

DRAFT FINAL

**Conceptual Model of Particulate Matter Pollution
in the California San Joaquin Valley**

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Executive Summary

The main objective of this work is to develop a conceptual model for the formation of particulate matter (PM) in the California San Joaquin Valley in the fall and winter seasons. A systematic approach was used to compile the findings of the 1995 Integrated Monitoring Study (IMS 95). Quantitative information is used as much as possible to build the conceptual model, whose framework is based on the chemical characteristics of PM and the physical processes responsible for the accumulation of PM.

The analysis of the chemical composition was based primarily on the chemical mass balance (CMB) work by Magliano (1997). Several primary sources were identified, including vegetative burning, mobile sources, and geological material (dust). Ammonium nitrate (NH_4NO_3), secondary organic aerosols (SOA), and ammonium sulfate composed the secondary fraction of PM. Each of these components was associated with precursor gases (e.g., ammonia (NH_3), nitric acid (HNO_3), volatile organic compounds (VOC), sulfur dioxide (SO_2)) and atmospheric oxidants (e.g., hydroxy radical (OH), ozone (O_3), and nitrate radical (NO_3)). We sought to identify the chemical pathways (gas-phase or aqueous-phase) leading to the formation of each component, and the limiting reagent in each case, so that further field work can be focused on the most important chemical processes and precursors.

The physical transport processes analyzed were associated with mass fluxes of PM and precursors into and out of the atmospheric system of the San Joaquin Valley, including horizontal transport (surface and aloft), vertical mixing, wet deposition, and dry deposition. Ground-level transport was limited due to low surface wind speeds. The effects of aloft transport were dependent on both the upper air wind speeds and the exchange of air between the surface and aloft. Rain was not associated with the PM episodes in the fall and winter seasons, so the wet deposition process of concern was the removal of PM by the settling of fog droplets. Dry deposition pertained to both particles and precursor gases.

Key aspects of the conceptual model are summarized in Table E-1.

Table E-1. Summary of Conceptual Models

	Winter (PM-2.5)	Fall (PM-10)
Chemical Composition and Transformations	<p>Ammonium Nitrate (46%)</p> <ul style="list-style-type: none"> ▪ Nitric Acid Sensitive ▪ Nitric Acid Formation Possibly Limited by Oxidants (OH, O₃, NO₃) Availability ▪ Oxidants May be VOC-Sensitive Rather Than NO_x-Sensitive <p>Organic Compounds (34%)</p> <ul style="list-style-type: none"> ▪ Primary (e.g., Vegetative Burning and Mobile Sources) ▪ Secondary (Anthropogenic or Biogenic Precursors) 	<p>Geological Material (57%)</p> <p>Ammonium Nitrate (16%)</p>
Transport Processes	<p>Limited Ground-level Transport</p> <ul style="list-style-type: none"> ▪ Calm Winds <p>Aloft Transport Possible</p> <p>Limited Vertical Mixing</p> <p>Wet Deposition (Fog)</p> <p>Dry Deposition Unknown</p> <p>Urban Influences (Primary Sources) on Regional Distribution (Secondary NH₄NO₃, SOA)</p>	<p>Limited Ground-level Transport</p> <p>Aloft Transport Possible</p> <p>PM Build-up Correlates with Reduced Mixing Height</p> <p>Limited Wet Deposition (Mild Fog)</p> <p>Dry Deposition Unknown</p> <p>Local Influences (Geological Material) on Sub-regional Distribution (Secondary NH₄NO₃)</p>

In the winter, PM-2.5 accounted for 70% to 80% of the PM mass measured in the rural and urban areas of the San Joaquin Valley. The dominant component of PM-2.5 was NH_4NO_3 , contributing an average of 46% to the PM-2.5 mass. Of the two precursors of NH_4NO_3 , NH_3 and HNO_3 , NH_3 was found to be abundant in the study area of IMS 95. Therefore, the conversion of NO_x to HNO_3 was of interest. There are two pathways for HNO_3 formation that involve the oxidants OH (gas phase only) and O_3 / NO_3 (gas and aqueous phases), respectively. The relative importance of these pathways is uncertain, although daytime production of nitrates likely involved OH. Since only a small fraction of NO_x is converted to HNO_3 (Kumar et al., 1998), it was possible that the oxidation system was limited by the availability of oxidants. During wintertime, these oxidants may be sensitive to VOC rather than NO_x . However, these inferences need to be confirmed.

Primary and secondary organic compounds constituted a significant portion of PM in the San Joaquin Valley, contributing on average 34% of the PM-2.5 mass. Primary components, such as mobile sources and vegetative burning, were strong contributors in urban areas such as Fresno and Bakersfield (up to 35%). The contribution of secondary organic aerosols was typically determined by the difference of total and apportioned organic mass. Schauer and Cass (1998) determined that a regional concentration of about $4.5 \mu\text{g}/\text{m}^3$ existed for secondary organic compounds in the San Joaquin Valley. This regional background can contribute 10% to 15% of the total PM-2.5 mass observed at the rural sites (e.g., Kern Wildlife Refuge).

Sulfates were a relatively small component of PM (6%) during the winter. Sulfates were produced as sulfuric acid either in the gas phase or in the aqueous phase. In the urban areas, precursor SO_2 was abundant (about 3 ppb). Daytime, gas-phase production could be a significant venue for the production of sulfate, although aqueous-phase production in fog was the focus of IMS 95. Aqueous-phase oxidizing agents include O_3 , H_2O_2 , and O_2 (reaction catalyzed by Mn^{2+} or Fe^{3+}). Of the three reactions, the O_3 and O_2 reactions are self-limiting. Their rates decrease with decreasing pH, which may result from the production of sulfates. Analyses of IMS 95 data revealed that the O_3 route was the most important of the three pathways (Collett et al., 1998a).

Stagnation was the single most important factor for the accumulation of PM within the San Joaquin Valley. During a stagnation event, the ground-level wind speed was typically less than 2 m/s, and, on some occasions, diffusion dominated over advection as the mode of pollutant dispersion. Ground-level transport was not a likely mechanism for distributing PM and precursors. Wind speeds aloft were typically higher (up to 10 m/s) and long-range transport aloft was a possible mechanism for pollutant dispersion. Vertical mixing was generally limited to less than 100 m at night and from 125 to 1100 m during the day. Midday vertical mixing of aloft air could be responsible for introducing precursors, transported aloft from upwind areas, to the southern part of the San Joaquin Valley.

Fog was prevalent in the valley during the winter season. In addition to serving as aqueous reactors for the production of secondary sulfate and possibly nitrate, fog droplets also facilitate the wet removal of PM ammonium, sulfate, and nitrate when they settle to the ground. Pandis et al. (1998) concluded that the net effect of fog episodes was the removal of nitrate and ammonium. Sulfates were removed at some sites while produced at others (e.g., Bakersfield).

Dry deposition was not studied during the winter study of IMS 95.

The fall study of IMS 95 was held in the Corcoran vicinity. The fall PM issue differed from the winter one in several aspects: (1) PM-10 exceeded the 24-hour average National Ambient Air Quality Standard, (2) geological material was the dominant component (57%) while NH_4NO_3 only accounted for 16% of PM-10, (3) vegetative burning was not a significant source, (4) fog was patchy. Fewer details were available for the fall analysis. It was expected that the production of NH_4NO_3 would be sensitive to HNO_3 , based on results from the winter IMS 95 and a previous analysis of summer photochemistry (Lu and Chang, 1998). However, further research is needed to understand the production of oxidants during the fall season and to assess the sensitivity of oxidants and HNO_3 to VOC and NO_x precursors. Excess organic compounds (OC) (unapportioned primary OC and SOA) contributed 10% to the PM-10 mass. A CMB analysis using tracer-based profiles may decipher this category further.

PM build-up in the Corcoran area correlated well with the 850 mb (1500 m or 5000 ft) temperature at Oakland airport, indicating that meteorology was responsible for the build-up of PM-10. A sub-regional build-up theory was supported by the zone-of-influence study, which identified a 5 to 15 km spatial distribution scale. Geological material was likely to be generated locally (a neighborhood scale of influence of 1 km was also identified), and contributed to higher PM measurements at the industrial sites relative to the residential and agricultural sites. However, no meteorological data were available at the monitoring sites to confirm the contribution of local wind-blown dust. The ground-level wind speed was typically less than 2 m/s, indicating the lack of surface transport. Aloft transport could not be evaluated without aloft wind speed, concentration, and mixing height data. Since fog was patchy, wet deposition was expected to be limited. Dry deposition of gases and PM was not investigated during the IMS 95 fall study.

The following key gaps in current knowledge were identified in the formulation of the conceptual model:

- Abundance of NH_3 with respect to HNO_3 in areas other than the IMS 95 monitoring domain in the San Joaquin Valley and during spring, summer, and fall
- Production route of HNO_3 and key oxidants (OH or O_3 / NO_3)
- Sensitivity of the oxidants to VOC and NO_x
- Precursors (anthropogenic and biogenic) of SOA
- Production route(s) of sulfate
- Buffering capacity of fogs and oxidant concentrations in fog
- Composition profiles of key San Joaquin Valley PM sources (geological material, vegetative burning, mobile sources)
- Aloft transport as a dispersion mechanism for PM and precursors
- Dry deposition of PM and precursors

1. Introduction

1.1 National Ambient Air Quality Standards (NAAQS) for Particulate Matter (PM)

The U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) in 1997. The standards pertain to particles with aerodynamic diameter of less than 10 μm and those with aerodynamic diameter of less than 2.5 μm :

- Annual average PM-10: Three-year arithmetic average of the annual arithmetic average PM-10 concentrations not to exceed 50 $\mu\text{g}/\text{m}^3$ at any monitoring site.
- 24-hour average PM-10: Twenty-four hour average PM-10 concentrations not to exceed 150 $\mu\text{g}/\text{m}^3$ for a three-year arithmetic average of annual 99th percentiles at any monitoring site.
- Annual average PM-2.5: Three-year arithmetic average of the annual arithmetic average PM-2.5 concentrations not to exceed 15 $\mu\text{g}/\text{m}^3$ for a single community-oriented monitoring site or the spatial average of eligible community-oriented sites.
- 24-hour average PM-2.5: Twenty-four hour average PM-2.5 concentrations not to exceed 65 $\mu\text{g}/\text{m}^3$ for a three-year arithmetic average of annual 98th percentiles at any population-oriented monitoring site.

Limited PM-2.5 measurements from central California indicate that the annual 15 $\mu\text{g}/\text{m}^3$ standard will probably be exceeded in several populated areas, especially in the San Joaquin Valley (Watson et al., 1998). These annual average concentrations are dominated by elevated concentrations that occur primarily during fall and winter. In addition, the 24-hour standard value for PM-2.5 (65 $\mu\text{g}/\text{m}^3$) was exceeded several times during the Integrated Monitoring Study of 1995 (IMS 95) and the 24-hour standard value for PM-10 (150 $\mu\text{g}/\text{m}^3$) was exceeded twice during IMS 95.

1.2 1995 Integrated Monitoring Study

IMS 95 was the planning study of the comprehensive data collection and modeling effort titled California Regional PM-2.5 and PM-10 Air Quality Study (CRPAQS). Under IMS 95, two studies were undertaken during the fall and winter of 1995 to understand the formation of PM in the San Joaquin Valley. The study domain of IMS 95 is shown in Figure 1-1.

Fall Study: The fall study was performed in the vicinity of Corcoran, CA, with one core site (community-representative / community-oriented site) and 22 satellite sites. The satellite sites were set up to collect ambient samples in agricultural, industrial, and commercial/residential neighborhood areas. Twenty-four hour average PM-10 samples were acquired daily from 11/1/95 to 11/14/95 at all locations. Daily 24-hour average measurements of ammonia (NH_3), light absorption, and PM-10 mass were also reported. Detailed component analyses (including PM elements, Cl^- , NO_3^- , SO_4^{2-} , volatilized NO_3^- , K^+ , NH_4^+ , OC, EC, and artifact OC) were performed on 9 daily samples from selected sites.

Winter Study: The winter study featured high-resolution three-hour average measurements for PM-10, PM-2.5, nitric acid (HNO_3), and NH_3 at four locations: Bakersfield, Chowchilla (northern boundary site), Fresno, and Kern Wildlife Refuge (non-urban site). Daily 24-hour average NH_3 , PM-2.5, and PM-10 measurements were taken at selected sites. In addition to PM-2.5 and PM-10, size resolved-samples were collected at Bakersfield using a Multi-Orifice Uniform Deposit Impactor (MOUDI). Limited continuous (hourly) PM-2.5 and PM-10 mass measurements were obtained using tapered element oscillating microbalances (TEOM) and beta-attenuation monitors (BAM), respectively. Hourly measurements of light scattering were also conducted using nephelometers. Component analyses were performed for samples on episode days. Supporting gas-phase measurements included hourly NO / NO_x (NO_2 by difference) and SO_2 (all days), and three-hour or 24-hour average samples of hydrocarbon and carbonyl compounds at the urban sites (episode days).

A second component of the winter study was conducted at Walnut Grove, California in the northern San Joaquin Valley to characterize the vertical variations in fog/cloud chemistry and

Figure 1-1. Study Domain of the 1995 Integrated Monitoring Study

physics. Three-hour average measurements of fog composition were obtained at three different heights (ground level, 140 m, and 230 m above ground level). Limited droplet size-resolved data (e.g., pH) were also taken.

1.3 Objectives of this Study

The objective of this analysis is to formulate a conceptual model for fall and winter PM concentrations in the San Joaquin Valley using primarily the information obtained during IMS 95. This conceptual model is a qualitative description of the physical and chemical processes that govern the formation of PM, which, to the extent possible, is supported by quantitative information. IMS 95 is the planning study for the comprehensive field program CRPAQS. Therefore, the conceptual model is an important link between the planning study and the comprehensive field program because it identifies the major characteristics of the meteorology and atmospheric composition of the area that are relevant to PM. The conceptual model is a valuable tool (1) to guide data collection priorities of CRPAQS and (2) to aid future model development and evaluation activities. The planning study approach being implemented in the San Joaquin Valley has been recommended for the general design of field program experiments used for PM model performance evaluation in other areas (Seigneur et al., 1998a).

1.4 Outline of the Report

We first describe the methodology used in the analysis. The applications of the methodology to typical winter and fall PM episodes are described in Sections 3 and 4, respectively. When appropriate, we provide some preliminary remarks regarding additional measurements that would be useful to complete our understanding of PM pollution in the San Joaquin Valley. However, a more elaborate discussion of data needs will be developed in a subsequent report. Finally, we conclude by addressing the questions we set out to answer in our work statement.

2. Methodology

Our methodology is based on a data-driven approach that uses the composition and physical characteristics of PM as the starting point. Working backwards in time, we use a structured approach to understand the chemical transformations and physical transport processes leading to the observed PM. PM precursors and oxidants may be transported over great distances to produce PM at a given location. Therefore, the transport processes of both PM and PM precursors are considered in formulating the conceptual model. By understanding what compounds contribute to PM formation and how PM episodes come about, we may begin to shape a general understanding about the specific chemical compounds and emissions sources that are the most influential for PM pollution in the San Joaquin Valley.

Figure 2-1 shows the framework for analyzing PM by chemical composition. The categories used in this work were identified by chemical mass balance (CMB) (Magliano, 1997). Several of these categories are primary emissions, including geological material (dust), primary mobile sources, and vegetative burning. Excess organic compounds (OC) consist of organic compounds that are not apportioned to specific sources. They may be primary emissions from sources that are not used in the CMB analysis, such as meat cooking, or secondary organic compounds formed in the atmosphere. Other categories are secondary compounds. The formation of nitrates, sulfates, and secondary organic compounds are analyzed further to identify important chemical reactions responsible for their production and the limiting reagents of the reactions.

Ammonium nitrate in the ambient atmosphere is produced by the combination of ammonia and nitric acid. Ammonia is emitted in the San Joaquin Valley primarily by livestock whereas nitric acid is formed in the atmosphere. The formation of nitric acid involves both NO_2 and oxidants, which are in turn formed from precursors, volatile organic compounds (VOC) and NO_x . Information regarding the limiting reagent in each of the transformation steps of this chemical system may be used to develop control decisions for particulate nitrate.

Sulfate is produced by the oxidation of SO_2 . The gas-phase oxidation process by OH radicals has a lifetime of about one week (Seinfeld and Pandis, 1998). Aqueous pathways are especially

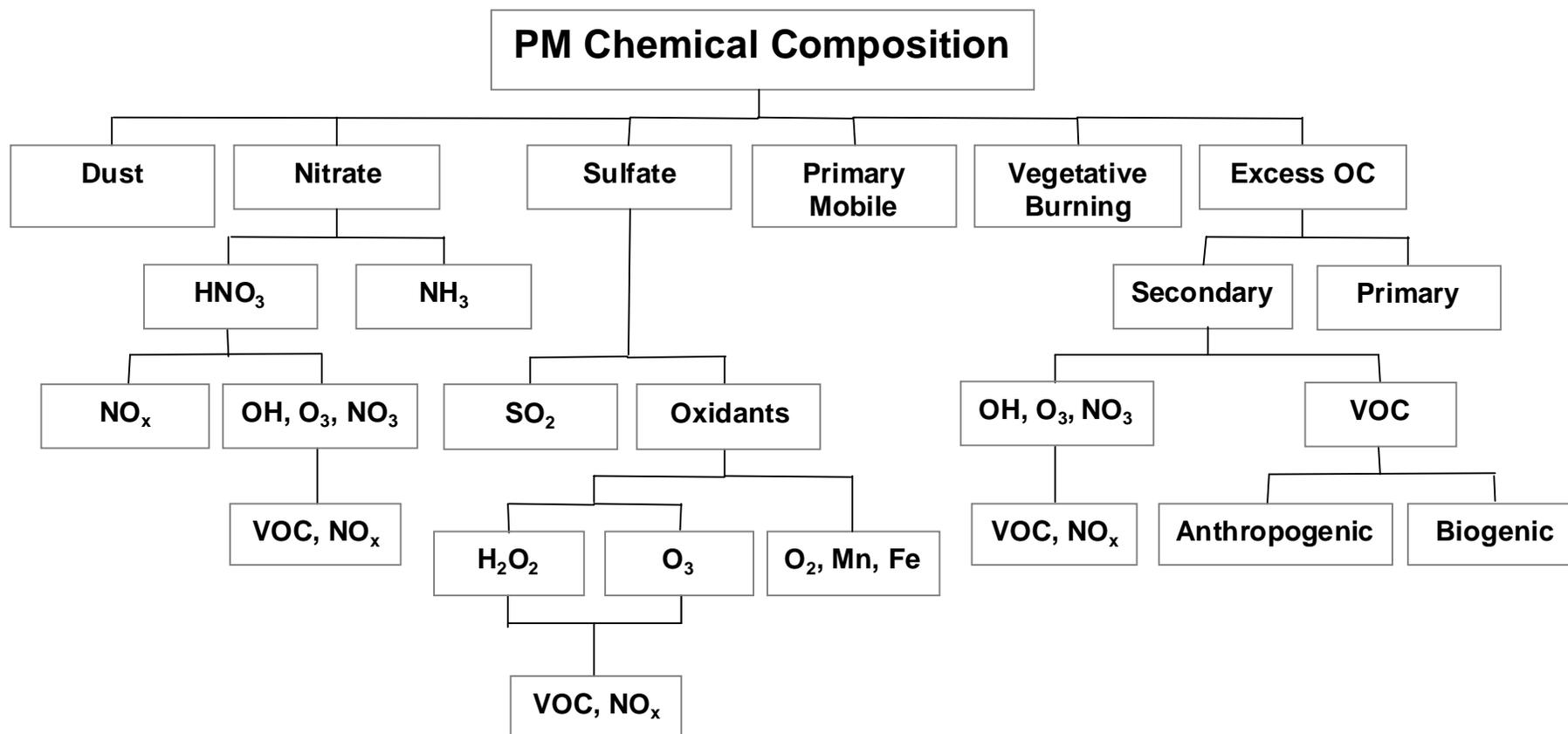


Figure 2-1. Breakdown of PM by Chemical Composition from CMB Analysis (Data Source: Magliano, 1997).

Precursors to PM components are also listed.

important during fog episodes in the San Joaquin Valley (Pandis et al., 1998). In the aqueous phase, O_3 , H_2O_2 , and O_2 (catalyzed by Fe^{3+} or Mn^{2+}) are the main oxidizing agents for dissolved SO_2 . The abundance of O_3 and H_2O_2 is determined by the photochemical reactivity of the system. Therefore, it is important to understand the relative abundance of SO_2 and the oxidants, and the dominant reaction(s) responsible for the formation of sulfates to inform the choices of control strategies for this PM component.

Secondary organic aerosols (SOA) are formed via atmospheric reactions of biogenic and anthropogenic VOC with oxidants, such as OH, O_3 , and NO_3 . Anthropogenic SOA precursors include aromatic compounds, and high molecular weight alkanes and alkenes. Monoterpenes and oxygenated compounds are examples of biogenic emissions that form PM. Therefore, a solid understanding of all VOC emissions within the San Joaquin Valley is essential. In addition, understanding the formation of oxidants (i.e., whether the system is in a VOC- or NO_x -sensitive regime) is also important for a proper assessment of SOA chemistry.

The transport processes that are important on the regional scale include horizontal advection, vertical mixing, wet deposition, and dry deposition (as shown in Figure 2-2). Because there is a secondary component in PM, transport processes for PM precursors (such as HNO_3 , NH_3 , NO_x , VOC, oxidants) also need to be considered. Horizontal advection is a function of wind flow, both at the surface and aloft, which carries gaseous and particulate pollutants from one location to another. The effect of upper-air transport depends upon vertical mixing. As the mixed layer grows during the day, aloft air is entrained into the surface layer system. If the upper air wind speed is high, an air parcel from an upwind location will be mixed in. Wet deposition removes pollutants and particles by scavenging during a rain or fog episode. Dry deposition pertains to the transfer of gaseous and particulate compounds to the surface where they are removed.

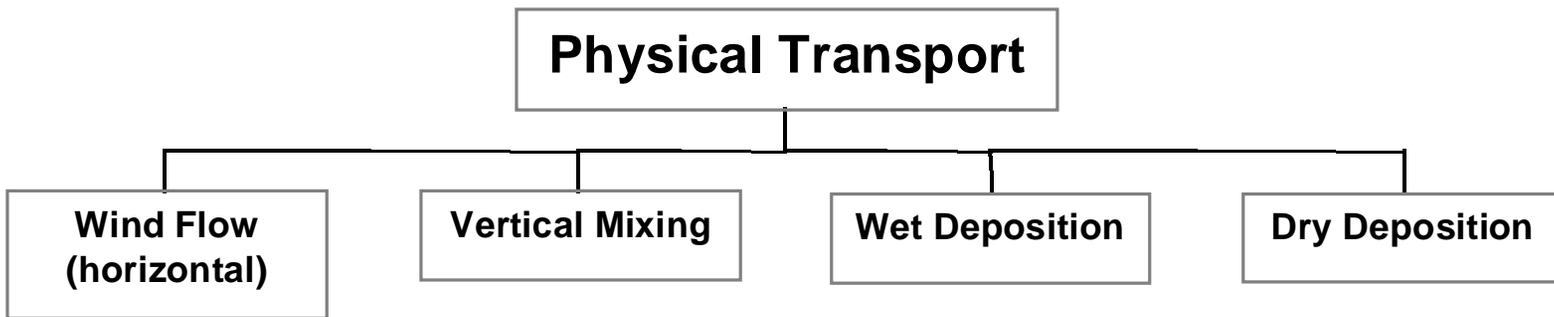


Figure 2-2. Transport Processes Important for the Formation, Accumulation, and Removal of PM.

3. Analysis of Winter PM-2.5 Episodes

3.1 PM-2.5 Problem in the Winter Episodes

The PM-10 24-hour average standard of $150 \mu\text{g}/\text{m}^3$ was not exceeded during the IMS 95 winter study in December, 1995 and January, 1996. Elevated PM concentrations in the winter were a direct result of increased PM-2.5 concentrations, which constituted on average 70-80% of PM-10 concentrations. PM-2.5 exceeded the new 24-hour average standard of $65 \mu\text{g}/\text{m}^3$ at the urban sites of Fresno (five times) and Bakersfield (once). Hence, we focus on the PM-2.5 problem within the San Joaquin Valley in the analysis of the winter episodes.

Figure 3-1 shows the PM-2.5 mass concentrations observed at the core sites during the winter study of IMS 95. The trends of PM were very different during the episodes observed on December 9-10, December 25-28, and January 4-6. The characteristics of PM and the associated meteorology are summarized in Table 3-1. Some of the differences may be explained by a combination of meteorological and emissions factors. For the early December episode, PM-2.5 peaked at Fresno and Bakersfield on December 10. On the same day, a reduction in PM-2.5 was observed at the northern boundary site of Chowchilla. However, PM continued to accumulate at Kern Wildlife Refuge until December 11. Warm temperatures aloft, particularly at Vendenberg (15°C) indicated a strong stagnation event. Fog was also prevalent during this episode, with the daily averaged relative humidity (RH) close to 90% in both cities. A large drop in the 850 mB (1500 m or 5000 ft) temperature was observed at the Oakland airport between December 9 and December 10. A drop in the 850 mB temperature was recorded from December 10 to December 12 at Vendenberg (Lehrman et al., 1998). These records suggested a meteorological event moving through the San Joaquin Valley from NW to SE during the PM episode, which may partly explain the observed temporal variations of PM observed at different sites. During the Christmas episode, Fresno experienced peak 24-hour average PM-2.5 concentration of over $100 \mu\text{g}/\text{m}^3$ on December 26. The other sites exhibited trends that were similar to one another, with maximum concentrations on December 27. PM concentrations at Bakersfield were about $15 \mu\text{g}/\text{m}^3$ higher than the rural sites on December 27 and 28. Of the three episodes studied in the

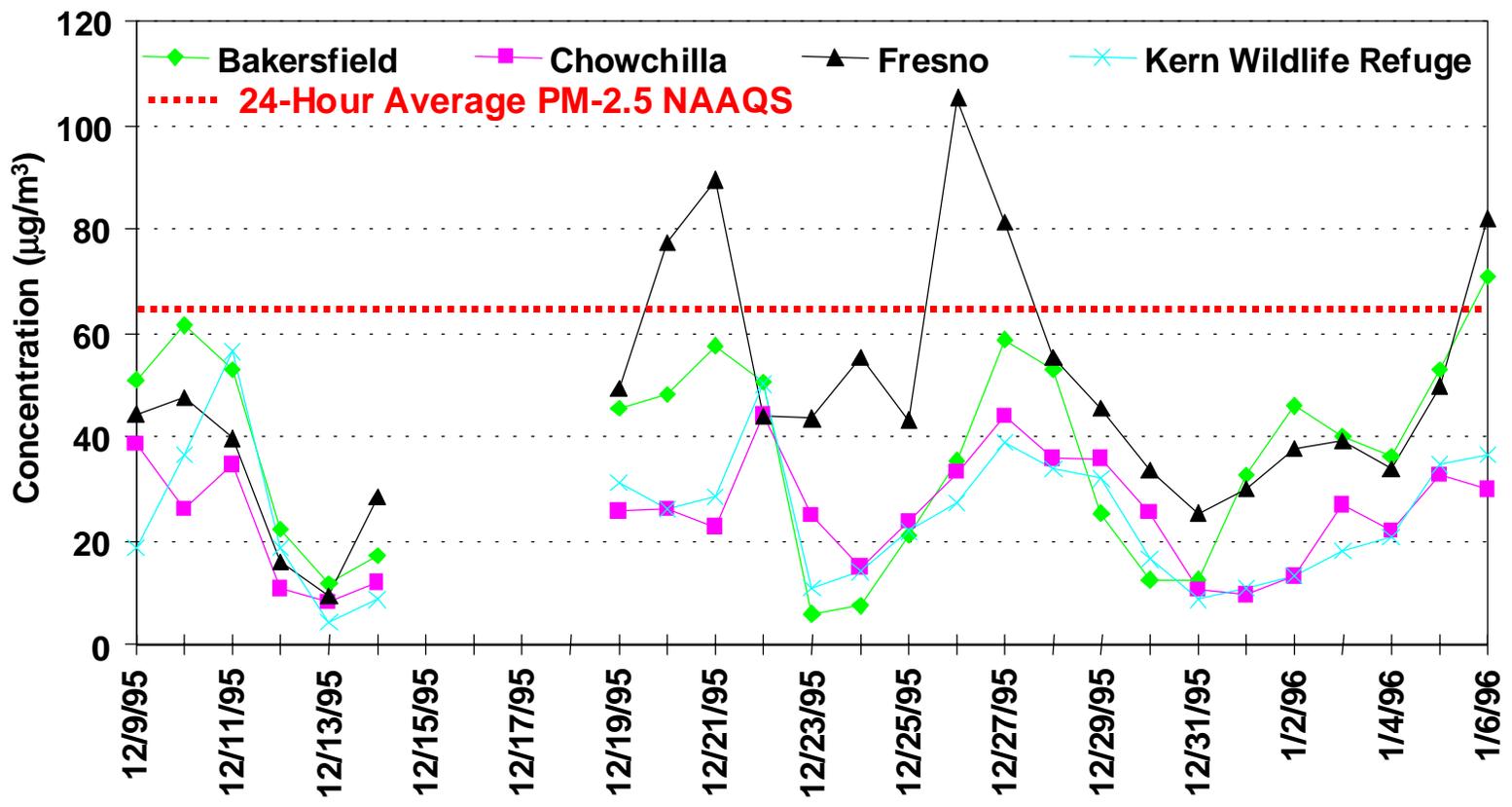


Figure 3-1. Temporal Variations of PM-2.5 Mass Concentrations during the IMS 95 Winter Study (Source: CARB, 1998)

Table 3-1. Characteristics of the Winter PM Episodes in the San Joaquin Valley
(Data Source: Chow and Egami, 1997; Lehrman et al., 1998)

Episode	December 9 – 10, 95	December 25 – 28, 95	January 4 – 6, 96
PM2.5 Observations	None of the core sites exceeded 24-hr PM-2.5 or PM-10 standard	PM-2.5 exceeded 65 $\mu\text{g}/\text{m}^3$ on two days at Fresno, but not at the other core sites	PM-2.5 exceeded 65 $\mu\text{g}/\text{m}^3$ on 1/6/96 at Bakersfield and Fresno, but not at the other core sites
Peak Time / Site	Peak concentrations observed at different sites on different days (Chowchilla 12/9, Fresno/Bakersfield 12/10, Kern Wildlife Refuge 12/11 Bakersfield on 12/10/95 (60 $\mu\text{g}/\text{m}^3$ PM-2.5, 75 $\mu\text{g}/\text{m}^3$ PM-10) Peak 3-hr concentration: 9 p.m. to midnight	PM peaked on December 26 (Fresno) or 27 (other sites), then decrease until December 31 Fresno on 12/26/95 (105 $\mu\text{g}/\text{m}^3$ PM-2.5, 125 $\mu\text{g}/\text{m}^3$ PM-10) Peak 3-hr concentrations: midnight to 6 am. (Lower peaks next two nights.)	PM concentrations on the rise at the 2 urban sites when monitoring period ended on 1/6/96; but rural sites same 24-hour PM on 1/5-1/6 Fresno on 1/6/96 (80 $\mu\text{g}/\text{m}^3$ PM-2.5, 100 $\mu\text{g}/\text{m}^3$ PM-10) Peak 3-hr concentration: 9 pm to midnight
Wind Speed	43 – 60% data* < 1 ms^{-1}	36 – 49% data < 1 ms^{-1} . SE winds at low levels	39 – 52% data < 1 ms^{-1} NW winds during the day at ground level. SE winds aloft at Bakersfield
Temperature (ground / upper air)	Ground level: 10 – 15°C; Warm aloft temperatures: 14 – 15 °C	Ground level: 0 – 15 °C Aloft temperature: 7 - 9 °C	Ground level: 7 - 15°C;Aloft Temperature: 10 – 15 °C
Mixing Height at 4 pm	125 – 175 m	250 – 900 m	450 – 1100 m
Fog	10 – 20 fog hours per day at Fresno and Bakersfield	5 – 10 fog hours per day at Fresno and Bakersfield	10 – 15 fog hours per day at Fresno and Bakersfield

* based on hourly-average vector wind at 42 sites in the San Joaquin Valley

winter, the Christmas episode was associated with the lowest temperatures aloft (about 8 °C) and lowest RH (80%). Pressure gradients from San Francisco to Las Vegas and Reno were negative. High pressure over the San Joaquin Valley resulted in low wind transport. The observed patterns of build-up were likely a result of reduced transport and increased anthropogenic emissions during the holiday season. Clear differences in PM-2.5 concentrations were observed between the urban sites and the rural sites during the January episode. Both Fresno (80 $\mu\text{g}/\text{m}^3$ PM-2.5) and Bakersfield (70 $\mu\text{g}/\text{m}^3$) exceeded the 24 hour-average PM-2.5 NAAQS of 65 $\mu\text{g}/\text{m}^3$ on January 6. An Alberta low pressure system preceded this episode (Lehrman et al., 1998). The pressure front may have transported pollutants from the Pacific coastal cities into the San Joaquin Valley. During the episode from January 4 to January 6, the temperature aloft increased while the pressure gradient weakened. Moderate fog was observed (average RH was 85%). PM concentrations at Chowchilla and Kern Wildlife Refuge were 50% lower than the urban sites. PM-2.5 accumulated slowly, if at all, at the rural sites during the last two days of the episode. These observations show that the spatial and temporal patterns of PM-2.5 vary among the episodes.

Diurnal profiles of PM were measured by collecting three-hour average samples in the winter IMS 95 study. Figure 3-2 shows the observed temporal behavior of PM-10 during the Christmas episode. Sharp peaks were observed in the evening at Fresno; weaker evening peaks were observed at Bakersfield on two of the episode days. The rural sites exhibited lower diurnal variability relative to day-to-day fluctuations, with higher PM concentrations during the day. These observations are generally consistent with the conclusions drawn using the visibility data obtained by nephelometers. Since measurements of light scattering could be made at time resolutions of less than one hour, they were used to assess the adequacy of the three-hour average PM samples for capturing changes in PM. Main et al. (1998) analyzed one-hour average nephelometer measurements (transformed to correct for RH effects) and concluded that three-hour samples adequately characterized the diurnal variations in light scattering and PM. Transformed data showed higher PM in the urban areas than in the rural areas. For Fresno and Bakersfield, higher transformed scattering values were observed at night than during the day. Main et al. (1998) also identified 4-7 p.m. as the time frame for increased scattering at Bakersfield, and 9 a.m. to 12 noon as the period of decrease scattering at Fresno. However,

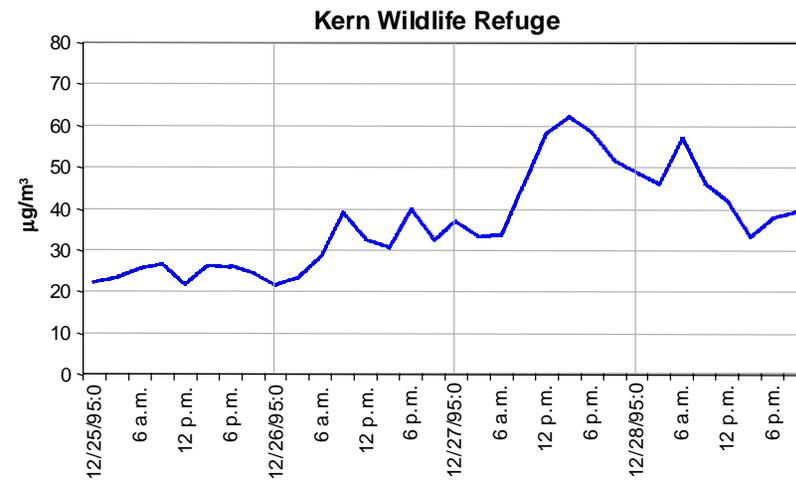
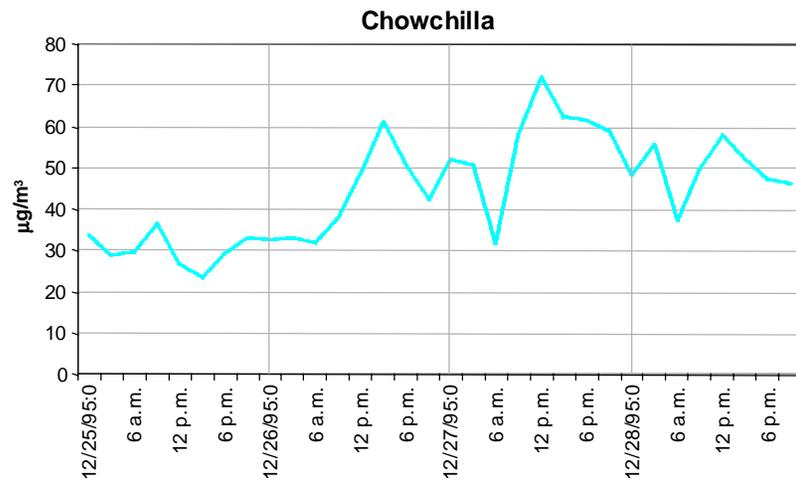
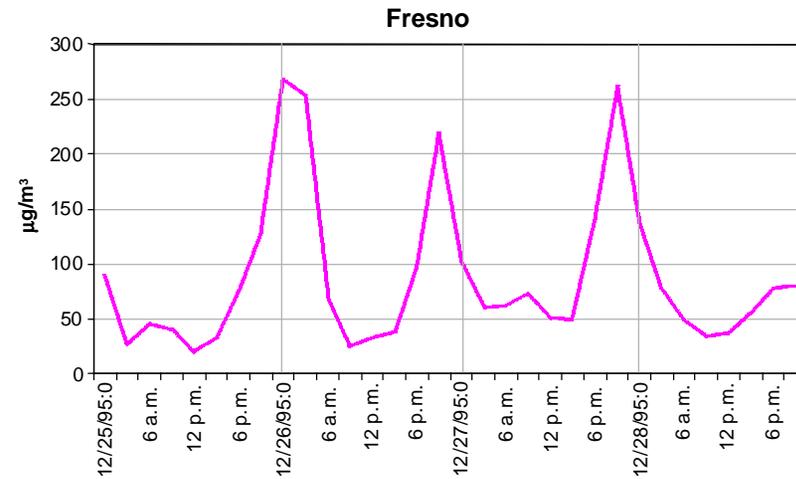
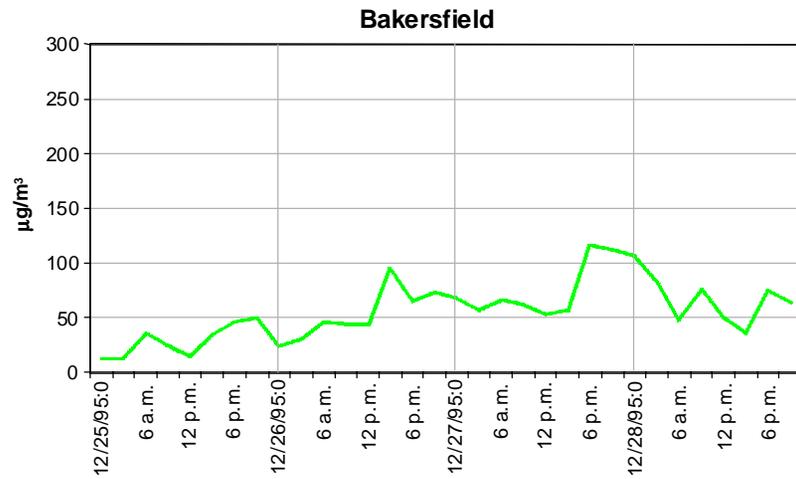


Figure 3-2. Three-hour Average PM-10 Measurements (Source: CARB, 1998)

during the Christmas episode, PM reductions took place earlier in the morning. The transformed readings at the rural sites were less reliable indicators of diurnal PM because fog was prevalent and the RH was too high for the application of the correction term. Main et al. (1998) observed little variation in the light scattering efficiency during the day at Kern Wildlife Refuge, which is consistent with lower PM observed at that site.

Richards et al. (1998) analyzed collocated nephelometer and PM-2.5 measurements and concluded that a heated nephelometer could provide readings that correlate very well with PM-2.5, even under high RH and foggy conditions. The scattering efficiency for PM-2.5 was $\sim 3.7 \text{ m}^2/\text{g}$, with higher efficiency from ammonium nitrate and sulfate ($\sim 4.2 \text{ m}^2/\text{g}$) and lower efficiency from other compounds ($\sim 2.9 \text{ m}^2/\text{g}$). The good correlation may be a direct result of the dominant fraction of ammonium nitrate, which also contributed significantly to scattering. McDade (1997) verified the extinction of the San Joaquin Valley particles using the observed data on the size distribution and composition of particles. Ammonium nitrate was found to be the largest contributor to light extinction.

3.2 Chemical Composition and Transformations

Table 3-2 shows the contributions of major sources to the concentration of PM-2.5 during the winter episodes. The PM-2.5 composition is displayed in a pie chart in Figure 3-3. Significant variability of the source contributions was observed at the core sites. Table 3-3 shows typical contributions of key components at urban and rural sites. PM at urban sites typically showed higher contributions from primary sources, while higher contributions from secondary compounds were observed at the rural sites. The chemical composition breakdown of the San Joaquin Valley winter PM-2.5 is shown in Figure 3-4, using the CMB categories reported by Magliano (1997).

Table 3-2. Chemical Mass Balance Analysis of PM in Winter in the San Joaquin Valley
(Data Source: Magliano, 1997)

Episode	Component	Contribution (Range at Core Sites)
Winter PM-10	Nitrate	40% (8 – 54%)
	Vegetative Burning ^(a)	12% (4 – 22%)
	Mobile Sources ^(b)	12% (4 – 21%)
	Geological material ^(c)	10% (6 – 16%)
	Excess OC ^(d)	8% (1 – 25%)
	Sulfate	6% (1 – 10%)
Winter PM-2.5 (70-80% of PM-10 mass)	Nitrate	46% (10 – 69%)
	Vegetative Burning	15% (5 – 35%)
	Mobile Sources	12% (7 – 19%)
	Excess OC	7% (0 – 23%)
	Sulfate	6% (1 – 12%)
	Geological material	0.6% (0.1 – 1 %)

(a) Vegetative Burning: based on combustion PM samples from fireplaces and agricultural burning.

(b) Mobile Sources: based on SCAQMD and Phoenix dynamometer profiles.

(c) Geological material: soil dust profiles determined from samples of soil and (paved and unpaved) road dust from Visalia, Bakersfield, and Taft.

(d) Excess OC: organic compounds not accounted for by the other source categories, including primary and secondary components.

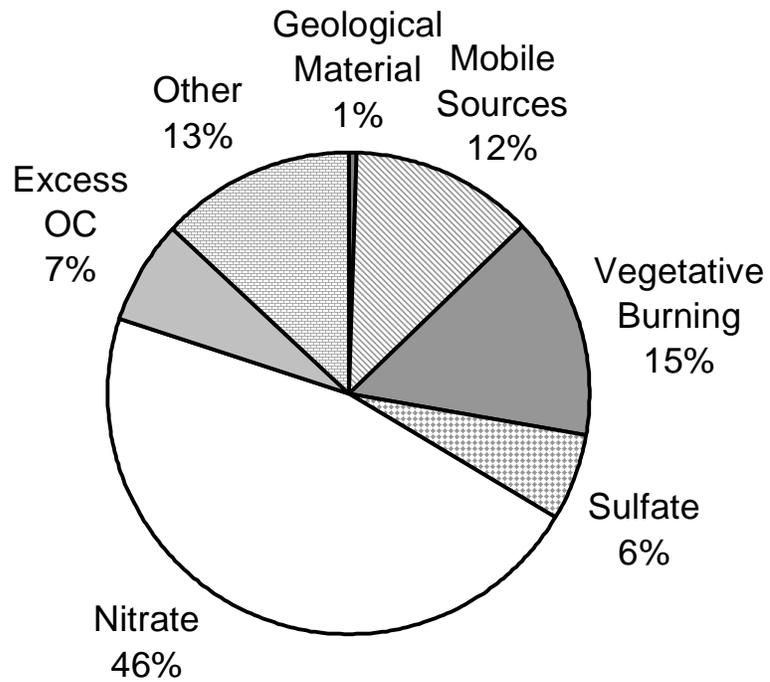


Figure 3-3. Source Contributions Based on Chemical Mass Balance Analysis of Winter PM-2.5
 (Data Source: Magliano, 1997)

Table 3-3. Differences in PM-2.5 Compositions at Urban and Rural Sites

(Data Source: Magliano, 1997)

	Urban	Rural
Average Mass on Episode Days	57 $\mu\text{g}/\text{m}^3$	31 $\mu\text{g}/\text{m}^3$
Nitrate	30%	50%
Vegetative Burning	21%	9%
Mobile Sources	14%	10%

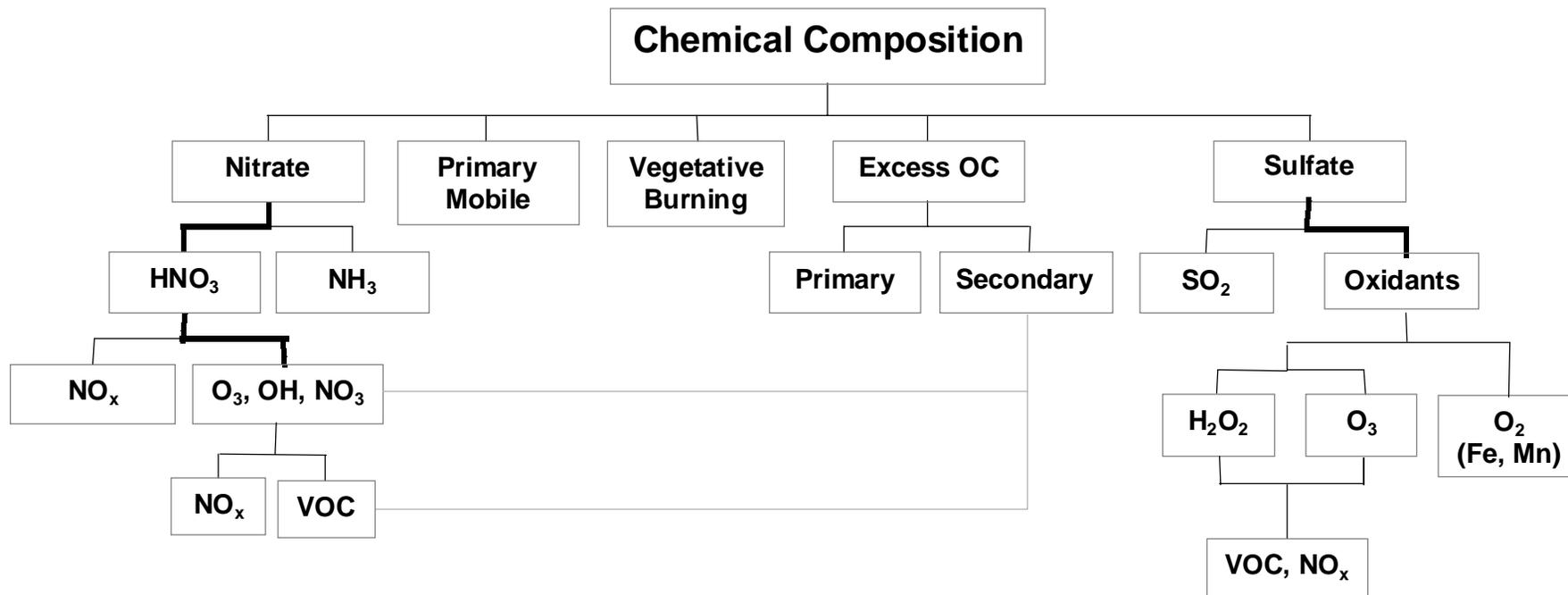


Figure 3-4. Breakdown of PM by Chemical Composition for a Typical Winter Episode

(bold lines represent the influential variables for the formation of secondary PM,

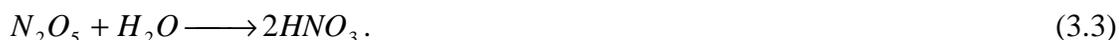
to the extent that sufficient information is available to determine which variables are the most influential).

Ammonium Nitrate

Ammonium nitrate was the most dominant compound found in PM-2.5 during IMS 95 winter episodes. The ranges of concentrations observed were 9.6 to 24 $\mu\text{g}/\text{m}^3$ at rural sites and 10.6 to 29.5 $\mu\text{g}/\text{m}^3$ at urban sites. At the non-urban sites, ammonium nitrate can contribute 50% or more to the total mass of PM-2.5. As indicated in Figure 3-4, ammonium nitrate is formed by the combination of ammonia and nitric acid:



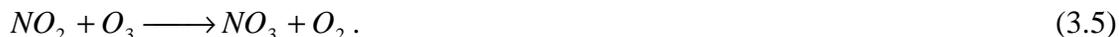
Ammonia (NH_3) is emitted mainly from dairies / livestock / poultry feedlots and natural soils (Haste et al., 1998), while nitric acid (HNO_3) is typically formed in the atmosphere. Kumar et al. (1998) showed that the formation of ammonium nitrate (NH_4NO_3) within the study area of IMS 95 was limited by the availability of HNO_3 in the winter, since 75 to 82% of the total nitrate was present in the particle phase. NH_3 sources were abundant, and 40-50% of the ammonia remained in the gas phase after neutralizing the particulate-phase nitrate. The ratio of NH_3 to HNO_3 was greater than 1.05 in 93% of the winter samples. The abundance of NH_3 relative to HNO_3 needs to be confirmed for areas west of Interstate 5 (Phil Roth, Personal Communication, 1998). The formation of HNO_3 may take place either in the gas phase or in water droplets. Gas-phase reactions that form HNO_3 are:



The hydrolysis reaction also takes place in the aqueous phase, with increased reaction rate. N_2O_5 is formed when NO_2 and nitrate radical (NO_3) combine:



NO₃ is formed when O₃ oxidizes NO₂:



During the day, the lifetime of NO₃ is usually short because the photolysis reaction of NO₃ is fast, and, consequently, the concentration of N₂O₅ is expected to be low.

The ambient formation of HNO₃ may be either NO_x-sensitive or oxidant-sensitive (OH in Reaction 3.2, NO₃ in Reaction 3.4, and O₃ in Reaction 3.5). Although information regarding the dominant reaction was not available, indirect evidence from the diurnal profile of total nitrate (peak concentrations in the afternoon) seemed to indicate that the NO₂ + OH reaction was an important nitric acid production route. Magliano (1997) also noted an increase in the NH₄NO₃ mass during the day (starting at 9 a.m.). At urban sites, NH₄NO₃ accounted for 20-25% of the evening mass and 40-45% of the midday PM-10 mass. The percentage contribution was relatively constant at rural sites. The analysis of Carr and Gray (1998) indicated that only a small fraction (12% in cities, 30% in rural areas) of the available NO_x was converted to nitric acid and nitrate during a typical episode. They concluded that the conversion of NO_x to nitric acid might be limited by the availability of oxidants. Thus, to understand which primary pollutants govern the formation of ammonium nitrate, we need to address the oxidation potential of the atmosphere and determine which pollutants (i.e., NO_x or VOC) are the most influential for the formation of oxidants in the system.

Organic Compounds

Organic compounds accounted for a substantial fraction (35%) of the PM-2.5 particle mass at the urban sites of Bakersfield and Fresno. In the San Joaquin Valley winter, sources of organic particles included mobile vehicles, vegetative burning (e.g., household wood burning), and other (excess) organic compounds (e.g., primary compounds from meat cooking or secondary organic compounds). The contribution from hardwood and softwood combustion was especially pronounced in the December 26-28 episode at Fresno, where wood combustion surpassed ammonium nitrate as the largest contributor of PM-2.5. (The contribution of vegetative burning

was 35% according to Magliano, 1997; combined hard and soft wood burning contributed close to 50% according to Schauer and Cass, 1998.) The vegetative burning contribution profile exhibited, not surprisingly, peaks in the evening samples at the urban sites, corresponding to domestic fireplace usage. On the other hand, in rural areas, the percentage contribution remained essentially constant throughout the day. The influence of the vegetative combustion source was weak at the Kern Wildlife Refuge core site (see Table 3-3). Motor vehicle particles also exhibited higher contributions at urban sites than rural sites.

Excess OC represents the fraction of OC that is not apportioned to any source in the CMB analysis. The large amounts of excess OC in many CMB runs may be an indication of the inadequacy of the current source profiles, which can result in mis-allocation amongst the various carbon-containing sources using the traditional CMB approach. Nonetheless, a fraction of excess OC corresponds to secondary organic aerosol. At present, there are no direct measurement techniques that allow the experimental distinction of primary vs. secondary organic compounds. Better source profiles or tracer compounds (e.g., Schauer and Cass, 1998) may increase the resolution of the CMB technique in that respect. With sufficient sensitivity, CMB or tracer techniques are tools to apportion ambient organic aerosols to their primary sources; and the amount of secondary organics may be determined by the difference of total organics and the primary fraction. Schauer and Cass (1998) reported that the fine organic compound mass that could not be attributed to direct particulate emissions averaged about $4.5 \mu\text{g}/\text{m}^3$ at both urban and rural sites in the winter. The un-apportioned mass was interpreted as a uniform regional background of secondary organic aerosols in the San Joaquin Valley during two different episodes. The secondary organic aerosol background contributed to a maximum of 16% of PM-2.5 to Fresno in the January, 1996 episode. Similar high contributions were also calculated at the Kern Wildlife Refuge, where secondary organics were the second largest contributor to PM-2.5 behind ammonium nitrate. The analysis and modeling results of Strader et al. (1998) were generally consistent with Schauer and Cass (1998), indicating that secondary organic aerosols should not be ignored in the apportionment of the PM concentrations.

Oxidant Chemistry

Oxidant chemistry may be VOC-sensitive or NO_x-sensitive. The sensitivity regime affects the response of the atmospheric system towards control measures placed on the precursors. A possible photochemical indicator (e.g., Sillman, 1995; Lu and Chang, 1998) is the ratio of HNO₃ (or HNO₃ + particulate nitrate) and H₂O₂ concentrations. These chemical species are produced by radical termination reactions and their relative importance sheds some light on whether the chemical system is VOC- or NO_x-sensitive. Figure 3-5 depicts the major chemical pathways of the VOC/NO_x/O₃ system. When NO_x is low, HO₂ radicals preferentially recombine to form H₂O₂ (left-hand side of Figure 3-5). When VOC is the limiting reagent, OH reacts preferentially with NO₂ to form HNO₃ (right-hand side of Figure 3-5). Consequently, the ratio of H₂O₂ and HNO₃ concentrations is a good indicator of the relative extents of NO_x and VOC sensitivity in the atmospheric system.

Lu and Chang (1998) investigated the summer ozone chemistry in the San Joaquin Valley, CA, and determined that much of the domain was sensitive to NO_x, or both VOC and NO_x. However, Jacob et al. (1995) reported a seasonal transition from NO_x-limited conditions during summer to VOC-limited conditions during winter for ozone production over the eastern United States. Therefore, the results of Lu and Chang (1998) may not be directly applicable to the winter conditions in the San Joaquin Valley. Typical concentrations of HNO₃ (1.5 ppb at urban sites, 2.4 ppb at rural sites) and H₂O₂ (0.2 ppb at urban sites, 0.3 ppb at rural sites) suggest that the oxidant chemistry of the San Joaquin Valley may be in the VOC-sensitive regime during the winter season. This result is preliminary because the indicator approach (i.e., HNO₃/H₂O₂ ratio) has not been evaluated for the type of meteorological conditions prevalent in the San Joaquin Valley winter.

Ammonium Sulfate

Although ammonium sulfate only accounted for 6% ($\leq 3.4 \mu\text{g}/\text{m}^3$ at Kern Wildlife Refuge; $\leq 3.7 \mu\text{g}/\text{m}^3$ at Bakersfield) of the PM-2.5 measured during IMS 95 in the San Joaquin Valley, it was the third largest component at the rural site of Kern Wildlife Refuge. The concentration of SO₂ in the urban areas averaged about 3 ppb during the winter episodes, and accounted for almost 80% of the total sulfur (18% sulfur in fine particles, 4% in coarse particles). Therefore, it was

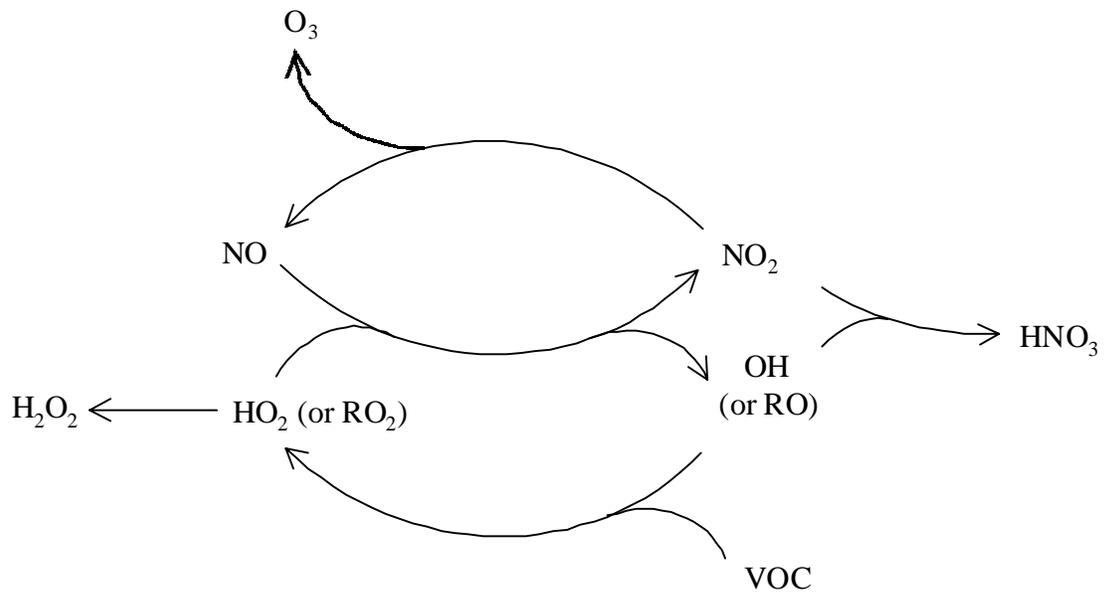


Figure 3-5. Simplified Description of Photochemical Smog Formation Showing the Two Major Interacting Cycles (NO/NO₂ and OH/HO₂ or OH/RO₂ and the Two Major Sinks for Radical Chain Termination: H₂O₂ (NO_x Sensitive) and HNO₃ (VOC Sensitive).

Source: Seigneur et al., 1998b

likely that the conversion of SO₂ to sulfates in urban areas was limited by the availability of oxidants. The situation at the rural areas was not as clear. The concentration of gaseous SO₂ was significantly lower in the rural areas (0.1 ppb, 20% of total sulfur), and fine and coarse sulfate accounted for 56% and 22% of the total sulfur, respectively. In-situ production of sulfate was probably limited. Therefore, transport of particulate sulfate was a factor to consider at rural locations.

Midday peaks observed at the rural sites (Magliano, 1997) and the abundance of sulfates in the PM-2.5 fraction (aqueous production of sulfates typically take place in coarse particles) seemed to be consistent with day-time gas-phase production of sulfate rather than production in fog droplets. Nonetheless, much effort was invested during IMS 95 to understand the aqueous-phase chemistry leading to the formation of ammonium sulfate during a fog episode. There are three major oxidation pathways for dissolved SO₂: oxidation by ozone, catalytic oxidation (dissolved Fe or Mn as catalysts) by oxygen, and oxidation by H₂O₂. Of these three pathways, only the H₂O₂ oxidation reaction is insensitive to pH. The other two reactions have kinetic rates that decrease as the pH decreases; therefore, they tend to be self-limiting since sulfate formation decreases the pH. Therefore, it was postulated that the kinetics of the SO₂ oxidation reaction(s) responsible for sulfate production may change because of pH changes within the fog droplets due to the production of acids.

According to the analysis of Collett et al. (1998a), ozone was the dominant oxidizing agent in 98% of the IMS 95 fog samples. This conclusion was reached based on two main assumptions: (1) dissolved Fe(III) comprised one quarter of total aqueous iron concentration, and (2) the gaseous concentration, from which the aqueous concentration was calculated, was assumed to be equal to the instrument's detection limit (DL) when it fell below DL. Sensitivity studies showed that if these assumptions were relaxed, all three pathways would be important for the formation of sulfate at urban sites, although sulfate production at the rural site will still be dominated by the ozone reaction. Therefore, it is important to have accurate measurements of the oxidants at the ppb level. Collett's group (1998b) found that at urban sites, there was some unexplained buffering capacity within the fog droplet such that the ozone reaction remained highly competitive throughout the fog episode. The fog drop buffering capacity, due to some dissolved

agent, could not be explained by the usual buffering agents, such as carbonate, acetate, and formate. Several phenol candidates were analyzed, but their concentrations did not explain the observed buffering. The authors postulated that a dissolved organic acid, such as humic acid, might be responsible for the buffering of fog droplets. This buffering capacity should be understood for accurate prediction of the chemical reaction pathways that govern sulfate production.

3.3 Transport Processes

Typical transport scales may be inferred by the spatial distribution of PM. For example, Table 3-3 shows that the primary sources, such as mobile sources and vegetative burning, contributed more to PM in the cities, where they are generated, than to PM in the rural areas. On the other hand, nitrate, a surrogate secondary compound, displayed relatively uniform distribution. Therefore, both urban-scale (primary sources) and rural-scale (secondary compounds) influences were observed for PM-2.5 in the winter.

Blanchard et al. (1998) analyzed the spatial representativeness of monitoring stations and the zone of influence of emissions sources. The spatial representativeness, defined as the fraction of the monitoring domain having concentrations within $\pm 20\%$ of the measurement, of the core sites was variable. For example, the Fresno core site was representative of the monitoring domain only 27% of the time, the Bakersfield core site 60%. However, the spatial representativeness increased to 90% by using two additional sites. Spatial representativeness is also a function of the PM component. Relative to primary components, secondary compounds were more uniformly distributed within each network, as indicated by the large area with similar concentrations. Representativeness was typically high when concentrations were high; however, representativeness and concentration do not necessarily track. Differences in mixing and transport conditions could explain some of the observations of increasing or decreasing spatial representativeness at peak concentration during an episode. Available data seem to indicate higher average spatial representativeness in the rural network (73%) than the urban ones (61% at

Bakersfield, 54% at Fresno) for PM-10. This is consistent with the urban sources at the cities and the dominance of the secondary compounds in the rural areas.

The zone of influence analysis (Blanchard et al., 1998) confirmed the observations of urban (10 km) and regional-scale dispersion (20 km). A mean urban background of $40 \mu\text{g}/\text{m}^3$ PM-10 was inferred. Collins (1998) concluded that the regional background averaged about $25 \mu\text{g}/\text{m}^3$ for PM-2.5. Concentrations measured at the boundary sites at the valley floor were very similar to the rural sites. Elevated boundary sites usually recorded concentrations lower than or similar to the background sites on the valley floor. For example, 24-hour PM-2.5 measurements recorded at the elevated boundary sites were between 10 to $20 \mu\text{g}/\text{m}^3$ on December 26 when the rural concentrations were 30 to $40 \mu\text{g}/\text{m}^3$. On January 5, when the rural PM-2.5 concentrations were about $35 \mu\text{g}/\text{m}^3$, the elevated boundary sites measured concentrations between 25 and $50 \mu\text{g}/\text{m}^3$. Despite the availability of concentration measurements at the boundary sites, fluxes across the boundary sites were poorly defined because of low and variable winds.

Fog and stagnation were typically the dominating features of the meteorological conditions. The temporal and spatial distribution of fog was observed using a network of Optec nephelometers. The light scattering measurements indicated the non-uniform pattern of fog. Fog was more frequent and longer in duration at the rural sites. Of the urban sites, Fresno tended to be foggier than Bakersfield. During the IMS winter study, ground level transport was limited to a length scale of about 4 km during a stagnation period of 3 to 5 hours (Carr and Gray, 1998). Advective transport gave way to diffusion during some periods of stagnant conditions. Carr and Gray observed both regional and local influences on nitrate production, although it was unclear whether the so-called regional influence was due to advective mixing, diffusion, or widespread / area sources.

As shown in Table 3-1, during the winter episodes, the maximum daily mixing height ranged from 125 m to 1100 m. The low mixing heights during several episodes were likely conducive to pollutant build-up within the valley. Dye et al. (1997) indicated that there were typically three layers within the San Joaquin Valley: the surface layer, the upper mixed layer, and the decoupled layer. The heights of the layers varied with time and location. The surface layer depth ranged

from a few hundred meters to about 1000 m. At night, the surface layer was further divided into an inversion layer of 50 – 100 m and a decoupled surface layer. The decoupled layer was roughly 2000 m above ground level. During two of the winter episodes, the mixed layer extended beyond the surface layer at some locations in the afternoon. Since the wind speeds aloft (up to 10 m/s) were typically higher than in the surface layer (0 – 300 m wind generally < 2.5 m/s) (Lehrman et al., 1998), transport of pollutants aloft and subsequent mixing into the surface layer may be a mechanism of distributing pollutants within the valley in a multi-day episode.

With reduced mixing heights of a few hundred meters and reduced length scales for horizontal transport, much of the pollutants were trapped within the San Joaquin Valley. The dominant sink processes were, therefore, wet and dry deposition. Wet deposition is likely to be a significant removal process because of the solubility of ammonium nitrate, nitric acid, and ammonia gas. During fog episodes, a fraction of the particles are activated to grow by absorbing water. As fog droplets settle more quickly than smaller particles, PM is removed as fog. Measurements were taken of wet deposition at Fresno during the early December PM episode. The observed removal fluxes were 169 $\mu\text{g}/\text{m}^3$ for sulfate, 1018 $\mu\text{g}/\text{m}^3$ for nitrate and 1291 $\mu\text{g}/\text{m}^3$ for ammonia. Therefore, the concentration of PM typically diminished after a major fog event, although the effect of wet deposition may be balanced by aqueous production of sulfate during patchy / local fog events. Model predictions of wet deposition fluxes were sensitive to assumptions used in the model. For example, when the wet deposition velocity was reduced by a factor of 2, the removal of nitrate was reduced by 25%. Pandis et al. (1998) calculated with their fog simulation model that the San Joaquin Valley scavenged nitrate and ammonium, but may produce or remove sulfate.

Dry deposition was not studied during IMS 95, although it may be a significant sink for both particles and precursor gases. For instance, nitric acid deposits fairly rapidly (compared to other nitrogen species such as NO or NO₂) because it has high affinity towards surfaces. Russell et al. (1985) determined that 75% of the atmospheric nitric acid could be removed in the California South Coast Air Basin in 24 hours via dry deposition.

4. Analysis of Fall PM-10 Episodes

4.1 PM-10 Problem in the Fall

Figure 4-1 shows the 24-hour average PM-10 mass concentrations observed at Corcoran (core and satellite sites) during the fall study of IMS 95. The spatial average PM-10 concentration in the Corcoran vicinity exceeded $150 \mu\text{g}/\text{m}^3$ on November 8 and 14. Table 4-1 summarizes the PM-10 observations and the associated meteorological conditions. Two episodes were monitored during the fall of 1995, separated by the passage of a low pressure system on November 8 and 9 through the valley. The chemical mass balance, with dominating contribution (> 50%) from dust and significant contributions from nitrates (16%) and excess organic compounds (10%) (see Table 4-2 and Figure 4-2), indicated the influence of both primary and secondary components on the PM-10 problem during the fall episodes (November 6-8, November 11-14). The chemical composition breakdown for the fall episodes is shown in Figure 4-3.

The key differences between the winter and the fall episodes are as follows:

- PM-10 concentrations were higher in the fall (maximum PM-10 was $180 \mu\text{g}/\text{m}^3$) than in the winter (Maximum PM-10 was $125 \mu\text{g}/\text{m}^3$).
- Geological material (dust) dominated the composition of the fall PM-10 (57%), but was a relatively minor component of PM-10 (10 %) and PM-2.5 (0.6%) in the winter.
- Secondary ammonium nitrate was the dominating component of PM-10 (40%) and PM-2.5 (46%) in the winter but not in the fall (16%).
- PM from vegetative burning contributed significantly (15%) in many sites, especially urban ones (21%), in the winter, but not in the fall.
- Fog was patchy and mild in the fall.

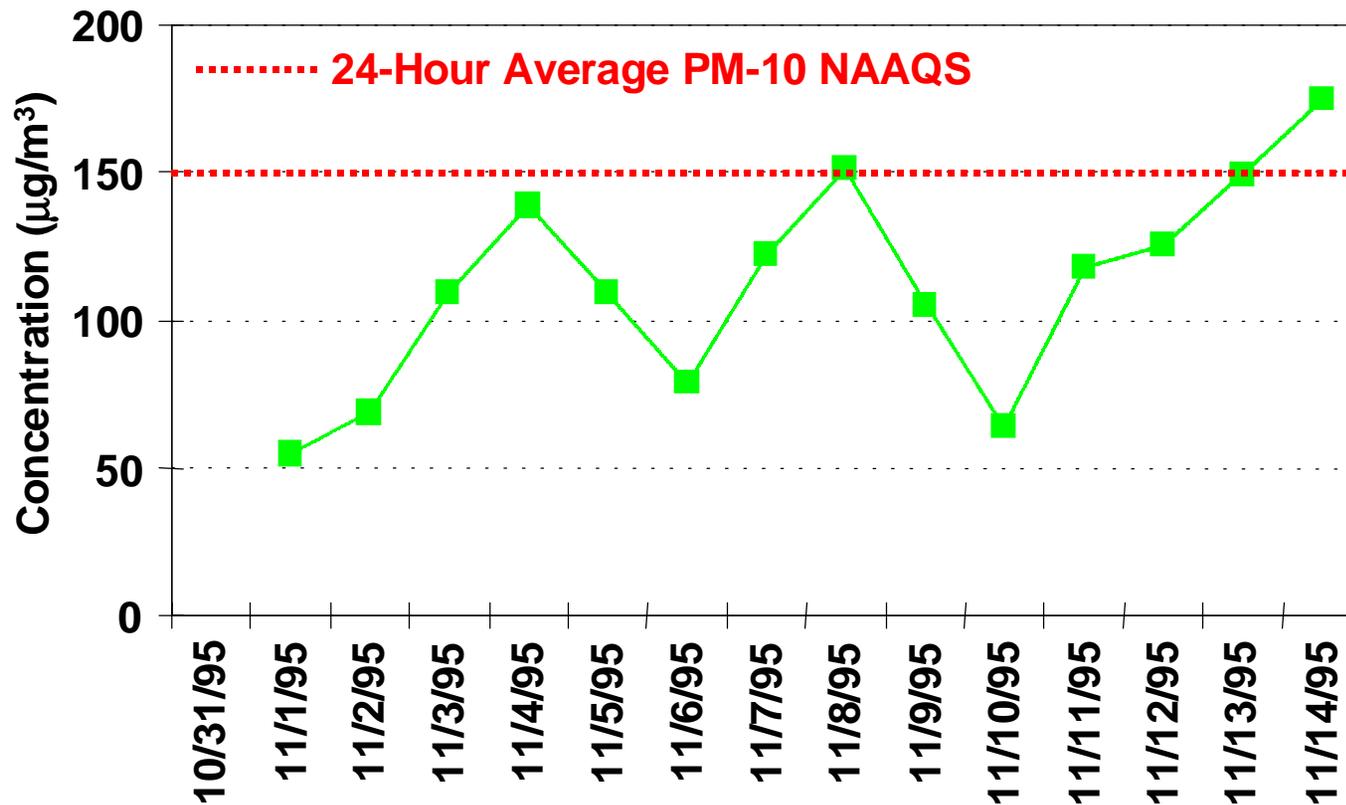


Figure 4-1. Temporal Variations of PM-10 Mass Concentrations during the IMS 95 Fall Study (Source: CARB, 1998)

Table 4-1. Characteristics of the Fall PM Episodes in the San Joaquin Valley

(Data Source: Chow and Egami, 1997; Lehrman et al., 1998)

Episode	November 6 – 14, 1995 (2 episodes, each 3-4 days; decrease in PM observed on November 9, 10)
PM-10 Observations	Concentrations correlate among sites. Corcoran core site and 20 satellite sites exceeded $150 \mu\text{g}/\text{m}^3$ 24-hr PM-10 on 11/14/95 Several sites exceeded $150 \mu\text{g}/\text{m}^3$ 24-hr PM-10 on four other days
Peak Time / Site	11/14/95, (time unknown, no hourly data available) Peak concentration at an industrial site next to railroad tracks
Wind Speed	Light winds ($< 2 \text{ ms}^{-1}$)
Temperature (ground / upper air)	Ground temperature: $20 \text{ }^\circ\text{C}$; Aloft temperature: $11 - 15 \text{ }^\circ\text{C}$
Mixing Height at 4 pm	No report of mixing height 500 mB height of 5820 m (stable condition)
Fog	Bakersfield: no fog (RH = 60%). Fresno: 1-5 fog hours nightly (RH = 70%) Corcoran day-time RH $< 50\%$; 80% at night

Table 4-2. Chemical Mass Balance Analysis of PM in the Fall in the San Joaquin Valley
 (Data Source: Magliano, 1997)

Episode	Component	Contribution
Fall PM-10 (core site)	Geological Material ^(a)	57%
	Nitrate	16%
	Excess OC ^(b)	10%
	Mobile Sources ^(c)	7%
	Vegetative Burning ^(d)	5%
	Sulfate	3%

(a) Geological Material: soil dust profiles determined from samples of soil and (paved and unpaved) road dust from Visalia, Bakersfield, and Taft.

(b) Excess OC: organic compounds not accounted for by the other source categories, including primary and secondary components.

(c) Mobile Sources: based on SCAQMD and Phoenix dynamometer profiles.

(d) Vegetative Burning: based on combustion PM samples from fireplaces and agricultural burning.

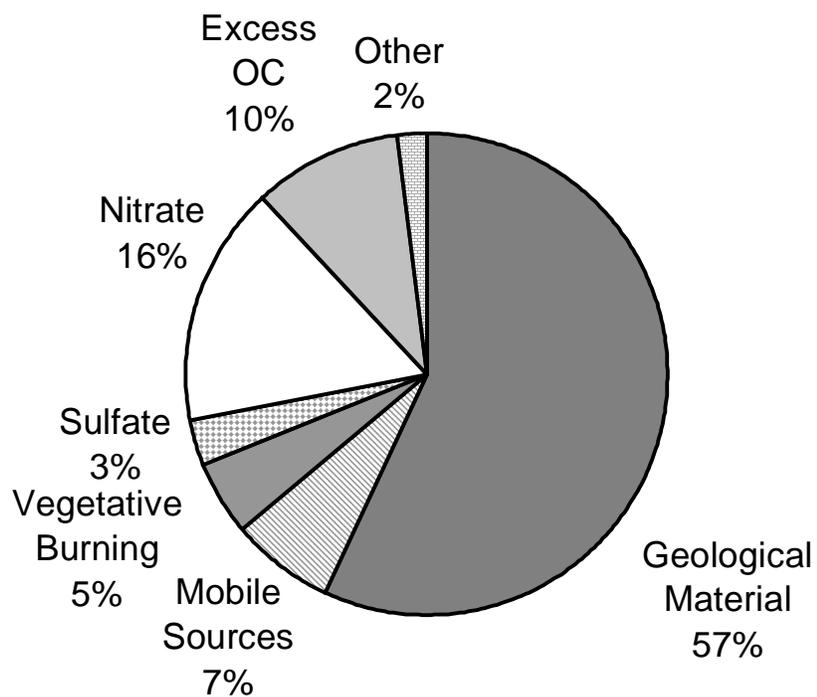


Figure 4-2. Source Contributions Based on Chemical Mass Balance Analysis of Fall PM-10
(Data Source: Magliano, 1997)

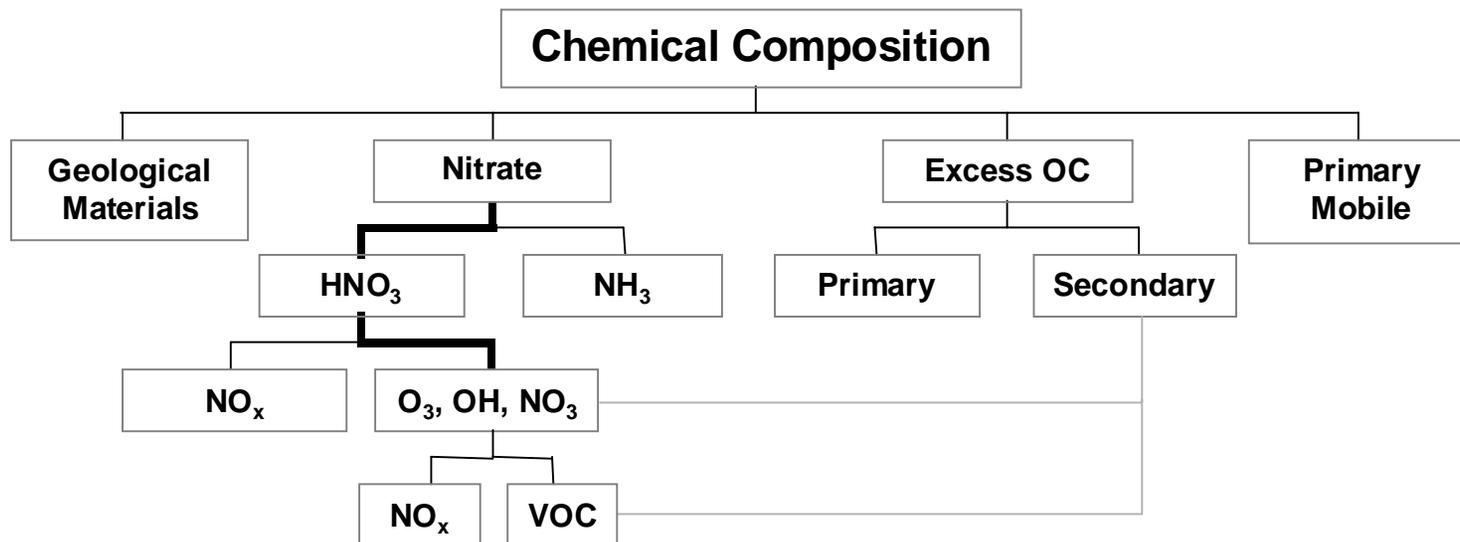


Figure 4-3. Breakdown of PM by Chemical Composition for a Typical Fall Episode
 (bold lines represent the influential variables for the formation of secondary PM,
 to the extent that sufficient information is available to determine which variables are the most influential)

4.2 Chemical Composition and Transformations

Geological Material

The largest component of PM-10 in November 1995 was geological material, i.e. dust (57%). Since dust is a primary component, it will be discussed further under transport processes in Section 4.3.

Ammonium Nitrate

Ammonium nitrate was the second most important component of PM-10 in the fall, accounting for about 16% of the mass at the Corcoran core site. The formation of ammonium nitrate warrants further discussion. One key question is whether the formation of nitrate is limited by the availability of nitric acid or ammonia. Kumar et al. (1998) showed that the atmosphere in the monitoring domain within the southern part of the San Joaquin Valley was ammonium rich in the winter. It is likely that the system is also more sensitive to nitric acid than to ammonia during the rest of the year, especially in the summer when the oxidant chemistry is NO_x-sensitive (Lu and Chang, 1998) and, therefore, not conducive to the formation of nitric acid. The nitric acid sensitivity should be confirmed for fall conditions, which have different reaction rates (due to different temperature and solar radiation), mixing conditions, and emissions. Fog was not prevalent during the fall and the atmosphere was relatively dry; therefore, it is postulated that the OH reaction (Reaction 3.2) may be more important than the N₂O₅ hydrolysis route (Reactions 3.4, and 3.3) in the production of HNO₃ in the fall. In order to confirm the important nitrate formation reactions, a better understanding of oxidant chemistry is needed for the fall season in the San Joaquin Valley, CA. Emphasis should be placed on studying the gas-phase oxidation pathways of NO_x to HNO₃, and the sensitivity of oxidants (OH, O₃, and NO₃) to NO_x and VOC.

Excess OC

Another PM component needing further investigations is the excess OC. These are the organic compounds that were not accounted for by the source profiles explicitly included in the CMB study. Excess OC includes both primary (e.g., from meat cooking) and secondary organic components. Tracer-based receptor modeling, similar to that described in Section 3.2, may be used to analyze the source of excess OC, and determine whether these are primary or secondary organic compounds.

4.3 Transport Processes

The spatial representativeness of the Corcoran core site was 87%, i.e., 87% of the area in the monitoring domain recorded PM-10 concentrations within $\pm 20\%$ of the core site (Blanchard et al., 1998). The average spatial representativeness over all sites in the Corcoran vicinity was 74%. During PM-10 episodes, the spatial representativeness tended to increase, indicating the sub-regional nature of the PM build-up, driven mostly by meteorology. The meteorological conditions are summarized in Table 4-1. As expected, secondary components were more uniformly distributed (87% spatial representativeness averaged over all sites) than primary components (the spatial representativeness of dust is 65%). The source zone of influence study revealed the presence of neighborhood scale influence (~ 1 km) and a 5 to 15 km sub-regional influence. The mean PM-10 background in the vicinity of Corcoran was $100 \mu\text{g}/\text{m}^3$. Boundary conditions could not be determined from the Corcoran network (Collins, 1998).

There is little direct evidence from which to infer the dominant physical transport processes affecting the concentrations of PM in the San Joaquin Valley in the fall. Collins (1998) showed that PM concentrations are generally highest during periods of light and variable winds which tend to come from the southeast. Lower PM concentrations were associated with stronger northeasterly winds. As shown in Figure 4-4, PM-10 concentrations correlate well with the aloft temperatures measured at Oakland, CA (850 mB temperature at about 1500 m or 5000 ft), indicating reduced mixing as a major cause of the observed PM episodes. Furthermore, both primary (e.g., dust) and secondary components (e.g., nitrates) increased during the fall episodes. These observations tended to support a sub-regional build-up of PM as the culprit of the pollution episodes under the particular fall conditions.

The dominance (57%) of dust or geological material in the PM composition also supported the sub-regional build-up hypothesis, as coarse materials are generally not transported over great distances. The correlation of PM-10 concentrations among the core and satellite sites (i.e., the fact that the concentrations at all sites increase and decrease together) indicated that meteorology

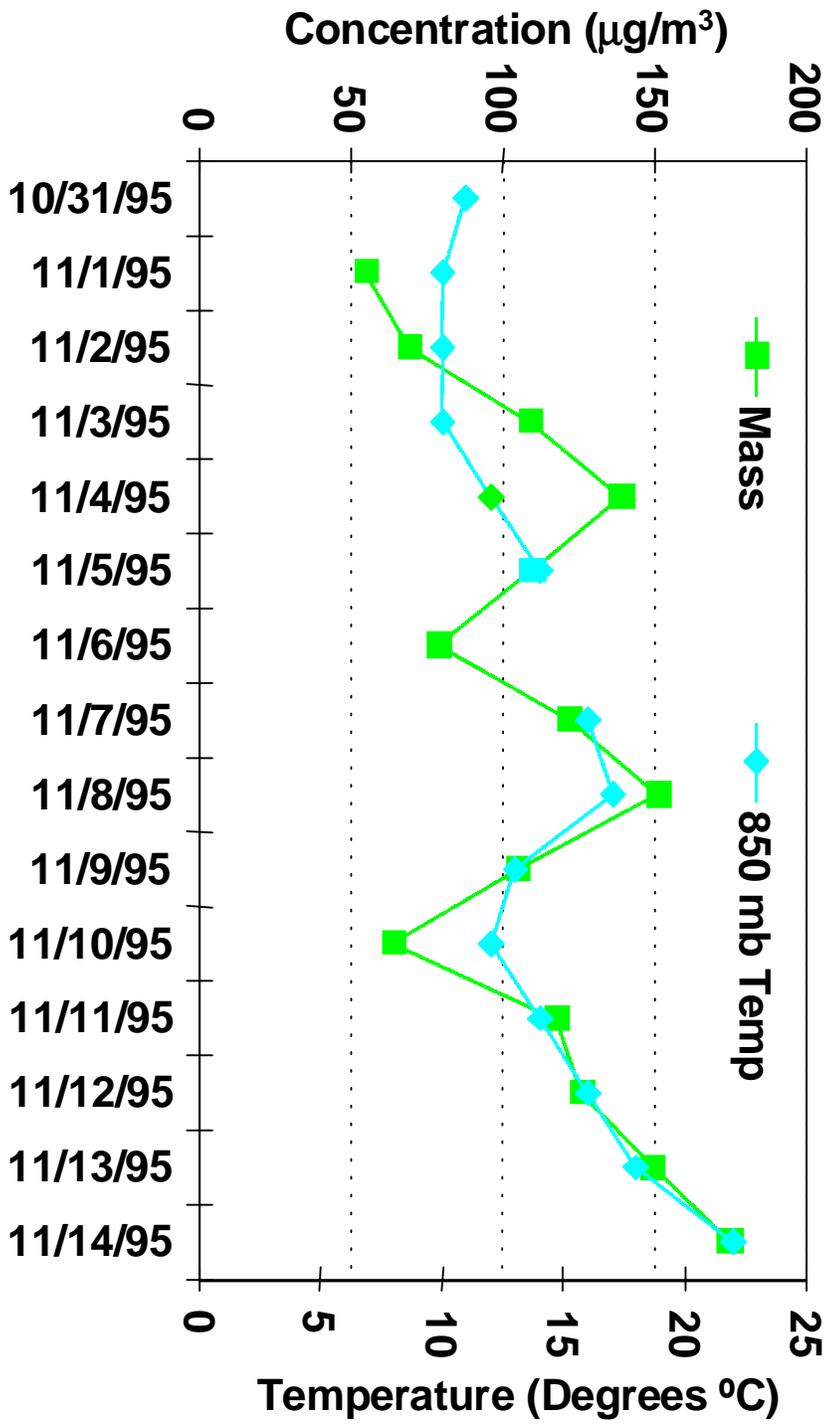


Figure 4-4. Fall PM-10 Mass at Corcoran and 850 mb Temperature (Source: CARB, 1998)

was the driving force behind episodes in the Corcoran area. Spatial variability recorded by the network was attributed to local influences. It was found that industrial sites tended to record higher concentrations than the residential sites. Average PM-10 concentrations were 134 $\mu\text{g}/\text{m}^3$ at the industrial sites, 113 $\mu\text{g}/\text{m}^3$ at the agricultural sites, and 112 $\mu\text{g}/\text{m}^3$ at the commercial / residential sites (Chow and Egami, 1997). However, because of the intermittent nature of the many PM-generating activities, observations of activities did not correlate well with the 24-hour data that were collected (Coe and Chinkin, 1998). No meteorological data were available at the monitoring sites to evaluate the contribution of local wind-blown dust.

Long-range surface transport from upwind pollutant sources to Corcoran was unlikely, as the surface wind speed was typically less than 2 m/s during the fall episodes in Corcoran. Mixing height, upper air winds, and concentration data are necessary to evaluate the impact of vertical mixing and long-range transport of precursors and PM aloft.

Wet deposition probably played a minor role in the dissipation of PM during the fall episode. No rain was reported during the PM monitoring period in November, and only patchy evening fog was reported in Fresno.

No information was available from IMS 95 to determine whether dry deposition provides a dominant sink for PM and PM precursors in the San Joaquin Valley in the fall. Depending on the size of the coarse material, e.g., dust, dry deposition could play a role in the PM balance at the Corcoran location.

5. Discussion

5.1 Synthesis of Winter Episodes

In the winter, PM-2.5 dominated PM in the San Joaquin Valley. Secondary ammonium nitrate was an important component of PM. It was shown that nitric acid limited the yield of this secondary compound, as ammonia was abundant within the IMS 95 study area. To control nitric acid formation effectively, it is necessary to develop a better understanding of the $\text{NO}_x/\text{VOC}/\text{oxidant}$ chemistry for the San Joaquin Valley. To that end, it may be desirable to conduct an extensive gas-phase measurement program to characterize speciated VOC, NO, NO_2 , O_3 , H_2O_2 , HNO_3 , and, if feasible, OH, NO_3 , HO_2 , and RO_2 within the San Joaquin Valley during winter. In particular, the formation of nitric acid should be studied in detail. Two chemical reactions are of interest: $\text{NO}_2 + \text{OH}$ and $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$. Since N_2O_5 is formed from the reaction of NO_2 with NO_3 , this reaction may be important in the evening or during a fog episode when NO_3 accumulates due to the lack of photolytic dissociation. N_2O_5 cannot be measured directly, but the formation rate of nitric acid via N_2O_5 hydrolysis may be inferred from measurements of NO_3 . Other oxidized nitrogen species, including HNO_3 , particulate nitrates, HNO_2 , PAN, and other organic nitrates, may also be measured to improve the understanding of nitrogen chemistry.

Secondary organic aerosols are another component that requires further study. During IMS 95, the relative contribution of secondary organic aerosols to PM was significant at the rural site. In addition to the transport and transformation of anthropogenic emissions from urban areas, the atmospheric reactions of biogenic compounds are also a source of secondary organic aerosols. The modeling results of Strader et al. (1998) may be useful in understanding the atmospheric organic-oxidant reactions in the foggy winter climate encountered in the San Joaquin Valley. Unfortunately, their implementation of the state-of-the-art secondary aerosol formation processes cannot be considered fully reliable for predicting PM in the San Joaquin Valley, because of some generic input data used in their simulation and uncertainties in the model formulation. In order to understand the formation of secondary organic aerosols, a better understanding of the VOC emissions inventory and oxidant chemistry is needed for both anthropogenic and biogenic

emissions, such as monoterpenes and oxygenated hydrocarbons. IMS 95 provided no information on the magnitude of biogenic emissions within the San Joaquin Valley. VOC emissions inventories, both anthropogenic and biogenic compounds, should be a focus of the forthcoming field campaign.

Sulfate seemed to be a minor (6%) component of San Joaquin Valley PM in the fall and winter. However, with abundant SO₂ in the southern part of the valley and the sensitivity of sulfate production to changes in oxidant concentrations, it is prudent to examine more closely the mechanisms for sulfate formation to assure that changes in precursor (NO_x or VOC) emissions designed to reduce ozone and other components of PM will not have adverse effects on the sulfate problem.

Oxidant production may be sensitive to NO_x or VOC. There is some evidence that ozone formation in the summer is sensitive to NO_x (Lu and Chang, 1998). However, data from IMS 95 seemed to indicate that the formation of oxidants and HNO₃ during the winter season was sensitive to VOC, although the indicator approach (Sillman, 1995; Lu and Chang, 1998) has not been verified for the cooler and foggier winter conditions. Oxidant chemistry should be further investigated to confirm the precursor (NO_x or VOC) sensitivity in the winter season. This basic understanding of the atmospheric system is important because any reduction of NO_x (e.g., for controlling summer O₃) may increase the abundance of HO₂ radicals and enhance the production of H₂O₂ (see Figure 3-5). Since ozone and H₂O₂ are both oxidizing agents of SO₂, the trade-off between the different reaction pathways needs to be understood.

Two areas of research needs identified by IMS 95 researchers are the source of fog buffering capacity and the sensitivity of ambient ozone measurements at the ppb levels. Modern ozone instruments with sub-ppb detection limit and sensitivity (Seigneur et al., 1998a and references therein) may need to be considered in future field studies. Accurate RH measurements are also needed to understand the importance of various aqueous-phase processes. Furthermore, McDade's finding (McDade, 1997) that light extinction was sensitive to particulate water confirmed the need for such measurements for determining light scattering by PM.

The accumulation of pollutants, e.g., NO_2 , HNO_3 , was associated with stagnant conditions with limited surface transport. Under these conditions, the regional uniformity of secondary pollutants (e.g., ammonium nitrate and secondary organic aerosols) within the San Joaquin Valley is intriguing. Was the time scale of reaction and deposition slower than the time scale of transport (advective or diffusive) under stagnant conditions? Or were widespread sources responsible for the regional scale concentrations of pollutants? In the fall episode, and in some winter episodes, the influence of regional sources was evident (Blanchard et al., 1998). It should be useful to better characterize the meteorological conditions that are associated with enhanced regional influence.

One question that IMS 95 did not sufficiently address because of its limited scope was the magnitude of above-ground transport. There is some evidence that transport of pollutants aloft and subsequent mixing into the surface layer (in the middle of the afternoon) may be a mechanism of distributing pollutants within the valley in a multi-day episode. Aloft measurements of concentrations will be needed to determine the magnitude of this mixing process.

Wet deposition is mostly a function of fog in the San Joaquin Valley PM episodes studied. The effects of fog are two-fold. First, particles that become fog droplets by absorbing water vapor are subsequently removed by gravitational settling. Second, fog droplets provide the aqueous medium for the production of sulfates. The net effect of a fog event depends on the length of the event, the availability of precursors, oxidants, and catalysts, and the composition of the original PM. It is probably advisable to study the wet deposition phenomenon further, and to understand if any recycling of PM and gaseous pollutants occurs through volatilization at the conclusion of the fog event.

Dry deposition information is needed to complete our understanding of major mass fluxes in the system. Direct measurements of dry deposition fluxes by the eddy correlation technique over a variety of land-use types are needed for both PM and precursor gases, including O_3 , HNO_3 , NH_3 , and other nitrogen-containing compounds.

5.2 Synthesis of Fall Episodes

A primary component of the fall PM-10 is geological material (dust), which accounted for over 50% of the mass according to CMB analyses. Limited information is available regarding the source of the dust particles. Given that wind speeds were typically less than 2 ms^{-1} , it seems unlikely that wind blown dust was a significant contributor to PM-10. Other sources of mechanically generated aerosols, such as paved and unpaved roads and farming activities, may be addressed by tracer experiments. Ammonium nitrate (16%) was the second most common component, followed by excess OC (about 10%), which included both primary and secondary components. Accurate geological material profiles and tracer-based organic profiles are needed for major San Joaquin Valley primary sources to increase the resolution of the CMB methods and to elucidate the importance of secondary organic compounds.

A sub-regional build up in the vicinity of Corcoran seemed to be a reasonable hypothesis during a multi-day episode. Although local sources were postulated to explain the spatial variability, there was no direct evidence to link observations of local emissions to elevated 24-hour PM measurements. The atmospheric lifetimes of particles due to settling are functions of particle diameters. The range of PM transport may be estimated if particle size measurements are available. This information may be used to infer the mechanism of sub-regional buildup of PM in the San Joaquin Valley during the fall season. To evaluate the effects of transport, upper level wind and mixing height data are required. Measurements of dry deposition of particles and precursor gases may be needed to refine estimates of areas of influence.

6. Conclusions

6.1 Summary of Conceptual Model

In the formulation of a conceptual model for PM during IMS 95, a data driven approach was used. Available information was systematically compiled into a framework based on the chemical characteristics of and transport processes associated with the observed PM. The key features of the conceptual models for the fall and winter PM episodes in the San Joaquin Valley are summarized in Table 6-1.

Table 6-1. Summary of Conceptual Models

	Winter (PM-2.5)	Fall (PM-10)
Chemical Composition and Transformations	Ammonium Nitrate (46%) <ul style="list-style-type: none"> ▪ Nitric acid Sensitive ▪ Nitric acid Formation Possibly Limited by Oxidants (OH, O₃, and NO₃) Availability ▪ Oxidants May be VOC-Sensitive Rather Than NO_x-Sensitive Organic Compounds (34%) <ul style="list-style-type: none"> ▪ Primary (e.g., Vegetative Burning and Mobile Sources) ▪ Secondary (Anthropogenic or Biogenic Precursors) 	Geological Material (57%) Ammonium Nitrate (16%)
Transport Processes	Limited Ground-level Transport <ul style="list-style-type: none"> ▪ Calm Winds Aloft Transport Possible Limited Vertical Mixing Wet Deposition (Fog) Dry Deposition Unknown Urban Influences (Primary Sources) on Regional Distribution (Secondary NH ₄ NO ₃ , SOA)	Limited Ground-level Transport Aloft Transport Possible PM Build-up Correlates with Reduced Mixing Height Limited Wet Deposition (Mild Fog) Dry Deposition Unknown Local Influences (Geological Material) on Sub-regional Distribution (Secondary NH ₄ NO ₃)

6.2 Comparison with the Conceptual Models of Watson et al. (1998)

Compared to previous conceptual models, ours place a stronger focus on understanding the chemical processes behind the formation of secondary compounds and, therefore, should provide a better balance between meteorology and chemistry in the analyses of the PM episodes. Watson et al. (1998) discussed the primary compounds in terms of their sources and secondary PM in terms of their precursors: NH_3 , SO_2 for sulfate, NO_x (HNO_3) for nitrate. We added another facet to the analysis of the secondary compounds and pointed out the need to address the availability of oxidants, which govern the chemical transformation of precursors to PM. Indeed, there was evidence to support that the oxidation of NO_x to HNO_3 was limited by the availability of oxidants, as was the oxidation of SO_2 to sulfate. In addition, different reactions, involving different oxidants, may contribute to the formation of secondary sulfate and nitrates depending on the time of day, the presence of fog and clouds, the amount of available light, relative humidity, etc. To understand these chemical systems, and to design effective control strategies, further work is needed to measure key oxidants accurately and to improve the understanding of the oxidant chemistry, particularly its sensitivity to NO_x or VOC. The effectiveness of any controls placed on the precursors will be dependent on the limiting reagents. In addition, it is important to coordinate the efforts to control oxidants in the summer (O_3) and in the winter (PM). Summer oxidants may be sensitive to NO_x . However, NO_x controls must be accompanied by methods to address VOC concentrations if the oxidants involved in the wintertime formation of secondary PM are more sensitive to VOC than NO_x .

Another component that was not analyzed in detail in Watson's approach is secondary organic aerosol (SOA) formation. Limited analyses seem to indicate that it could be a non-negligible contributor at the rural sites and at the urban sites under some circumstances. Better emissions inventories / profiles and measurements of ambient VOC at urban and rural sites may be useful in deciphering the importance of this component.

Watson et al. (1998) narrated the events that led to PM formation that involve (1) the accumulation of PM and precursors over night, (2) mixing with aloft air in the morning and early afternoon (reduction in PM and precursors), (3) photochemical production and accumulation

aloft (clear sky) of oxidants, nitric acid, and secondary aerosol, (4) entrainment of secondary aerosol by stratus cloud droplets (5) aqueous oxidation of sulfur, (6) radiation inversion separating pollutants aloft and those accumulating at the surface, and (7) mixing of ammonia and nitric acid by upper air transport. This analysis seems to be consistent with available information. However, some components of their analysis are hypotheses that, at this point, cannot be confirmed with available evidence. Aspects of this conceptual model that require verification include the aloft production of oxidants and secondary compounds, the role of cloud droplets, and upper air transport as a mechanism of pollutant dispersion. The removal processes of wet and dry deposition were not addressed in the conceptual model of Watson et al. (1988). Our analysis of the physical transport and removal processes, based loosely on mass balance arguments, confirmed the lack of ground level advection and reduced vertical mixing as the principal meteorological conditions associated with PM build-up. We acknowledged the possibility of aloft transport as a mechanism for pollutant dispersion under apparently stagnant conditions, and pointed out the possibility of widespread sources of precursors and diffusion as explanations of the regional distribution of pollutants. To complete our understanding of the mass fluxes within the valley, there is also a need to understand the wet and dry removal processes.

Watson et al. (1998) proposed a separate conceptual model for the fall. We concur with the basic features of the fall conceptual model, with primary sources responsible for local influences and secondary compounds responsible for the “subregional influence.” The key differences between the fall and the winter conceptual models are the contribution of dust and the lack of fog. Watson et al. (1998) also proposed that the stronger along-valley flows transport particles into the Mojave Desert, although IMS 95 was too limited in its geographical scope to evaluate the full range of transport. Several measurements should be taken to verify several aspects of Watson’s model: particle size distribution information will aid the determination of particle lifetimes and the distance of dust dispersion; and measurements of photochemical oxidants will be useful in determining the sensitivity of the oxidant system for nitric acid production.

6.3 Answers to Specific Questions on PM Episodes in the San Joaquin Valley

In the statement of work, several questions were raised. We now address these questions based on the results of our analysis. Where appropriate, quantitative descriptions are provided based on the data from specific episode days, January 5 (winter) and November 14 (fall).

What are the causes of excessive PM-10 and PM-2.5 concentrations in the SJV?

The chemical components that contributed to PM build-up were identified. In the fall, PM-10 contained a significant amount of geological material (see Table 4-2). Ammonium nitrate and organic compounds also contributed to the accumulation of PM. On November 14, the relative contributions from geological material, ammonium nitrate, and organic compounds (mobile sources + vegetative burning + excess organic compounds) were 58%, 21%, and 14%, respectively. In the winter, ammonium nitrate was the major component of PM-2.5 (see Table 3-2). Nitrate contributions averaged 41% at the urban sites and 64% at the rural sites on January 5. Primary organic sources such as vegetative burning and mobile sources also contributed to fine particles, particularly at the urban sites (30% on January 5, 60% on December 26 in the Fresno area). Contributions of sulfates to PM-2.5 were observed in rural areas (10% on January 5).

What is the influence of meteorology, emissions, chemistry, and deposition on PM concentrations?

Meteorology: In both the fall and winter seasons, stagnant conditions (i.e., lack of advective transport) seemed to be the major cause of high PM in the sub-regional or regional scale. Warm aloft temperatures (15 to 20 °C in the fall; 10 to 15 °C in the winter) curtailed vertical mixing. Ground-level transport was an unlikely mechanism for pollutant distribution. The effects of upper-level transport were not clear, because of the lack of ambient concentration data aloft.

Emissions: The effects of urban-scale emissions were observed in the winter where primary emissions typically contributed to more PM at the urban sites than at the remote sites. For example, on January 5, mobile sources and vegetative burning combine to account for 30% or 15 $\mu\text{g}/\text{m}^3$ PM at urban sites, but only 16% or 5 $\mu\text{g}/\text{m}^3$ at rural sites. No direct link was found

between a locally observed emission activity and high PM at a single monitoring site in the fall, although higher average concentrations observed at the industrial sites than residential and agricultural sites may be attributable to local emissions.

Since secondary PM components were prominent in the fall and winter seasons, the emissions of gaseous precursors also need to be addressed, including NH_3 , NO_x , SO_2 , and VOC. Improvements in the emission inventories for VOC are also important for understanding the production of oxidants in the San Joaquin Valley.

Chemistry: Ammonium nitrate was the top component of PM-2.5 during the winter study. On average, 40 to 50% of the total ammonia was in the gas phase during IMS 95. The average phase partition of ammonia during the January, 1996 episode was as follows: 43% in PM-2.5, 10% in PM-10, 1% in fog droplets, and 46% as gaseous ammonia. Because of the abundance of NH_3 in the area, the formation of ammonium nitrate seemed to be limited by the availability of HNO_3 , a secondary compound. A large fraction of nitrates were associated with the particulate phase; only 18-25% of nitrate existed in the gas phase as nitric acid. An oxidant study is recommended to understand the oxidation pathways of NO_x to HNO_3 , and the sensitivity of key oxidants (OH or O_3/NO_3) to NO_x and VOC. A comprehensive understanding of the availability of oxidants will also be beneficial in the analysis of secondary organic aerosols and secondary sulfates.

Deposition: Fog episodes caused a net removal of PM by wet deposition, especially for ammonium and nitrate, removing 40 to 46 % (by mass) of ammonia and 15 to 29% of the nitrate present before the fog episode at Bakersfield and Fresno in the early December episode (Pandis et al., 1998). Sulfate formation in fog was estimated to exceed sulfate removal by fog settling at some sites (e.g., Bakersfield on December 10, 1995) but not all. Dry deposition was not studied during IMS 95; dry deposition may be a significant removal pathway for HNO_3 and other PM precursors.

What differences are observed for PM and PM components and precursor species among urban, rural, and industrial areas?

Winter: Episodes during the winter IMS study showed that PM concentrations were higher at the urban sites than the rural sites. During the January episode, PM averaged $51 \mu\text{g}/\text{m}^3$ at the urban sites, and $32 \mu\text{g}/\text{m}^3$ at the rural sites. In general, the urban sites contained larger contributions from anthropogenic primary sources, such as wood burning and mobile vehicle emissions, than rural areas. The average ammonium nitrate (NH_4NO_3) over all episode days was $18.7 \mu\text{g}/\text{m}^3$ at urban sites, and $17.8 \mu\text{g}/\text{m}^3$ at rural sites. Although the concentrations of NH_4NO_3 are similar, PM at rural sites was always dominated by NH_4NO_3 (> 50%). Contributions from secondary organic compounds and sulfates could also be non-negligible (20%) according to the analysis of Schauer and Cass (1998) and Magliano (1997). Due to the predominance of secondary compounds in the winter, which tended to be regionally distributed, conclusions regarding the distribution of PM between industrial and residential sites were not clear. There was some evidence that within the winter saturation network at Bakersfield, the residential and transportation sites recorded higher PM ($70 \mu\text{g}/\text{m}^3$ PM-10) than the industrial sites ($45 \mu\text{g}/\text{m}^3$). Larger contributions were observed of mobile sources, vegetative burning, and geological material (possibly road dust) at these sites, potentially reflecting the proximity to sources. However, more analyses in more areas are needed to confirm these observations.

Precursors to secondary PM include HNO_3 (NO_x), NH_3 , SO_2 , and VOC. The concentrations of HNO_3 at the urban sites were lower than or equal to those at the rural sites. For example, during the January episode, the urban sites recorded 1.1 to $1.2 \mu\text{gN}/\text{m}^3$ HNO_3 (4.4 to $4.5 \mu\text{gN}/\text{m}^3$ in the PM phase) while the Kern Wildlife Refuge site recorded $1.2 \mu\text{gN}/\text{m}^3$ of HNO_3 ($3.9 \mu\text{gN}/\text{m}^3$ in the PM phase). Although total oxidized nitrogen was higher in the urban areas, NO_x was also 10 times more abundant than in the rural areas. Total oxidized nitrogen was 29% (by mole) at Kern Wildlife Refuge, compared to only 10 to 13% at the urban sites, indicating the aged nature of the air parcel at the rural site. Ammonia seemed more abundant in Bakersfield than at the other core sites, possibly due to area sources southwest of the city (Haste et al. 1998). SO_2 was also more abundant in the cities than at Kern Wildlife Refuge. The distribution of sources again explained the difference. Gas-phase organic concentrations exhibited strong diurnal fluctuations in the urban areas, with about $400 \mu\text{gC}/\text{m}^3$ in the morning and only $250 \mu\text{gC}/\text{m}^3$ in the afternoon. No

specific information is available regarding the gas-phase concentrations of organics at the rural sites.

Fall: During the fall episodes, higher PM-10 was observed in industrial areas than at the other sites. On November 14, an industrial site near railroad tracks recorded the highest concentrations of PM ($273 \mu\text{g}/\text{m}^3$), while the average PM-10 in the Corcoran area was only $180 \mu\text{g}/\text{m}^3$ (Magliano, 1997). The absolute contribution of secondary components, such as ammonium nitrate, was fairly constant. For example, on the same day, the contribution of secondary ammonium nitrate ranged from 35.2 to $40.4 \mu\text{g}/\text{m}^3$. Therefore, the site-to-site variability was attributed to changes in impacts due to primary emissions of geological material (83 to $146 \mu\text{g}/\text{m}^3$) and organic compounds (mobile sources + vegetative burning + excess organic compounds accounted for 9.6 to $55.4 \mu\text{g}/\text{m}^3$) (Chow and Egami, 1997; Magliano, 1998).

What are the chemical processes for the formation of secondary aerosols, especially during foggy conditions when the photochemical processes may be limited?

Nitrate: Ammonium nitrate is formed by the combination of NH_3 and HNO_3 . Ammonia was found to be abundant in the San Joaquin Valley; therefore, the formation of this secondary compound was limited by the availability of nitric acid. Nitric acid is formed when NO_2 reacts with OH or O_3 (with subsequent reaction of NO_3 with NO_2 to form N_2O_5 , followed by reaction of N_2O_5 with water). The dominant reaction (i.e., $\text{NO}_2 + \text{OH}$ or $\text{NO}_2 + \text{O}_3$) cannot be identified with the available data. The fact that total nitrate peaked in the afternoon suggests that the $\text{NO}_2 + \text{OH}$ reaction may be dominant. The sensitivity of oxidants to VOC and NO_x needs to be evaluated. The abundance of NO_x relative to oxidized nitrate seems to provide evidence that wintertime conditions may be conducive to a VOC-sensitive oxidant system. However, more data are needed to confirm these hypotheses.

Sulfate: Sulfate was fully neutralized as ammonium sulfate. In addition to the gas-phase oxidation of SO_2 by OH, aqueous reactions in the fog could be an important source of sulfate in the San Joaquin Valley. Of the reaction pathways with O_3 , H_2O_2 , and O_2 (catalyzed by Fe or Mn), model simulations and data analyses based on IMS 95 results indicated that the O_3 reaction dominated within fog droplets. However, because of uncertainties in the gas-phase oxidant

concentrations, this finding should be re-evaluated when accurate measurements of oxidants are available at the ppb level.

Organics: Secondary organic aerosols (SOA) may contribute to a significant fraction of PM (e.g., 8% of PM-2.5 in Bakersfield, 13% in Kern Wildlife Refuge during the January 4-6 episode). SOA is formed in the oxidation of anthropogenic and biogenic VOC. Strader et al. (1998) found aromatic compounds to be efficient SOA producers in their model. However, a more thorough understanding of the contributions of the various VOC categories to the formation of SOA would require better information on the emissions inventories of biogenic and anthropogenic VOC. Strader et al. (1998) also found that clouds and fog reduced the photochemical production of secondary organic aerosols by a factor of 2 or 3 from the maximum clear sky conditions because of reduced availability of photons. The thermodynamic interactions between fog droplets and SOA are unknown.

What is the influence of fog on PM concentrations?

The influence of fog is two-fold. First, it serves as an aqueous reactor for the formation of sulfate and nitrate. Second, fog drops settle to the ground and remove PM with them. The net effect of a fog episode depends on the pre-fog concentrations, duration of fog, and the availability of oxidants. Nitrate and ammonium are typically removed, while sulfate may be produced or removed. During the December 10 episode, fog was found to remove 29% and 46% of the nitrate and ammonia that were present in the atmosphere before the fog occurrence in Bakersfield. However, with sulfate production over-balancing the wet removal, a 7% by mass increase of sulfate after the fog was predicted by the computer model (Pandis et al., 1998).

What is the spatial influence of primary emissions and secondary aerosol precursors during each conceptual model scenario relevant to the IMS 95 fall and winter sampling periods?

In the fall, spatial variability observed among different site types supported a local scale of influence of primary emissions, although a link between locally observed, often intermittent, emission activities and high 24-hour average PM measurements at a specific site was not identified. Blanchard et al. (1998) identified a 1-km neighborhood scale for primary sources and

a 5 to 15 km sub-regional scale for the distribution of secondary PM. In the winter, elevated primary source contributions of wood combustion in the CMB analysis in the urban areas indicated an urban-scale primary source influence. HNO_3 , a secondary gaseous pollutant, was fairly uniformly distributed in urban areas, and tended to increase as a percentage of total nitrogen at the rural site of Kern Wildlife Refuge where the air parcels were more aged (Kumar et al. 1998). Relatively high levels of NH_3 were detected at urban sites far from emission sources (Haste et al., 1998). Haste et al. (1998) used a 25-km radius when comparing ambient NH_3/NO_x ratios to inventory values. On the other hand, Pandis et al. (1998) noted a SO_2 plume in Bakersfield on December 19, 1995, indicating that this precursor was not as well-mixed as ammonia and nitric acid.

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