia sources, how much do they emit, and when do they emit it?
 - Feedlots and dairies are the largest ammonia emitters. Water treatment plants are moderate emitters. Chicken, turkey coops, and fertilizer application are not large emitters.
 - Most feedlots, dairies, and water treatment plants are locatable on Dept. of Water Resources maps. Some new ones have been added that do not appear on these maps.
- What are the gaseous and particulate chemical compositions of source emissions that provide precursors for secondary organic formation and permit source sub-categories to be distinguished from each other?
 - Profile species are needed to unambiguously determine contributions from the following source types: 1) diesel exhaust; 2) cold start exhaust; 3) visible exhaust emitters; 4) hot stabilized exhaust; 5) residential wood combustion, 6) agricultural burning; 7) forest wildfires and prescribed burning; 8) meat cooking; 9) secondary organic aerosol; 10) paved road dust; 11) unpaved road dust; 12) construction dust; and 13) agricultural dust from different crops and farming operations.
- For the highest PM concentrations, which source contributions are most likely, based on CMB source apportionments and time and place of occurrence?
 - Secondary ammonium nitrate and motor vehicle exhaust are the largest contributors to high PM_{2.5} levels. These sources, along with fugitive dust, are the largest contributors to PM₁₀. More specific source sub-category contributions are needed to further develop effective control strategies. Residential wood combustion can be a significant PM_{2.5} contributor in neighborhoods.
- What quantities of NO_x are emitted aloft relative to quantities emitted at the surface, and under what conditions do these mix to the surface?
 - Point source emitters do not have tall stacks in the SJV. Nearly all of the NO_x from point, area, and mobile sources is emitted into the valleywide layer in the SJV. Only in the Bay area are significant, but not major, quantities of NO_x emitted from tall stacks.
- How well can emissions data be reconciled with ambient data?
 - Emission inventory ratios for PM/NO_x and SO_x/NO_x are 1.5 to four times higher than ambient ratios, indicating that emissions for PM and SO_x may be

overestimated. However, emission inventory ratios for NMHC/NO_x, and CO/NO_x are about two times higher than ambient ratios, indicating that NMHC and CO emissions may be underestimated. Ambient and emissions inventory derived ratios for NH₃/NO_x are within ±25% agreement when emissions within an approximate 25 km radius of the ambient monitor are included in ratio comparisons (Haste et. al. 1998).

- Can specific source activities be detected at given sites to confirm source influences?
 - No strong positive correlations were observed between observations of PM activities and high outliers of Chemical Mass balance (CMB) source categories during IMS95. This lack of correlation is consistent with the small zone of influence observed for specific emitters and with the dominance of urban and regional scale contributions over neighborhood scale contributions at community-representative sites (Coe et. al. 1998).
- How well are dynamic atmospheric process and the formation of secondary aerosols from primary and secondary aerosol precursors understood?
 - During IMS95, NO, NO₂ and NH₃ accounted for 78% of the nitrogen; the majority of nitrogen occurs in the gas phase rather than the particle phase. On average, ~12% of the NO_x oxidizes to nitrate at in the cities and ~30% in non-urban areas such as Kern Wildlife Refuge.
 - NO is oxidized to NO₂ and HNO₃ in the daytime via photochemical reactions and the aerosol phase is thermodynamically favored both day the night.
 - Gaseous compounds account for approximately 95% of the carbonaceous species. Gaseous alkanes (>C₂) are the most abundant species.
 - Gas phase sulfur species dominate at the urban sites, with 77% of all sulfur in the gas phase. Particle sulfate dominates, at 78% of total sulfur, in non-urban areas. Sulfate is formed primarily from daytime photochemistry in urban areas and from transport and fog reactions in non-urban areas (Kumar et. al. 1998).

3.2.6 How accurate and prevalent is the manmade fugitive dust conceptual model?

- What is the extent of vertical mixing of surface dust emissions generated by manmade activities?
 - More than half the PM₁₀ concentrations in a 10 m vertical profile of dust emissions remains within the first two meters (Watson et. al., 1996).
- How do the processes of transformation, dispersion, and deposition reduce concentrations with distance from the source?
 - Dust concentrations from a single emitter are within 10% of PM₁₀ concentrations ~100 m downwind of the emitter.
- What conditions would cause large dust contributions to the PM_{2.5} size fraction?

- Large dust concentrations are found when many suspended dust sources emitting on an urban-scale contribute small increments to the urban-scale total.

3.2.7 How accurate and prevalent is the high wind fugitive dust conceptual model?

- How does the atmosphere interact with different surfaces in central California to inject dust into the atmosphere? Which surfaces are most susceptible to large emissions rates? What are surface properties conducive to and that mitigate against suspension and transport by high winds?
 - Unknown.
- What is the extent of vertical mixing of surface dust emissions generated by the atmosphere?
 - The extent of vertical mixing for windblown dust in central California is unknown.
- How do the processes of transformation, dispersion, and deposition reduce concentrations with distance from the source?
 - Unknown.

3.2.8 How accurate and prevalent is the clear sky stagnation model?

- To what extent is ammonium nitrate limited by ammonia in urban and non-urban areas?
 - During summer, temperatures are sufficiently high that most nitrate remains in the gas phase, and dilution is sufficient to keep the ammonium nitrate concentrations low.
 - Ammonia limitations during fall are not understood.
- To what extent will further SO₂ reductions free up ammonia to create ammonium nitrate?
 - Ammonium sulfate levels are sufficiently low and ammonia levels are sufficiently high that changes in sulfate levels do not affect ammonium nitrate levels.
- To what extent does this conceptual model co-occur with the low wind fugitive dust situation in urban and non-urban areas?
 - High nitrate concentrations correspond with low wind fugitive dust contributions during fall.

3.2.9 How accurate and prevalent is the stagnation with fog model?

- To what extent is ammonium nitrate limited by the availability of ammonia or nitric acid, especially on the west side of the SJV?

- There is no ammonia limitation during winter. Temperatures are sufficiently low and ammonia is sufficiently abundant that more than 50% reductions in ammonia levels are needed to detect changes in ammonium nitrate levels.
- How is NO_x oxidized to nitric acid in a stagnant, cloudy environment with little photochemistry?
 - This may occur above the surface mixed layer.
- To what extent is secondary organic formation a contributor in this situation and how is it formed under clouds if it is important?
 - Secondary organic aerosol forms during winter and can account for ~20% of $\text{PM}_{2.5}$ organic carbon.
 - Although photochemical processes are slower than during summer, they occur over long residence times for surface precursors that are mixed aloft under the valleywide layer.
 - Clouds and fog slow down the production of secondary compounds, reducing concentrations by a factor of two to three from maximum clear sky levels. Schauer et al. (1998) found that the amount of organic carbon that could not be accounted for via primary sources was the same at both urban and rural sites ($\sim 4.5 \mu\text{g}/\text{m}^3$). This is in general agreement with the amount found by Strader et al. (1998).
- How does deposition, owing to fog droplet growth, balance creation of secondary aerosol in fog droplets?
 - Fog deposition is the main removal mechanism for soluble ammonium nitrate and precursor gases. Fog deposition for sulfate is slightly less than fog formation for sulfate.
- How significant does the drop size-dependence of the fog chemistry have on aerosol formation and deposition in fogs?
 - Droplet composition varies with drop size. Both large and small drops are alkaline. Small drops are enriched in inorganic ion species and are less alkaline than large drops. Nitrate is associated with smaller drops than sulfate. Ammonium is in large and small drops, corresponding with both sulfate and nitrate in those drops. The enrichment of inorganic ions in small drops results in a lower sedimentation rate relative to that which would be estimated from average droplet composition. Mathematical simulation of the size-dependent fog drop composition results in a sulfate concentration 30% higher than predicted by a bulk fog model simulation (Collett et al. 1998).
- How does acidification of drops due to aqueous phase acid production limit aerosol formation in fog drops?
 - Acid buffering is not completely caused by ammonia, bicarbonate, acetate, and formate found in IMS95 urban fog samples. This additional buffering capacity

supports rapid rates of sulfate production. Inclusion of the enhanced buffering in fog simulations results in an increase in sulfate aerosol present following the fog episode of approximately 50%. While a specific substance was not identified, potential sources of the buffering are organic solutes (Collett et. al. 1998).

- How does the ammonia generated in rural areas mix with the oxides of nitrogen generated along roadways and in urban areas under low wind, stagnant conditions?
 - Ammonia mixes above the surface layer into the valleywide layer during the afternoon on each day of stagnation between storms. It then mixes with urban NO_x emissions during the night and early morning. Photochemical mechanisms are slow, but residence times are long enough to create sufficient amounts of nitric acid that interacts with this ammonia for mixing to the surface throughout the SJV on the following day.
- To what extent is the regional nature of secondary ammonium nitrate and ammonium sulfate due to well-defined transport between upwind and downwind regions, or is it primarily due to slow diffusion over multi-day stagnation periods?
 - Wintertime flows in the valleywide layer, above the surface layer, are highly variable in direction, but of sufficient intensity to mix materials throughout the SJV and even into the San Francisco Bay area. There is no consistent transport direction from episode to episode. Bakersfield emissions may affect Fresno concentrations under some conditions, and vice versa under other conditions.
- How do primary particles generated from residential wood combustion, vehicle exhaust, cooking, and road dust in an urban area arrive at non-urban areas and other distant urban areas under low wind, stagnant conditions?
 - Primary contributions from urban areas mix from the surface layer to the valleywide layer between 1000 to 1900 PST in urban areas and mix down from aloft in non-urban areas. Nighttime and morning winds above the surface and valleywide layer are sufficient to move these pollutants throughout the SJV.
- How do elevated oxides of nitrogen emissions from industrial sources get into the shallow mixed layer?
 - Although industrial stacks in the SJV may inject NO_x above the surface layer, it remains within the valleywide layer where it can undergo transformation owing to most stacks being <50 m tall. These elevated emissions may have a larger influence on nitric acid formation owing to less opportunity for deposition to the surface.
- How much ozone is above the valleywide layer and how much of it gets into the mixed layer?
 - Ozone levels above the valleywide layer are 30 to 40 ppb. There is sufficient ozone within the valleywide layer to make it the dominant oxidant for aqueous-phase conversion of sulfur dioxide to sulfate.

- Where does fugitive dust come from when winds are low and the ground is wet?
- Fugitive dust contributions are low, <30% of PM₁₀, when winds are low and the ground is wet. Dust contributions are probably most influenced by nearby emitters, specifically paved road dust resulting from non-urban trackout in urban areas.

3.2.10 How will emissions reductions affect PM concentrations measured at receptors?

- Which contributions to PM are proportional to emissions rates and which are not?
 - Reductions in directly emitted particles in urban areas will result in proportional reductions at urban receptors, on average.
 - The extent to which secondary nitrate and organic aerosols during winter will respond to precursor reductions is unknown.
- What are the limiting precursors for ammonium nitrate and ammonium sulfate and by how much are they limiting?
 - Lacking 50% reductions in ammonia emissions, urban ammonium nitrate reductions require reductions in NO_x or VOC precursor emissions rather than in ammonia emissions. The times and locations of the most effective reductions are unknown.
- Over what distance, and at what times, will reductions in a specific emissions source be detectable as PM reductions at receptors?
 - Reductions in directly emitted particles will affect the urban areas in which those reductions are effected.
 - The extent to which precursor reductions from one city affect secondary aerosol concentrations in another city are unknown.
- What is the demonstrated effectiveness of different emissions reduction methods?
 - Vehicle inspection and maintenance programs do not target primary particle emissions or NO_x, nor do they adequately evaluate or control cold start and visible emissions.
 - Few unpaved roadway suppressants have demonstrated effectiveness. A durability specification can be set based on easily measured surface properties (Watson et. al. 1996).
- What are the major sources of imprecision in source contribution estimates determined by different types of models, and which improvements would have the greatest effect on reducing those imprecisions?
 - Unknown. Models have not been adequately evaluated or challenged.

- How are PM levels likely to change owing to population growth, planned changes in industrial and agricultural practices, and currently implemented or proposed emissions reduction strategies?
 - Unknown. Population is likely to increase, but urbanization may reduce agricultural emissions and increased vehicle miles traveled may be offset by lower-emitting vehicles
- How will emissions reductions affect the concentrations of other regulated pollutants and visibility impairment in the San Joaquin Valley, nearby Class I areas and in the Mojave Desert?
 - Unknown.
- To what extent will NO_x and VOC reductions that reduce PM_{2.5} concentrations in central California affect ozone?
 - Unknown.
- How will emissions changes in primary particles and precursor gases that reduce PM_{2.5} affect visibility in the Mojave desert?
 - Unknown.

3.2.11 How is visibility affected by PM_{2.5} and meteorology in central California

- What are the accuracy, precision, validity, and equivalence of light extinction, scattering, and absorption measurements?
 - Variations in the size distribution and composition of winter aerosol has a small enough effect on light scattering efficiency that PM_{2.5} concentrations can be estimated from measurements by: 1) a heated nephelometers; 2) an unheated nephelometer and an accurate RH measurement; or 3) an ASOS visibility sensor plus an accurate RH measurement.
- Where, how much, how long, and how often does visibility reduction occur in the SJV and in the Mojave Desert?
 - During winter, some fog events are valleywide, while others affect only one end of the SJV or the other. Fog events at Stockton, Modesto, and Merced are similar to one another, while Fresno fog patterns are more similar to those in Bakersfield. Higher wintertime light scattering at night observed at rural sites compared to urban sites is due to the greater presence of fog outside the cities.
 - There is minimal effect on visibility in the desert during winter due to aerosol generated in the SJV and other central California source regions. The SJV and the South Coast Air Basin supply the majority of visibility reducing PM_{2.5} to the Mojave Desert during summer.

- Where, how much, how long, and how often do different chemical constituents contribute to different levels of visibility reduction in the SJV and in the Mohave Desert?
- During winter, ammonium nitrate is the largest contributor to light extinction, with organic carbon, elemental carbon, and sulfate contributing substantially on some days. Crustal material is usually a small contributor during the winter.
- During summer, organic carbon, elemental carbon, and ammonium sulfate are the largest contributors to light extinction, especially once concentrations reach the Mojave Desert where high temperatures and a dearth of ammonia cause available ammonium nitrate to evaporate.

3.3 Data Analysis Methods and Data Requirements

Data analysis activities for CRPAQS have been specified to answer the questions in Section 3.2. These activities have been completed for measurements from prior special studies and long-term monitoring networks and from a series of technical support studies conducted as an Integrated Monitoring Study in the SJV during 1996-96 (IMS95, Solomon and Magliano, 1998; Blanchard et. al., 1998; Chow and Egami, 1997; etc.). The activities specified by Watson et. al. (1996) still apply to the data to be acquired by the monitoring plan discussed here, but they need to be revised to incorporate new approaches devised during the IMS95 data analysis efforts, to respond to the more specific knowledge gaps identified in Section 3.2, and to accommodate requirements of the new PM_{2.5} standards.

3.4 Modeling Methods and Data Requirements

Air quality modeling is an essential tool for understanding source-receptor relationships and for estimating the effects of future emissions scenarios. These mathematical simulations of atmospheric movements and chemistry are also used as part of data analysis activities. There is no universally “best” or “valid” model. Model complexity does not necessarily imply model sophistication. Every model application should: 1) determine model applicability by examining the availability of appropriate data inputs and inclusion of physical and chemical phenomena; 2) identify the potential emissions sources and their emissions characteristics; 3) evaluate model outputs and performance measures; 4) identify and evaluate deviations from model assumptions; 5) identify and remediate input data deficiencies; 6) verify consistency and stability of source contribution estimates; and 7) evaluate results with respect to other data analysis and source assessment methods.

Model results are sometimes evaluated only with respect to how well they duplicate measured concentrations of the relevant pollutant at a few receptors. A better approach is to stress models to an extent that they fail, and in such a way that the nature of those failures can be diagnosed. Applying both source and receptor models to the same pollution problem is one way in which that stress can be applied.

The San Joaquin Valley and surrounding regions must develop control plans that address both the annual average and the 24-hour standards for PM₁₀ and PM_{2.5}. Exceedances of each of these standards have contributions from both primary and secondary material and

they occur over a number of different seasons and meteorological scenarios (Watson et al., 1997). Therefore air quality models that can be reliably used to estimate both annual average and 24-hour PM concentrations over a broad spectrum of conditions are needed.

No single model will be adequate to address all aspects of PM. Instead, a suite of modeling methods are proposed, each with specific strengths and ranges of applicability. Each will be used to meet a stated objective. Taken as a group, they are intended to satisfy a broad range of needs. Moreover, each of these air quality modeling approaches depend to one extent or another on “foundation models” to provide information on emissions and meteorology. Emissions and meteorological models are an integral component of the suite of modeling approaches which will comprise a comprehensive modeling system for PM.

A separate modeling protocol (Magliano et al. 1998) describes the models, their formulations and assumptions, and methods to apply and evaluate them for the annual and intensive operating periods. Measurements are acquired to serve the needs of the following model types:

- **Conceptual models:** These models describe the relevant physical and chemical processes that affect emissions, transport, and transformation. They are the starting point for any source apportionment process. Conceptual models take advantage of the large body of scientific knowledge already acquired. They identify the sources that are likely to be present and eliminate those that are not. They examine meteorological conditions that affect concentrations and focus further modeling on the conditions conducive to the high concentrations. Although the conceptual models described earlier in this chapter are consistent with current information, they are not yet verified. Field study measurements are designed to test them as hypotheses, and they will likely change. Several changes have already been made with respect to the earlier versions stated by Watson et al., (1997) as a result of IMS95 data analysis.
- **Emissions models:** An emissions model estimates temporal and spatial emission rates based on activity level, emission rate per unit of activity, and meteorology. Emissions models are often empirically derived from tests on representative source types, such as paved and unpaved roads, motor vehicle exhaust, biota, and industries. Emissions models are used to construct emissions inventories that are used as the basis for control strategy assessment. All of the modeling methods proposed for CRPAQS rely on emissions models to one extent or another.
- **Meteorological models:** Meteorological models describe transport, dispersion, vertical mixing, and moisture in time and space. Meteorological models consist of straight line, interpolation (termed diagnostic), and first principle (termed prognostic) formulations, with increasing levels of complexity and requirements for computational and data resources. The straight line model is applied to hourly wind directions from a single monitor, assuming an air mass travels a distance equal to the wind velocity in the measured direction, regardless of the distance from the monitoring site. This model is applicable for a few hours of transport in flat terrain, typically for evaluating a single emissions source. Interpolation models integrate wind speed and directions from multiple measurement locations, including upper air measurements provide by remote

sensors or balloon launches. The more advanced of these models allow barriers, such as mountains, to be placed between monitors. Wind fields, therefore, show different directions and velocities at different horizontal and vertical positions. Interpolation wind models are applicable to domains with a large number of well-placed monitors and for estimating the movement of air masses from many sources over transport times of more than half a day. The number and placement of monitors, especially upper air monitors, is especially important in mountainous terrain and in coastal areas where winds are unusual. First principle models (Stauffer and Seaman, 1994; Seaman et al., 1995; Koracin and Enger, 1994a, 1994b) embody scientists' best knowledge of atmospheric physics and thermodynamics, employing basic equations for conservation and transfer of energy and momentum. Also known as "prognostic models," first principle models purport to need no data other than values from a sparse upper air network for interpolation. They are computationally intensive, often requiring supercomputers but are becoming more practical and cost-effective as workstation and desktop computers become more powerful. Modern versions use "four-dimensional data assimilation" that compare model-calculated wind, humidity, and temperature fields with measurements and "nudge" model outputs toward observations. A more complex meteorological model is not necessarily a better model for a specific application. The MM5 meteorological model has been adopted as the platform for central California air quality studies (Seaman et. al., 1995).

- **Chemical models:** These models describe transformation of directly emitted particles and gases to secondary particles and gases. Chemical models also estimate the equilibrium between gas and particle phases for volatile species. Chemical models have been or are being developed for: 1) photochemical formation of ozone, sulfate, nitrate, and organic particles in clear air (Seinfeld and Pandis, 1998); 2) sulfate and nitrate formation in fogs and clouds (Seinfeld and Pandis, 1998); 3) inorganic aerosol equilibrium (Kim et. al., 1993); and 4) organic aerosol equilibrium (Pankow et. al., 1994). Chemical models are reasonably well developed for ozone and inorganic particles, but they are still under development for organic particles and gases. Chemical models can be embedded in source-oriented dispersion models, or they can be applied to infer source contributions or limiting precursors as a receptor model using measurements from a monitoring site.
- **Source dispersion models:** Source-oriented dispersion models use the outputs from emissions, meteorological, and chemical models to estimate concentrations measured at receptors. They include mathematical simulations of transport, dispersion, vertical mixing, deposition, and chemical models to represent transformation. The most common source dispersion models are Gaussian plume, puff, and grid formulations. Gaussian plume models (Schulze, 1990; Freeman et. al., 1986; Schwede and Paumier, 1997) are most often associated with the straight line wind model and estimates a bell-shaped concentration field in the vertical and horizontal directions from the wind direction. These models are commonly used to evaluate potential effects of primary emissions from ducted sources, such as industrial stacks. Puff, or trajectory, models treat emissions from a variety of sources as independent entities that are moved in a curvilinear wind field generated by a diagnostic or prognostic wind model. Grid models place transfer pollutants between boxes with pre-defined vertical and horizontal dimensions (Bowman

et. al., 1995; Byun and Dennis, 1995; Yamartino et. al.). The 3-D grid-based photochemical SAQM-AERO model is the main platform that has been developed for central California studies.

- **Receptor models:** Receptor models (Cooper and Watson, 1980; Watson, 1984; Javitz et. al., 1988) infer contributions from different primary source emissions or precursors from multivariate measurements taken at one or more receptor sites. Receptor models are based on the same scientific principles as source dispersion models, but they are inferential rather than predictive of source contributions. They include: 1) Chemical Mass Balance (CMB) for estimating source contributions; and 2) inorganic aerosol equilibrium for estimating limiting ammonium nitrate precursors (Watson et. al., 1994a; Blanchard et. al., 1997).

The CMB receptor model (Friedlander, 1973; Cooper and Watson, 1980; Gordon, 1980, 1988; Watson, 1984; Watson et. al., 1984; 1990; 1991; Hidy and Venkataraman, 1996) solves equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The source profile abundances (i.e., the mass fraction of a chemical or other property in the emissions from each source type) and the receptor concentrations, with appropriate uncertainty estimates, serve as input data to the CMB model. The output consists of the amount contributed by each source type represented by a profile to the total mass and each chemical species. The CMB calculates values for the contributions from each source and the uncertainties of those values.

Chemical equilibrium models can be used to predict the effects of emission reductions on secondary aerosols by constructing a set of model-predicted isopleths of particulate nitrate concentration as a function of total (aerosol plus gas phase) nitrate and ammonia concentrations. By locating an actual sample on the isopleth diagram, predictions of sample responses to reductions in total ammonia or total nitrate can be obtained. A drawback of the isopleth approach is that it requires hundreds of model runs to construct the isopleth diagrams. An alternative approach uses two indicators which can be derived from ambient measurements to identify the transition between the ammonia- and nitrate-limited portions of the isopleth plots (Blanchard et. al., 1997). These indicators are quantities defined as excess ammonia and the ratio of particulate to total nitrate.

- **Rollback Models:** Linear rollback (Barth, 1970; deNevers, 1975; Cass, 1981; Cass and McRae, 1981, 1983) is the most commonly used method for control strategy development, although it is not often identified as such. Rollback assumes that atmospheric concentrations in excess of background are proportional to aggregate emission rates. Reducing excessive concentrations of a pollutant to levels below a pre-set standard requires emissions reductions that are proportionally equal to the relative amount by which the standard is exceeded. Speciated linear rollback has the fewest complex data requirements, but it also carries large uncertainties. These uncertainties might not, however, be larger than those associated with any other modeling approach. They may be acceptable for selecting among different pollution control measures, or at least narrowing the scope of viable alternatives.

Linear rollback does not consider the effects of meteorological transport between source and receptor or of differences in gas-to-particle conversion for different precursor emitters. It is most valid for spatial and temporal averages of ambient concentrations that represent the entire airshed containing urban-scale sources. The effect of transport from distant sources located outside the airshed is compensated by subtracting background concentrations, measured nearby but outside the airshed, from ambient levels prior to determining needed emissions reductions. Linear rollback also assumes for secondary particles, such as ammonium nitrate and ammonium sulfate, that one of the precursors limits particle formation.

3.4.1 Annual Average Source Attribution

The proposed approach for annual average modeling will use a combination of models: 1) a parameterized grid-based aerosol model combined with a diagnostic wind model run on a daily basis for a full year; 2) an enhanced version of the grid-based model run for up to 60 episodic days which represent typical meteorological regimes to provide an improved understanding of the accuracy and reliability of the full 365 day model simulations; and 3) the Chemical Mass Balance (CMB) receptor model to determine contributions from different source categories combined with a windfield/transport model to estimate the contributions from probable source areas to each source type for each apportioned sample.

While each method will be applied to all components of PM and the results compared to each other, the CMB method is expected to be more reliable for estimating primary PM, while the grid based modeling approaches are expected to be more robust for addressing secondary PM. The conditions under which these models supply reliable and unreliable results is evaluated by data analysis methods.

3.4.1.1 Daily Grid-Based Aerosol Modeling

Reasonably-priced computing platforms are sufficient to support meteorological and air quality modeling on a daily basis for a full year using a grid-based aerosol model with representative chemical transformation mechanisms. The grid-based model proposed for CRPAQS will likely be a simplified version of UAM-AERO or SAQM-AERO and will include full gas phase chemistry, a chemical mechanism suitable for simulating secondary aerosol formation (such as SAPRC), an equilibrium module for sulfate/nitrate/ammonia partitioning, and a parameterized aqueous phase fog chemistry module.

The model will be run for fine and coarse size fractions. Three-dimensional wind fields will be generated using a diagnostic wind model, while mixing heights, temperature, humidity and fog fields will be generated from interpolation of observations from the measurement network. The model will be applied to the full central California study domain.

Recent experience suggest that a year of simulation currently takes approximately 30 to 45 days in elapsed time on a DEC-ALPHA class system. Further advances in the calculation speed of computing systems are expected prior to the 2002-2005 time frame when the modeling will actually take place.

Efficient data management and automated processing of the input data will be essential. The model will require daily three-dimensional wind, mixing height, temperature, relative humidity, and fog fields. This will require a network of surface and upper air wind and temperature measurements collected via RASS and sodar systems, and at least several daily soundings to provide relative humidity profiles. Fog fields can be generated from airport observations of fog and newer ASOS systems, accurate relative humidity measurements, and potentially data from a network of unheated nephelometers. Frequent measurements of gaseous and aerosol concentrations for defining boundary conditions is required. At minimum, a site is needed on each of the four modeling domain boundaries. Data on gaseous and aerosol concentrations aloft, while desirable, will likely only be available during the winter intensive program.

Daily estimates of spatially, temporally, speciated and size fractionated emissions are also needed. The emissions should be corrected for diurnal temperature and wind speed variations and should also reflect changes in activity patterns. The emissions data will be generated through emissions studies that will be conducted during the field program, as well as ongoing work by the ARB. Despite the advances that have been made in improving inventories, the emissions data are likely to remain the weakest link in the modeling process. Appropriate sensitivity studies will be needed to address the uncertainties in the emissions inputs.

3.4.1.2 Representative Regimes Modeling

Detailed performance evaluation of 365 days of model simulation results is problematic, both in terms of the quantity of data to review and the monitoring data needed to support a detailed performance evaluation. Understanding whether the model is accurately simulating the true process dynamics requires hourly resolution for both aerosol species and gaseous precursors. This type of data is not built into the annual program both from a resource and cost perspective. For this reason, a subset of the days/episodes will be selected for more detailed performance evaluation and enhanced sensitivity testing. The improved understanding gained in examining these selected days will be used to better interpret the results and understand the uncertainties associated with the full suite of modeled days.

It is expected that approximately 60 days will be examined in greater detail. The subset of days selected must represent a statistical sampling of the various meteorological and emissions regimes which make up the annual average. Selection of these regimes can be done through methods such as CART analysis which evaluates the meteorological phenomena which explain the variability observed in the ambient data. Careful thought will need to be given to the influence of local and activity driven emissions patterns which may also drive differences in PM episodes. Because fall and winter episodes dominate the annual average, it may be advantageous to simulate all days during the winter intensive study, augmented with selected days from the fall and summer. The winter program will also be the main source of the detailed time-resolved chemical measurements that will be needed to support a diagnostic model performance evaluation.

The refinements that can be included in the modeling system for the subset of days will include replacement of the diagnostic meteorological model with a prognostic

meteorological model such as MM5, more detailed size resolution, and full aqueous phase fog chemistry for the winter episodes. Improved representation of daily emissions activity data may also be included.

3.4.1.3 Receptor Modeling

The CMB receptor model will be used to determine source contribution estimates at each monitoring site with speciation data using source profiles generated by emissions studies. In the past, the species measured at source and receptor have consisted of elements, soluble ions (including potassium and sodium as well as ammonium, sulfate and nitrate) and carbon. The CRPAQS long-term monitoring program will include measurements of specific organic compounds on seasonally composited particle phase samples to distinguish among organic source sub-types. These will be further supplemented during winter with detailed organic compounds in the gas and particle phases at a larger number of locations and during fall with organic compounds and single particle characterization. These more detailed source apportionment results will be used to develop profiles for apportioning the carbon and geological material during the remainder of the year.

The relative contributions of various source areas to each CMB source type will be determined from transport calculations using the parameterized grid-based modeling system. Primary source types such as woodsmoke, diesel exhaust, and geological material will be modeled as inert tracer species with appropriate deposition losses, while secondary species will be modeled with upper and lower bounds for expected chemical reaction rates. The effects of potential control strategies will be assessed via one of two methods: 1) linear rollback of present and future emissions in each source area with the fractional source type contribution from each source area, or 2) execution of the transport calculations with the parameterized grid-based modeling system to re-assess source-receptor relationships based on proposed emission reduction programs. Because the rollback approach is much simpler from a calculation and resource perspective, it can potentially be used to address a wider range of sensitivity questions than the transport approach. The more detailed transport calculations however can be used to assess the validity of the rollback approach and provide uncertainty estimates on the broader range of the rollback results.

As discussed previously, the rollback calculation is most appropriate for temporal and spatial averages. The rollback approach will evaluate a number of scenarios including: 1) spatial/temporal species averages; 2) temporal species averages for each core site; and 3) several of the highest PM_{2.5} samples at each site. The spatial/temporal seasonal averages are the most appropriate for linear rollback emissions reduction estimates. The other scenarios will indicate some of the uncertainty associated with area wide emissions reductions applied to single sites or single samples, but they are not valid for determining potential effects of emissions reductions.

3.4.2 Wintertime Episodic Source Attribution

Emissions, meteorological, chemical and physical, source, and receptor models will be applied to episodes, primarily to understand the causes of the highest PM_{2.5} concentrations that might affect a 24-hour average PM_{2.5} concentration, as well as episode average PM_{2.5}

that have been shown in Section 2 to be a major cause of annual average PM_{2.5} exceedances. As with the annual average approach, secondary and primary source contributions will be treated by the same models, but different models are considered more applicable to one or the other.

3.4.2.1 Emissions Model

Separate studies (Magliano et. al., 1998; Shimp et. al., 1998) will be carried out during CRPAQS field studies to: 1) estimate traffic volumes, makeup, and the distribution of primary particle emission rates; 2) create chemical profiles for emissions from cooking, cold start exhaust, visible exhaust, diesel exhaust, residential burning, and suspended dust; and 3) determine day and site specific events that might affect concentrations. Coe et. al., (1998) found that visible activities or emissions were poorly correlated with elevated concentrations at nearby sites, thereby confirming saturation study results. Chow and Egami (1997) and Blanchard et. al. (1998) found that the zone of influence is small for most sources when averaged over several hours. Measurements needed to evaluate emissions models are: 1) measurements close to and downwind of large emitters, specifically of carbon and ammonia; 2) detailed chemical measurements at receptors that can be compared with proportions in speciated inventories; and 3) short duration (5 min to 1 hr averages) measurements of particles, precursor gases, and meteorology that can be related to the locations and emissions rates of sources.

3.4.2.2 MM5 Meteorological Model

MM5 will be the primary meteorological model applied to simulate: 1) mixed layer depths and their evolution, including the shallow surface layer as well as the valleywide layer; 2) moisture fields, including the formation of fogs and clouds at ground level and between the surface layer and the valleywide layer; 3) vertical air movements, including that between the surface and valleywide layer and between the valleywide layer and clear air aloft; 4) horizontal transport under stagnant air conditions within the surface layer, the valleywide layer, and in clear air aloft. MM5 has not yet been demonstrated to represent these phenomena during winter time conditions, and many of the required measurements will be needed to evaluate its performance as well as to drive its operation.

MM5 input data consist of wind speed, wind direction, temperature, atmospheric pressure, and relative humidity at ground level, within the surface and valleywide layers, and above the valleywide layer. Ten-meter resolution is needed within the surface layer, 30-50 m resolution is needed in the valley wide layer, and 100 m resolution is needed above the valleywide layer up to ~2000 m agl. Time resolution is at least hourly for these measurements. Measurements are needed where large differences are expected, although this is largely unknown for winter.

Locations that represent different phenomena that should be simulated by the meteorological model include: 1) flows near mountain passes where air might travel between basins (IMS95 valleywide layer depths exceeded 800 m on occasion, above pass elevations but not above the surrounding mountains); 2) patchy fogs and clouds in the SJV and

neighboring air basins; 3) river valley flows, especially along the Sierra Nevada foothills; and 4) channeling within the valleywide layer when winds encounter surrounding mountains.

Verification measurements include mixed layer depths estimated by manual interpretation of vertical measurements, observed fog and relative humidity, and instrumented tower measurements of vertical and horizontal turbulence and fluxes. These will not be used as model inputs; instead they will be used to evaluate the mechanisms and performance of MM5 for simulating wintertime meteorology.

3.4.2.3 Chemical and Physical Models

Chemical and physical processes to be simulated include chemical equilibrium, fog liquid water and chemical content, dry and aqueous phase conversion of inorganic gases to particles, and conversion of heavy hydrocarbons to secondary organic particles. These will be applied in enclosed box, one dimensional (vertical), or simple trajectory (straight line or diagnostic) modes as illustrated by Pandis et. al. (1997, 1998) to evaluate the chemical and physical mechanisms, to identify the most and least significant mechanisms (e.g. aqueous reaction with ozone is the major pathway to sulfate, ammonium nitrate is not nitrate limited), and to place upper and lower bounds on secondary aerosol contributions to $PM_{2.5}$ from different types of emissions (e.g. diesel vs. gasoline for secondary organic aerosol).

These models require high time resolution surface measurements of: 1) precise temperature and relative humidity at aerosol sites; 2) high time resolution sulfate, nitrate, ammonia, nitric acid, and organic and elemental carbon concentrations; and 3) ozone concentrations accurate to 0.5 ppb at levels <5 ppb. They require aerosol measurements of: 1) $PM_{2.5}$ alkaline species; 2) light and heavy hydrocarbons; and 3) fog chemistry.

Similar measurements aloft would be useful at two levels: 1) at ~100 m agl, which is typically above the surface layer, often in the low-lying stratus clouds, and through which pollutants in the surface layer and elevated valleywide layer mix between 1800 and 1000 PST; and 2) near the top of the valleywide layer (~300 to 600 m agl) where solar radiation may be higher than at the surface and where oxidants from the clear air aloft can mix into the surface layer.

3.4.2.4 SAQM-AERO Air Quality Model

SAQM-AERO is a model specifically tailored to central California that incorporates some, and eventually will incorporate all, of the chemical models described above (Chang et al 1996). Only those portions of SAQM-AERO that result in significant sensitivities to changes in precursors, as determined by the simpler chemical modeling, will be “turned on” in SAQM-AERO model applied to CRPAQS.

SAQM-AERO will be applied to the entire central California study region during wintertime episodes, with emphasis on sulfate and nitrate formation. It will integrate the emissions, meteorological, and chemical and physical models. Input data are the same as needed by these other models, but over a larger domain. Technology and financial constraints will limit the number of sites that can acquire complete measurements, so less costly but representative measurements will be needed to determine how well data from the

detailed measurement locations can be extrapolated. Measurement locations are needed at boundaries, in selected urban areas, and above the valley-wide layer to initialize and drive SAQM-AERO.

3.4.2.5 CMB Receptor Model

The CMB receptor model will be applied to the speciated ambient chemical measurements, using source profiles generated by emission studies. The profiles and ambient data will be complete, including light hydrocarbons, heavy hydrocarbons, particulate organic compounds, organic and elemental carbon, ions (sulfate, nitrate, ammonium, chloride, potassium and sodium) and elements. Sources to be apportioned include those identified by the emissions inventory. All of these measurements are needed over <24 hour time periods when changes in contributions are expected owing to changes in emissions rates or meteorology.

3.4.3 Fall Episodic Source Attribution

Emissions, meteorological, chemical and physical, source, and receptor models will be applied during fall, but the spatial scale is not as large for secondary material as during winter. The clear sky stagnation conceptual model will be studied with emphasis on fugitive dust and ammonium nitrate. Owing to the large fugitive dust contributions during fall, PM_{2.5} measurements will be supplemented with PM₁₀ measurements.

The modeling will also aid in the understanding of high average PM_{2.5} concentrations that have been shown in Section 2 to be a major cause of annual average PM_{2.5} exceedances. Secondary and primary source contributions will be treated by the same model although different models are considered more applicable to one or the other.

3.4.3.1 Emissions Model

Emissions studies during the fall field program will focus on dust and ammonia, with measurements near to and distant from these sources. In particular, micrometeorological measurements are needed to characterize the vertical motions to evaluate dust suspension models.

3.4.3.2 Meteorological Model

MM5 will also be the prime model, but with a much finer grid resolution to simulate the mixing aloft and transport of fugitive dust.

3.4.3.3 Chemical and Physical Models

Suspension/deposition models will be applied to determine the heights achieved by surface-based dust and ammonia emissions and the degree to which these are transported by heat and momentum transfer for deposition at the surface.

Equilibrium modeling will be applied to measurements taken upwind and downwind of a large ammonia source to determine the extent to which ammonium nitrate equilibrium changes with precursor gas concentrations.

3.4.3.4 SAQM-AERO Air Quality Model

This model will be applied in the manner described for annual average modeling.

3.4.3.5 CMB Receptor Model

The CMB receptor model will be applied to the speciated ambient chemical and single particle elements, to be determined by the Fugitive Dust Characterization Study. These profiles will consist of particles only and not of gases.