APPENDIX B

WEIGHT OF EVIDENCE

SAN JOAQUIN VALLEY PM2.5 SUPPLEMENTAL ANALYSIS

1. INTRODUCTION

The State Implementation Plan or SIP serves as a demonstration of attainment for the national ambient air quality standards (NAAQS or federal standards). The attainment demonstration comprises analyses used to determine the set of control measures needed to meet the NAAQS by the attainment year. These analyses typically include air quality modeling, which generally guides the selection of the most effective pollutants to control and the magnitude of needed emissions reductions. The Weight of Evidence (WOE) analysis provides a set of complementary analyses that supplement the SIP-required modeling. These analyses can include consideration of measured air quality, emissions, and meteorological data, evaluation of other air quality indicators, and additional air quality modeling.

A WOE approach looks at the entirety of the information at hand to provide a more informed basis for the attainment strategy. Because all methods have inherent strengths and weaknesses, examining an air quality problem in a variety of ways offsets the limitations and uncertainty that are inherent in air quality modeling. This approach also provides a better understanding of the overall problem and the level and mix of emissions controls needed for attainment.

The United States Environmental Protection Agency (U.S. EPA) recognizes the importance of a comprehensive assessment of air quality data and modeling and encourages this type of broad assessment for all attainment demonstrations. In their modeling guidance, they further note that the results of supplementary analyses may be used in a WOE determination to show that attainment is likely despite modeled results which may be inconclusive (U.S. EPA 2007). Under the U.S. EPA guidance, future year modeled annual average design values that fall between 14.5 and 15.5 ug/m^3 should be accompanied by a WOE demonstration to determine whether attainment will occur. This range in modeled design values reflects the uncertainty in predicting absolute PM2.5 concentrations that is inherent in air quality modeling, and therefore recognizes that an improved assessment of attainment can be derived from examining a broader set of analyses.

U.S. EPA recommends that three basic types of analyses be included to supplement the primary modeling analysis in the WOE approach:

1) analyses of trends in ambient air quality and emissions,
2) observational models and diagnostic analyses, and
3) additional modeling.

Each analysis is weighted based on its ability to quantitatively assess the ability of the proposed control measures to yield attainment. The scope of the WOE

analysis is different for each nonattainment area. The level of detail appropriate for each area depends upon the complexity of the air quality problem, how far into the future the attainment deadline is, and the amount of data and modeling available. For example, less analysis is needed for an area that is projecting attainment near-term and by a wide margin, and for which recent air quality trends have demonstrated significant progress, than for areas with more severe air quality challenges. The following sections present the WOE assessment for PM2.5 in the San Joaquin Valley Air Basin for each of the areas outlined in the U.S. EPA guidance.

2. ASSESSMENT OF RECENT AIR QUALITY AND EMISSION TRENDS

a. Current Air Quality

According to U.S. EPA's guidance, even though air quality models are regarded as the most appropriate tool to assess impacts in emission changes, it is also possible to extrapolate future trends in PM2.5 based on measured historical trends of air quality and emissions. Strength of the evidence produced by emissions and air quality trends is increased if an extensive monitoring network exists and if there is good correlation between past emission reductions and current trends.

Along with the South Coast, the San Joaquin Valley Air Basin has one of the most severe PM2.5 problems in the nation and represents a considerable challenge in attaining the federal PM2.5 standards. These standards consist of both a 24-hour standard of 65 ug/m^3, and an annual average standard of 15 ug/m^3. While the majority of monitors with complete data in the San Joaquin Valley still exceed the annual PM2.5 standard, PM2.5 air quality has shown considerable improvement since 1999 when monitoring data for assessing compliance with the federal PM2.5 standard began. When the San Joaquin Valley was first designated nonattainment for the federal PM2.5 standards, the basin exceeded both the annual and the 24-hour PM2.5 standards. However, based on 2004-2006 data, the San Joaquin Valley meets the federal 24-hour PM2.5 standard of 65 ug/m^3 throughout the basin. Thus attaining the annual standard is the primary challenge in this State Implementation Plan.

The San Joaquin Valley Air Basin is a lowland area bordered by mountains to the east, west, and south. The mountains act as air flow barriers, with the resulting stagnant conditions favoring the accumulation of emissions and pollutants. To the north, the Valley borders the Sacramento Valley and Delta lowland, which allows for some level of pollutant dispersion. As a result, PM2.5 concentrations are higher in the southern and central portions of the Valley, where geography, emissions, and climate pose significant challenges to air quality progress. Chapter 3 and Appendix E of the District Plan provide detailed information on the conceptual model of PM2.5 formation in the Valley.

Currently, eleven sites routinely monitor PM2.5 in the Air Basin. Table 1 provides the 2006 annual standard design values and the annual average values for 2004, 2005, and 2006 for each monitoring site with complete data. The design value is a statistic that is used to describe the air quality status of a given area relative to the level of the federal standard. The annual design values represent the average of the mean annual PM2.5 concentrations measured during the three year period. Table 2 provides the 24-hour standard design value for each monitoring site with complete data and the yearly 98th percentile value of the 24-hour concentrations measured in 2004, 2005, and 2006. The 24-hour design value represents the average of the yearly 98th percentile of the 24-hour concentrations measured during the three year period. Attainment is reached when the design value is at or below the corresponding federal standard.

As shown in Table 1, current 2006 annual average design values (reflecting the 2004 through 2006 period) range from 12.9 ug/m^3 to 18.9 ug/m^3. The San Joaquin Valley monitoring sites with the highest PM2.5 annual design values are located in the southern and central portions of the basin, including Bakersfield and Visalia. Monitors located in the northern portion of the Valley, including Stockton, Modesto, and Merced have lower annual PM2.5 design values and attain the annual PM2.5 standard. As shown in bold in the table, the high site for the region is the Bakersfield–Planz monitor with a PM2.5 design value of 18.9 ug/m^3.

Table 1. PM2.5 Annual Average Values

	Annual Average (ug/m^3)			2006 3-year Annual Average Design Value (ug/m^3)
Monitor	**2004**	**2005**	**2006**	
Clovis-N Villa Avenue	15.8	16.0	16.8	16.2
Bakersfield-410 E Planz Road	17.4	19.9	19.3	**18.9**
Bakersfield-5558 California Avenue	19.0	17.9	18.7	18.5
Bakersfield-Golden State Highway	18.1	18.9	18.6	18.5
Corcoran-Patterson Avenue	17.3	17.6	16.7	17.2
Fresno-1st Street	16.4	16.9	16.8	16.7
Fresno-Hamilton and Winery	17.0	16.9	17.6	17.2
Merced-2334 M Street	15.3	14.1	14.8	14.7
Modesto-14th Street	13.6	13.9	14.8	14.1
Stockton-Hazelton Street	13.2	12.5	13.1	12.9
Visalia-N Church Street	17.0	18.8	18.8	18.2

Table 2. PM2.5 98th Percentile 24-hour Values

Monitor	Annual 98th Percentile (ug/m3)			2006 3-year Average of 98th Percentile Design Value (ug/m3)
	2004	2005	2006	
Clovis-N Villa Avenue	42.4	77.0	51.3	57
Bakersfield-410 E Planz Road	78.6	66.4	50.6	**65***
Bakersfield-5558 California Avenue	59.3	63.6	60.5	62
Bakersfield-Golden State Highway	53.8	74.9	64.4	64
Corcoran-Patterson Avenue	49.4	74.5	50.1	58
Fresno-1st Street	52.0	71.0	51.0	58
Fresno-Hamilton and Winery	49.4	71.2	55.0	59
Merced-2334 M Street	43.0	48.3	43.8	45
Modesto-14th Street	45.0	55.0	52.0	51
Stockton-Hazelton Street	36.0	44.0	42.0	41
Visalia-N Church Street	54.0	65.0	50.0	56

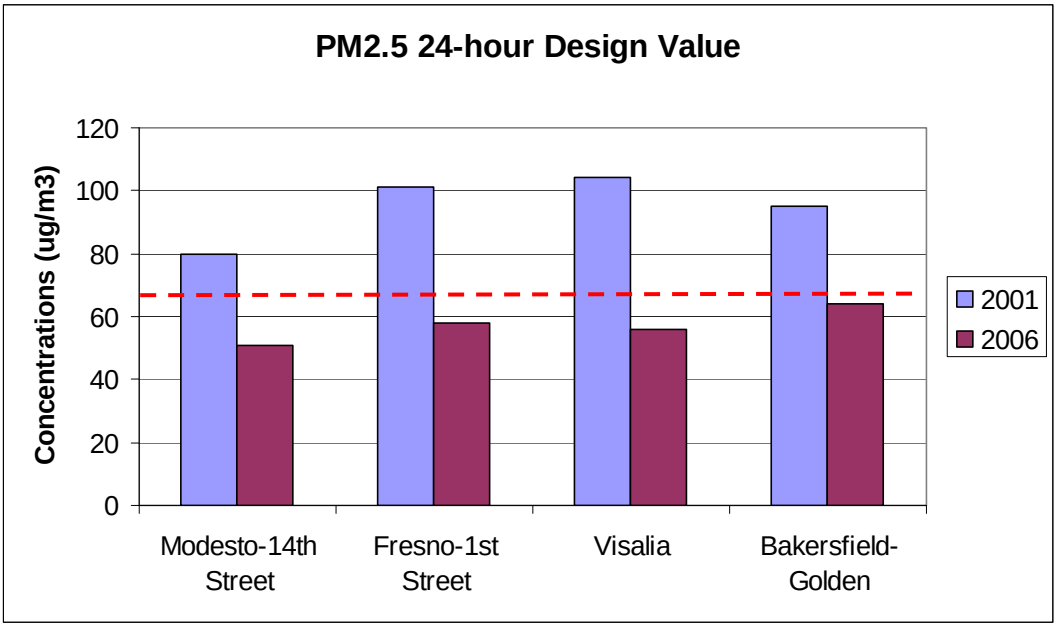
*The 24-hour standard is exceeded when the design value is over 65 ug/m^3

As previously mentioned, all monitors in the San Joaquin Valley currently attain the federal 24-hour PM2.5 standard. As shown on Table 2, 2006 24-hour PM2.5 design values (reflecting the 2004 through 2006 period) range from 41 ug/m^3 to 65 ug/m^3. Monitoring sites with the highest 24-hour PM2.5 design values are located in the southern portion of the Valley, around Bakersfield. As shown in bold on the table, the high site for the region is Bakersfield-Planz with a 24-hour PM2.5 design value of 65 ug/m^3.

b. Recent PM2.5 Mass Trends

Trends observed in the San Joaquin Valley show that considerable progress has occurred in the San Joaquin Valley over the last five years due to the ongoing emissions control program. As shown in Figure 1, 24-hour design values have decreased approximately 40 percent and, as discussed above, based on the 2004 through 2006 data, attain the federal standard at all sites in the Basin.

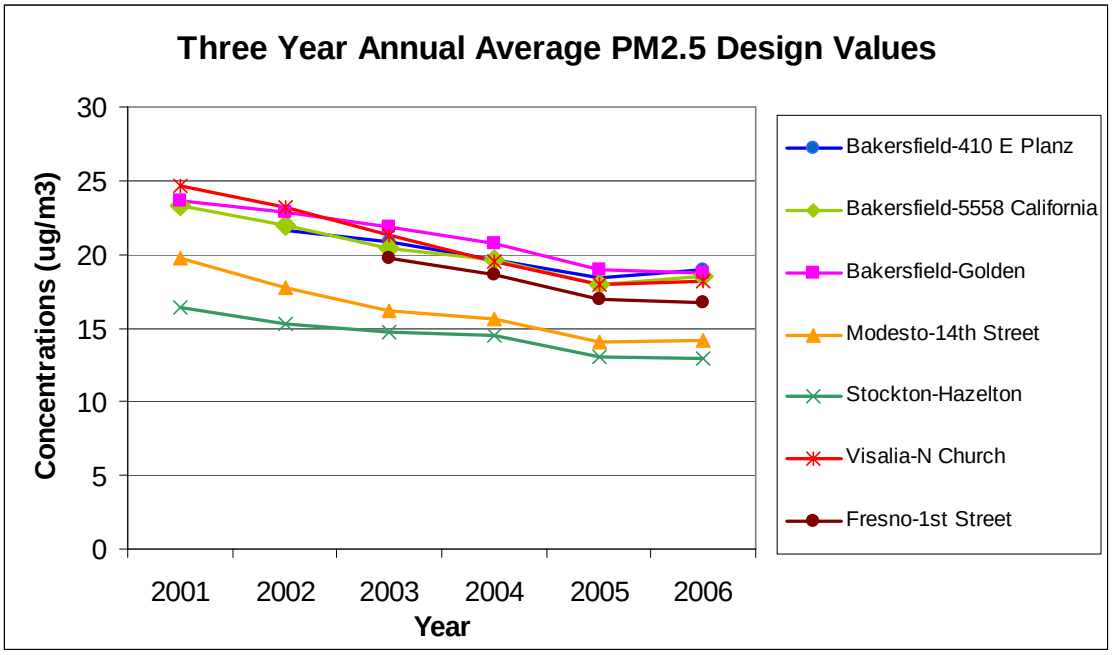
Figure 1: Comparison of 2006 to 2001 PM2.5 24-hour Design Values



All San Joaquin Valley monitors with complete data also show a significant decrease in annual average design values (Figure 2). In 2001, all monitoring sites in the Basin had annual design values greater than 16 ug/m^3, with the Visalia site at approximately one and a half times the level of the standard. By 2006, design values decreased throughout the basin, and only those sites in the southern and central portions of the Valley are still greater than 16 ug/m^3. Bakersfield–Planz is the current high site, with a design value which is 26 percent above the standard. The greatest rate of progress has occurred in the northern and central basin. From 2001 through 2006, the Modesto site design value dropped 28 percent, from 19.7 ug/m^3 to 14.1 ug/m^3, while the Visalia site design value dropped 26 percent from 24.7 ug/m^3 to 18.2 ug/m^3. As a result, all monitoring sites in the northern portion of the Valley now attain the annual PM2.5 standard of 15 ug/m^3. In contrast, the Bakersfield-Golden site dropped 22 percent from 23.6 ug/m^3 to 18.5 ug/m^3 and the Bakersfield-California site dropped 21 percent from 23.3 ug/m^3 to 18.5 ug/m^3. This trend is further illustrated in Figure 3 which depicts maps of the spatial variations in annual average concentrations in 2001 as compared to 2006.

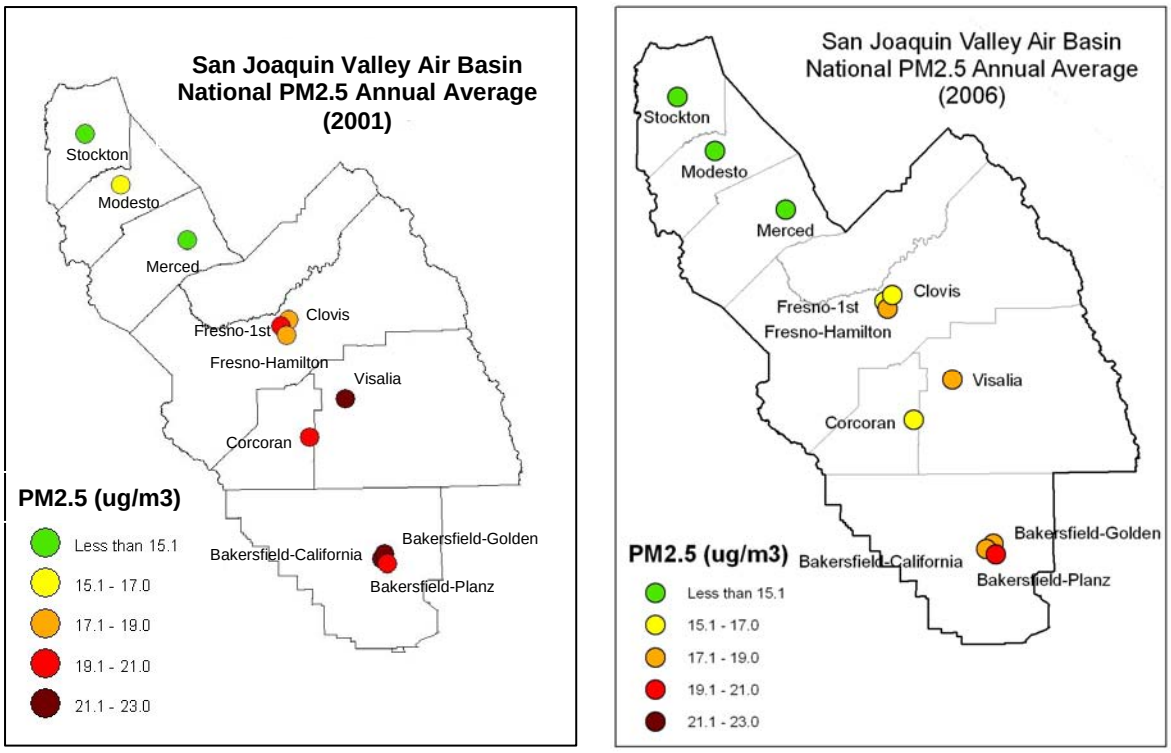
Trends in 24-hour and annual average design values were further evaluated using the nonparametric statistical analysis test, known as the Theil test, that U. S. EPA uses in national air quality trend analysis[1]. This method tests for whether upward or downward trends are real (significant) or a chance product of year-to-year variation (not significant). Theil test results indicate the 2001 to 2006 downward trends in 24-hour and three-year annual average PM2.5 concentrations are statistically significant.

Figure 2: Trends in Annual Average PM2.5 Design Values



[1] U.S. EPA , *National Air Quality and Emissions Trends Report,* Publication No. EPA 454/R-03-005, Office of Air Quality and Standards, Air Quality Strategies and Standards Division, Research Triangle Park, North Carolina. 2003. http://www.epa.gov/air/airtrends/aqtrnd03/

Figure 3: 2001 and 2006 Annual Average Values



The progress observed in both the annual and the 24-hour PM2.5 standards reflects the linkage between the two standards. The annual average is comprised of individual 24-hour samples which vary throughout the year. In the San Joaquin Valley, PM2.5 concentrations exhibit a pronounced seasonal variation, with significantly higher monthly average concentrations during the late fall and winter (November through January). PM2.5 concentrations from April through September are generally below 15 ug/m^3. Therefore 24-hour PM2.5 concentrations during the fall and winter seasons strongly drive the annual average concentrations. During the late fall and winter, stagnant air, cool temperatures, and high humidity can lead to a build-up of PM2.5 over a period of several days to weeks.

Analyses of the changes in the distribution of the 24-hour concentrations between 2001-2003 and 2004-2006 indicate that the decrease in both 24-hour and annual average concentrations is the result of the downward shift in the distribution of daily PM2.5 concentrations during the fall/winter period. This can be seen in the decrease in the monthly average concentrations during the fall/winter months between 2001 and 2006 at Bakersfield-California and Fresno (Figures 4 and 5).

Figure 4: Changes in Seasonal Pattern at the Bakersfield-California Monitoring Site

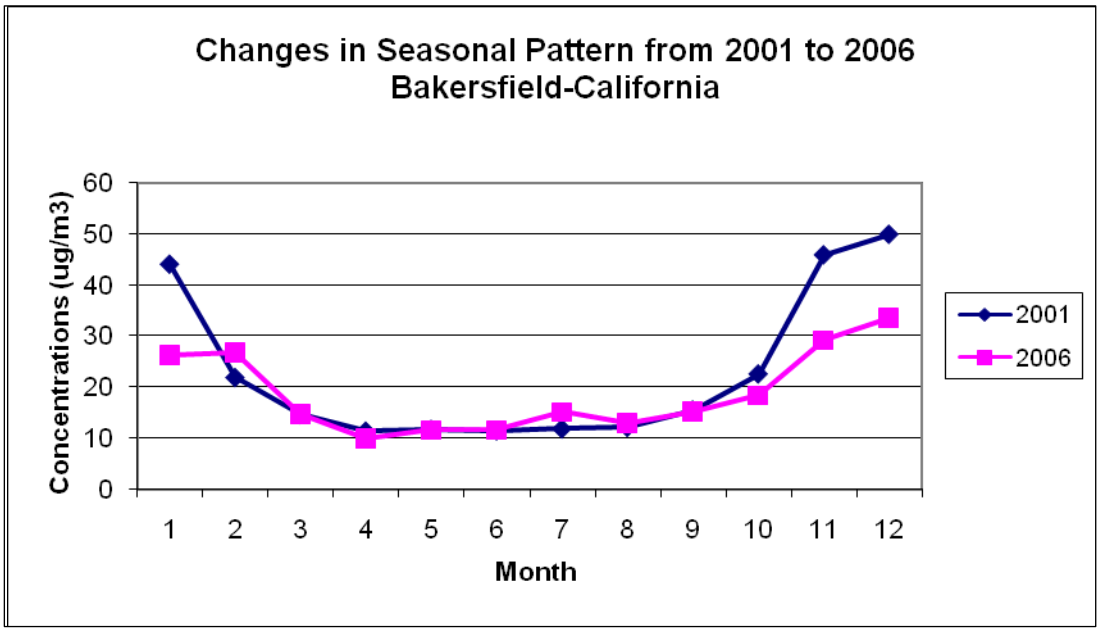
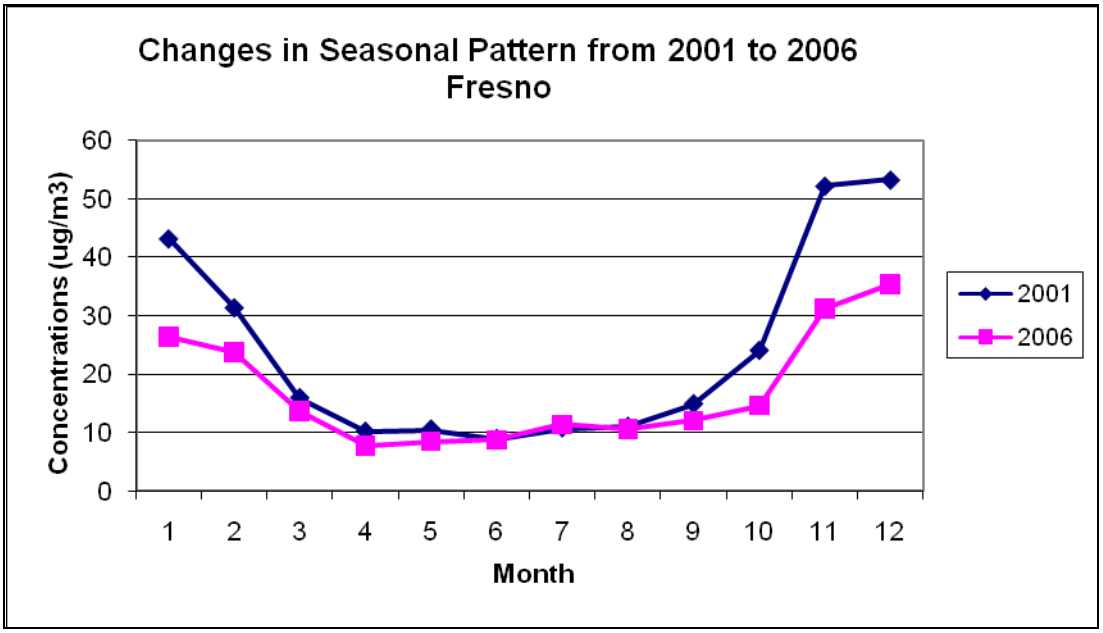


Figure 5: Changes in Seasonal Pattern at the Fresno Monitoring Site



A comparison of the changes in the frequency distribution of 24-hour concentrations over the last few years provides another means of understanding progress. Data collected from 24-hour samples during 1999-2001 at the Bakersfield site indicate that 6 percent of the samples had concentrations greater than 65 ug/m^3 (Figure 6). In comparison, during the 2004-2006 period, the number of samples with PM2.5 concentrations greater than 65 ug/m^3 fell to 1 percent. During both periods, 45 percent of the samples had concentrations above the level of the annual PM2.5 standard of 15 ug/m^3.

At the Fresno site data collected during the 1999–2001 period indicate that approximately 8 percent of the samples had concentrations greater than 65 ug/m^3 (Figure 7), while during the 2004-2006 period, only 1 percent of the samples had concentrations greater than 65 ug/m^3. In addition, during 1999-2001, 46 percent of the samples had concentrations above the level of the annual PM2.5 standard of 15 ug/m^3, while during the 2004-2006 period, the number of samples with concentrations greater than 15 ug/m^3 fell to 34 percent. This analysis, together with the analysis of monthly average PM2.5 trends, further illustrate that progress to date in the annual average is primarily linked to reductions in peak concentrations from October through March.

Figure 6: PM2.5 Concentrations at Bakersfield-California 1999-2001 versus 2004-2006

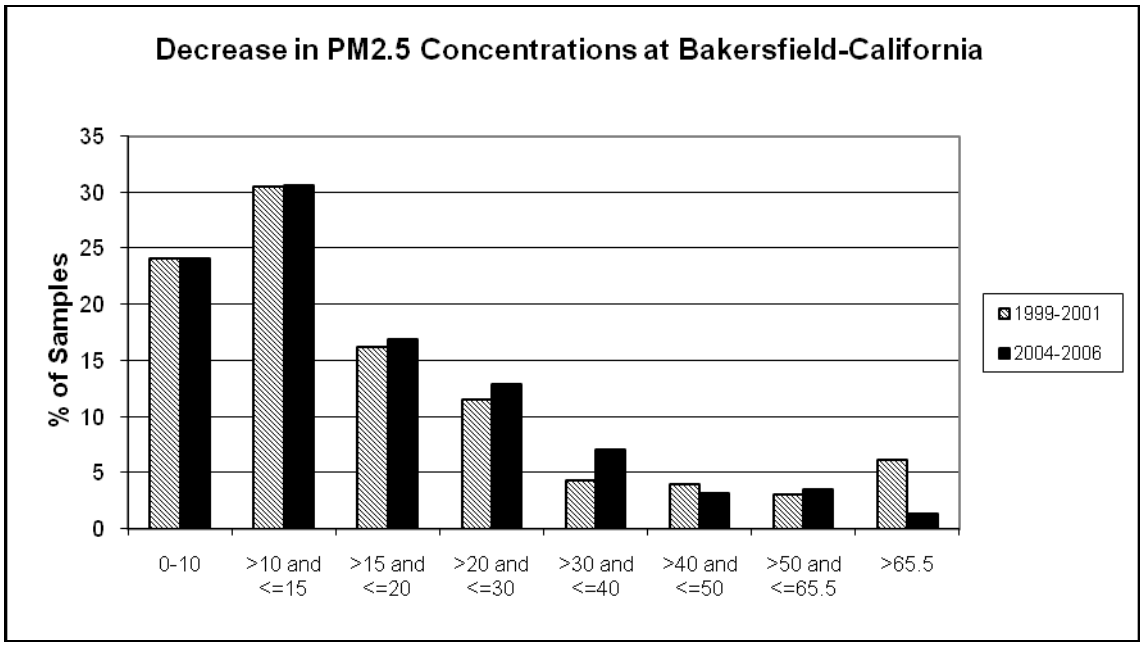
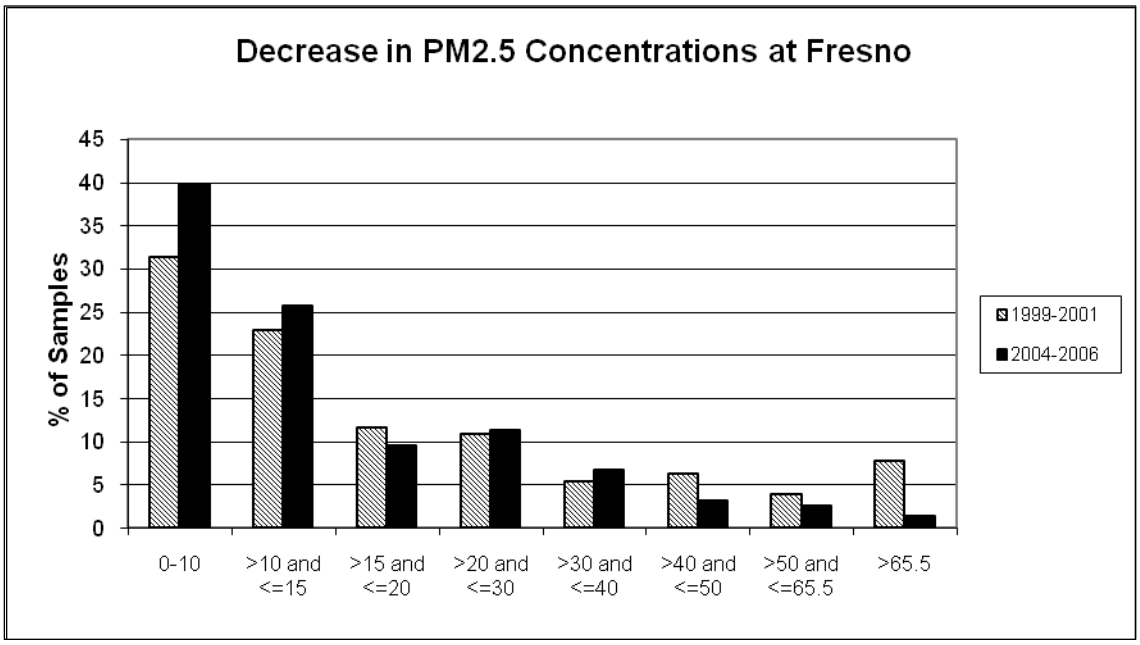


Figure 7: PM2.5 Concentrations at Fresno 1999-2001 versus 2004-2006

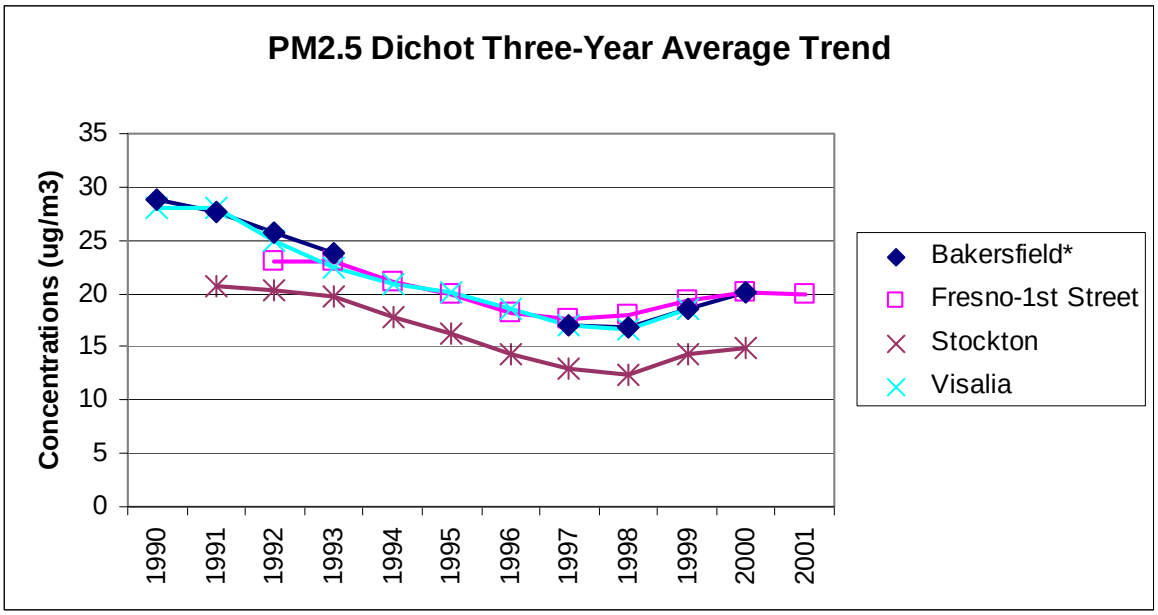


c. Historical PM2.5 Mass Trends

The PM2.5 Federal Reference Method (FRM) network that is used for comparison to the federal standard was deployed in 1998 and 1999. However, PM2.5 data have been routinely collected in the San Joaquin Valley Air Basin since the late 1980s using dichotomous samplers that were operated for research purposes. The PM2.5 dichotomous data correlate very well with the FRM data (r=0.98), but are biased lower than the FRM by 12 percent, therefore an absolute comparison to the FRM can not be made. However, the relative changes in the dichotomous data do provide a longer-term context for assessing progress. Figure 8 depicts PM2.5 concentrations at four sites. At all of these sites, the 3-year average concentrations decreased until 1998, then increased until 2000. At two of the three highest sites, Bakersfield and Visalia, the 3-year average concentrations decreased about 40 percent from 1990 to 1998 (the Bakersfield site trend has a gap from 1994 to 1996). PM2.5 concentrations at Bakersfield then increased 19 percent from 1998 to 2000. The dichotomous data record at the third high site, Fresno, started in 1992. From 1992 to 1998, PM2.5 concentrations decreased 21 percent, followed by a 12 percent increase from 1998 to 2000. PM2.5 concentrations at the low site, Stockton, decreased 40 percent from 1991 to 1998, followed by a 20 percent increase from 1998 to 2000. The period between 1999 and 2001 included a number of adverse winter episodes which likely lead to higher annual averages during this period. However, overall concentrations declined 20 to 30 percent over the period from

1990 through 2001. Looking at dichotomous data and FRM data together therefore illustrates an overall long-term improvement in PM2.5.

Figure 8: Trends in Three-Year Average PM2.5 Concentrations Measured with Dichotomous Samplers



d. Chemical Composition and Emissions Trends

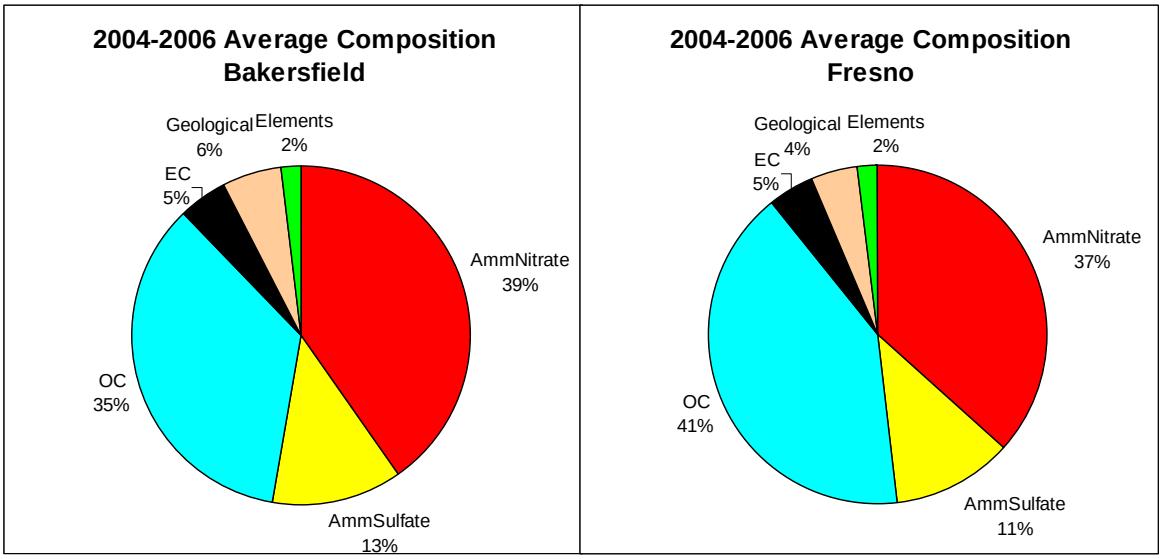
Current Chemical Composition

Particulate matter (PM) consists of many different chemical components. Investigating these different components and how they vary by site and season provides us with a better understanding of their complexity and responses to the emission control program. This mix of chemical components consists of both directly emitted PM such as geological material and elemental carbon (soot), known as primary PM, as well as PM formed in the atmosphere from the reactions of precursor gases, known as secondary PM. These precursor pollutants include nitrogen oxides (NOx), sulfur oxides (SOx), reactive organic gases (ROG), and ammonia. NOx, SOx, and ammonia combine to form secondary ammonium nitrate and sulfate. ROG can form secondary organic carbon, as well as participate in the production of secondary ammonium nitrate.

In the San Joaquin Valley, chemical components are routinely measured at four sites, Bakersfield, Fresno, Visalia, and Modesto. These sites represent urban areas in different portions in the air basin. The chemical composition of PM2.5, seasonal variability, and trends in these components at two of these sites,

Fresno and Bakersfield are discussed below to provide further insight into the linkage between observed progress and ongoing emission reductions.
The annual average PM2.5 chemical composition for Bakersfield and Fresno is shown in Figure 9. Ammonium nitrate and organic carbon are the major constituents at both sites. However, at Bakersfield, ammonium nitrate constitutes a higher percentage (39 percent) of PM2.5 than organic carbon (35 percent), while the reverse (37 percent ammonium nitrate and 41 percent organic carbon) occurs in Fresno. Ammonium nitrate is formed in the atmosphere from chemical reactions of NOx emitted from motor vehicles and stationary combustion sources. Stagnant, cold, and damp conditions in the winter promote the formation and accumulation of ammonium nitrate. Burning activities, such as residential wood combustion, cooking, and direct tailpipe emissions from mobile sources are major sources of organic carbon. Ammonium sulfate is also formed in the atmosphere from chemical reactions of SOx emitted from combustion sources. Ammonium sulfate constitutes about one tenth of ambient PM2.5 at both sites. Elemental carbon resulting from mobile and stationary combustion sources, and geological material from roads and other dust producing activities also contribute to PM2.5 at both sites, but to a lesser extent.

Figure 9: 2004-2006 Average Chemical Composition of PM2.5 at Bakersfield and Fresno



Figures 10 and 11 illustrate the seasonal variability in chemical components that make up PM2.5 for the Bakersfield and Fresno sites averaged over 2004 through 2006. As discussed previously, PM2.5 concentrations are highest during the fall and winter. These higher concentrations are driven by increases in ammonium

nitrate and carbon. At the Bakersfield site (Figure 10), ammonium nitrate is highest during the fall and winter months (November through January) and lowest from April through September. Ammonium nitrate concentrations at Fresno follow the same trend. Cold and humid conditions during the fall and winter favor the formation of ammonium nitrate in the atmosphere from chemical reactions of nitrogen oxides emitted from mobile and stationary combustion sources. At the Fresno site (Figure 11), organic carbon has a similar trend as that of ammonium nitrate. At the Bakersfield site, organic carbon is also highest during the fall and winter months, but at this site organic carbon levels start high in January, decrease until April and then increase almost linearly until reaching a maximum in December. Increased activity in residential wood combustion during the fall/winter period is one cause of higher organic carbon concentrations. At both locations, elemental carbon component remains fairly constant throughout the year, while the ammonium sulfate component is more prevalent from May through September, and the geological components from April through October.

Figure 10: Seasonal Variation in PM2.5 Chemical Components at Bakersfield

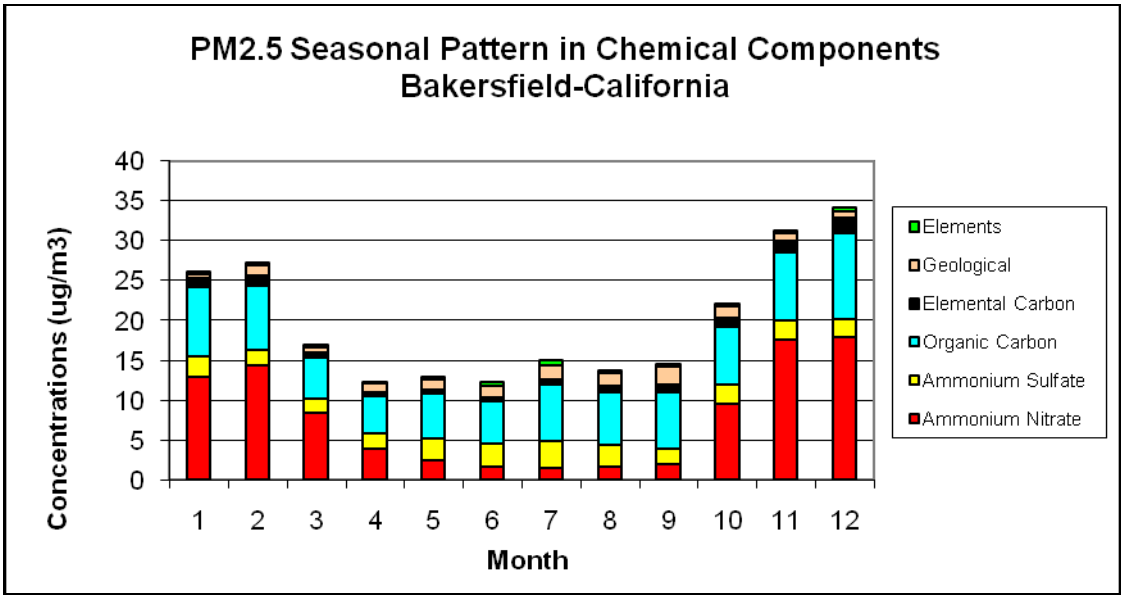
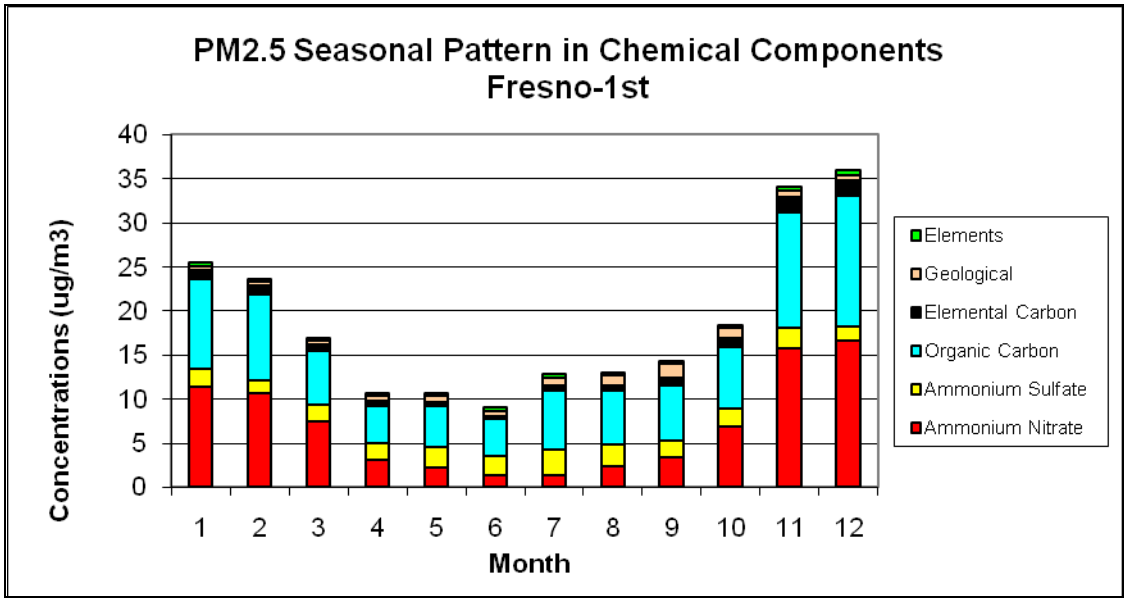


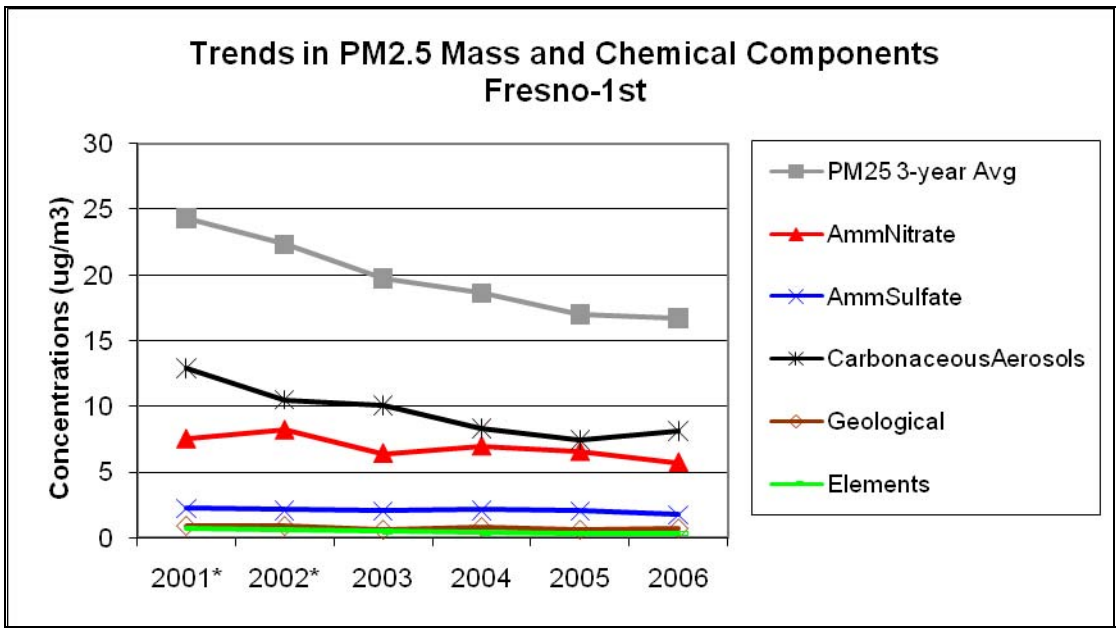
Figure 11: Seasonal Variation in PM2.5 Chemical Components at Fresno



Chemical Composition and Precursors Trends

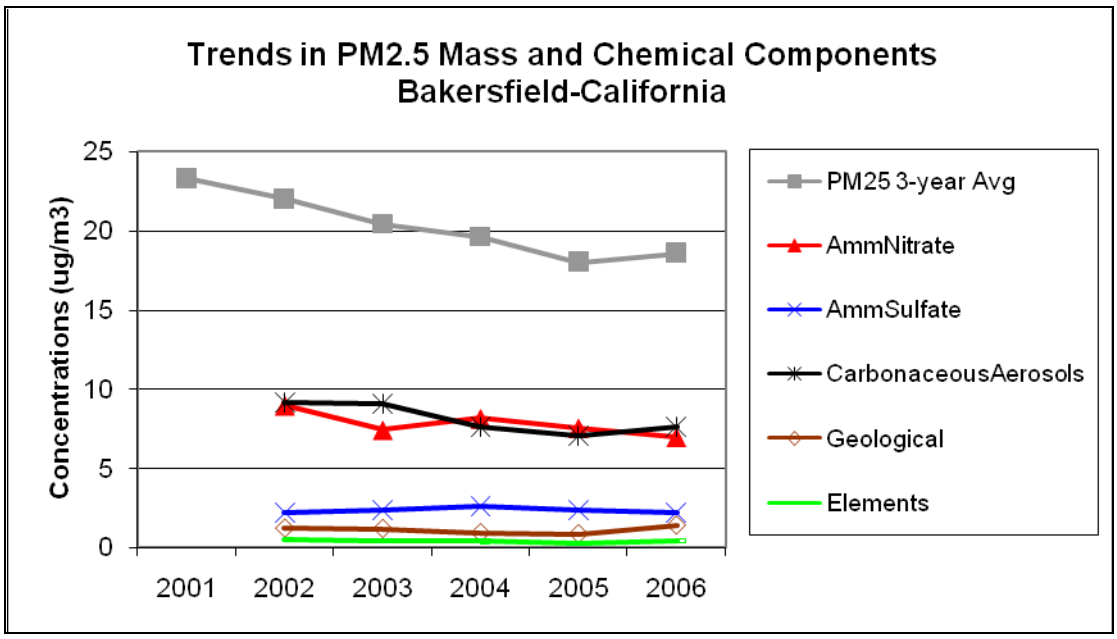
As discussed previously, monitoring sites in the San Joaquin Valley have shown PM2.5 concentrations decreasing from 2001 to 2006. Trends in individual chemical components and precursor concentrations, as well as emissions inventory trends were evaluated to understand the main chemical components responsible for this progress and to evaluate the response to our ongoing control program. Figures 12 and 13 illustrate recent trends in PM2.5 concentrations and its individual chemical components at Fresno and Bakersfield. Improvements in PM2.5 in the San Joaquin Valley can be mostly attributed to reductions in carbonaceous aerosols and ammonium nitrate. In Fresno, carbonaceous aerosols have dropped 37 percent, and ammonium nitrate concentrations have dropped 24 percent. The overall improvement in PM2.5 mass observed in Fresno is therefore due in most part to reductions in carbonaceous aerosols (63 percent), with a smaller portion of the remaining PM2.5 improvement due to reductions in ammonium nitrate (24 percent). In Bakersfield, carbonaceous aerosols have dropped by 16 percent and ammonium nitrate concentrations dropped by 23 percent since 2002. Therefore 41 percent of the overall reduction in PM2.5 mass is due to reductions in carbonaceous aerosols, while 59 percent is due to reductions in ammonium nitrate. Understanding the role of carbonaceous compounds in PM2.5 pollution, the San Joaquin Valley Air Pollution Control District made the Valley's Residential Wood Combustion Rule more stringent in 2003, which may have contributed to the observed decrease in carbonaceous aerosols.

Figure 12: Trends in PM2.5 Mass and Chemical Components at Fresno



* The three-year design value is not considered valid.

Figure 13: Trends in PM2.5 Mass and Chemical Components at Bakersfield-California



Concentrations in ambient NOx, a precursor to nitric acid and ammonium nitrate decreased steadily from 2001 through 2006. Figures **3**-14 and **3**-15 illustrate the

short-term trends in the Basin average NOx compared to ammonium nitrate concentrations in Fresno and Bakersfield. Ambient NOx concentrations in the Valley have shown a modest decrease of 15 percent. Ammonium nitrate concentrations were highest in 2002 at both sites, with a small decrease between 2001 and 2006 at Fresno of 7 percent.

While the short-term trends for ammonium nitrate have been modest, longer-term records show concomitant decreases between ambient NOx and ammonium nitrate as well as between ambient SO2 and ammonium sulfate. Figure 16 shows trends in the basin three-year average ambient NOx concentrations and the corresponding ambient nitrate measurements from the PM10 network extending back to the late 1980s. The hills and valleys in the ammonium nitrate concentrations reflect the effects of the varying meteorology on ammonium nitrate formation. Since 1987, ambient NOx has decreased 50 percent while ammonium nitrate decreased by 35 percent. Figure 17 shows the trends from 1987 to 1996 in the basin three-year average ambient SO2 concentrations and ammonium sulfate measurements from the PM10 network. During this period SO2 decreased by 42 percent with a concurrent decrease in PM10 sulfate of 39 percent.

Figure 14: PM2.5 Ammonium Nitrate Compared to NOx – Fresno

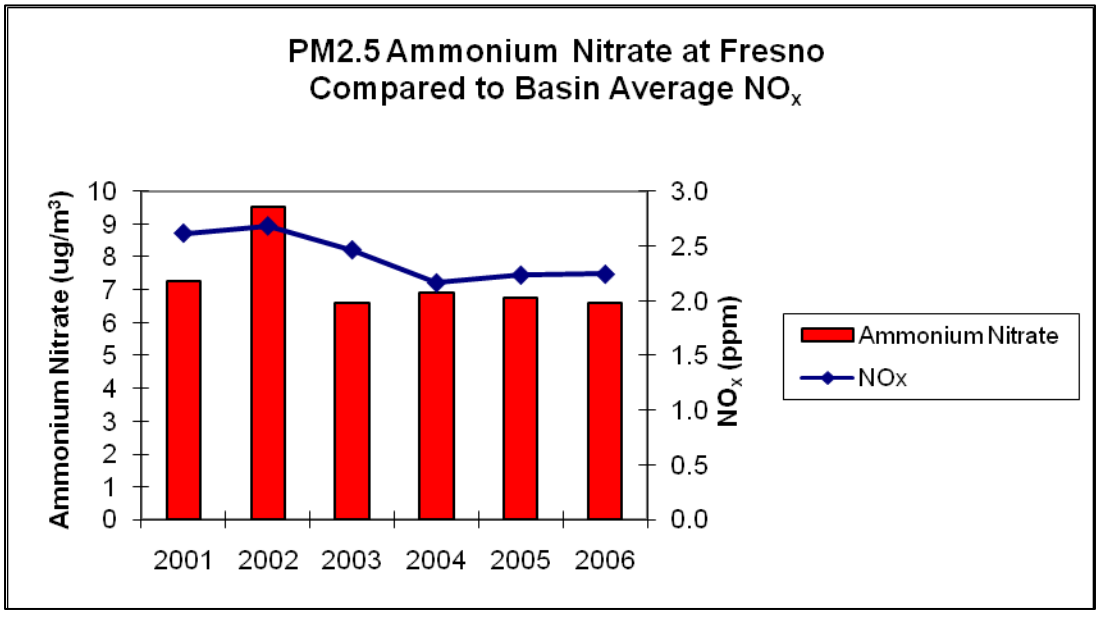


Figure 15: PM2.5 Ammonium Nitrate Compared to NOx - Bakersfield

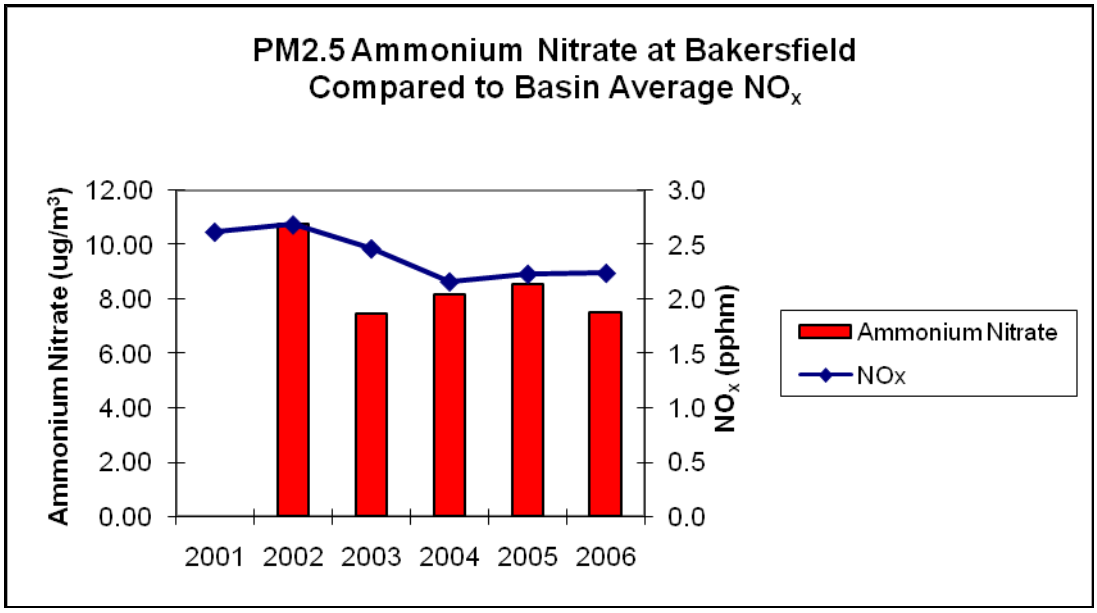


Figure 16: Long-Term Trends in Three-Year Average Concentrations of PM10 Nitrate and NOx in San Joaquin Valley

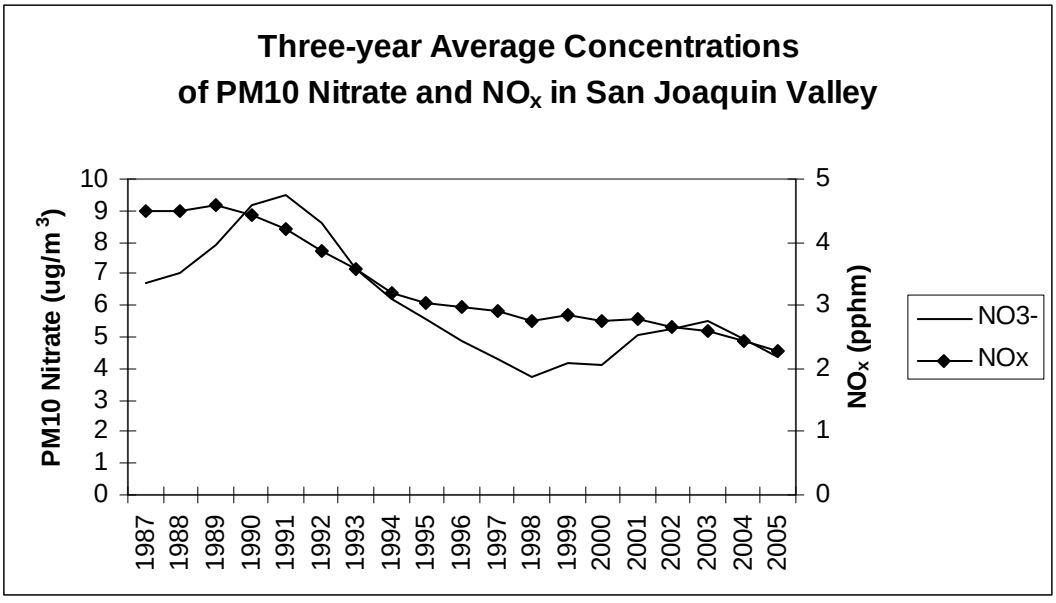
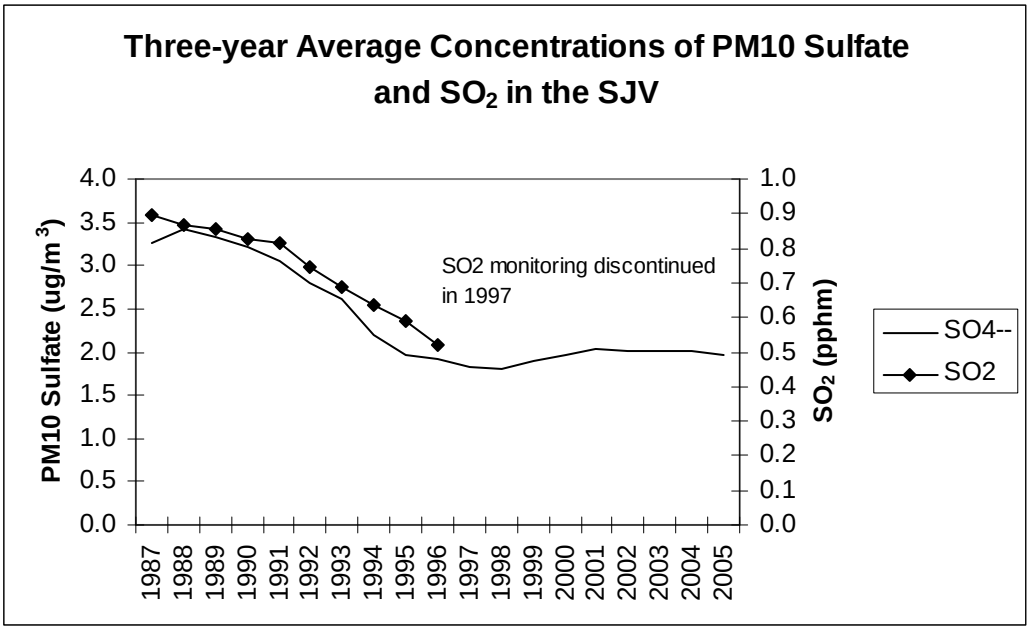


Figure 17: Long-Term Trends in Three-Year Average Concentrations of PM10 Sulfate and NOx in the San Joaquin Valley

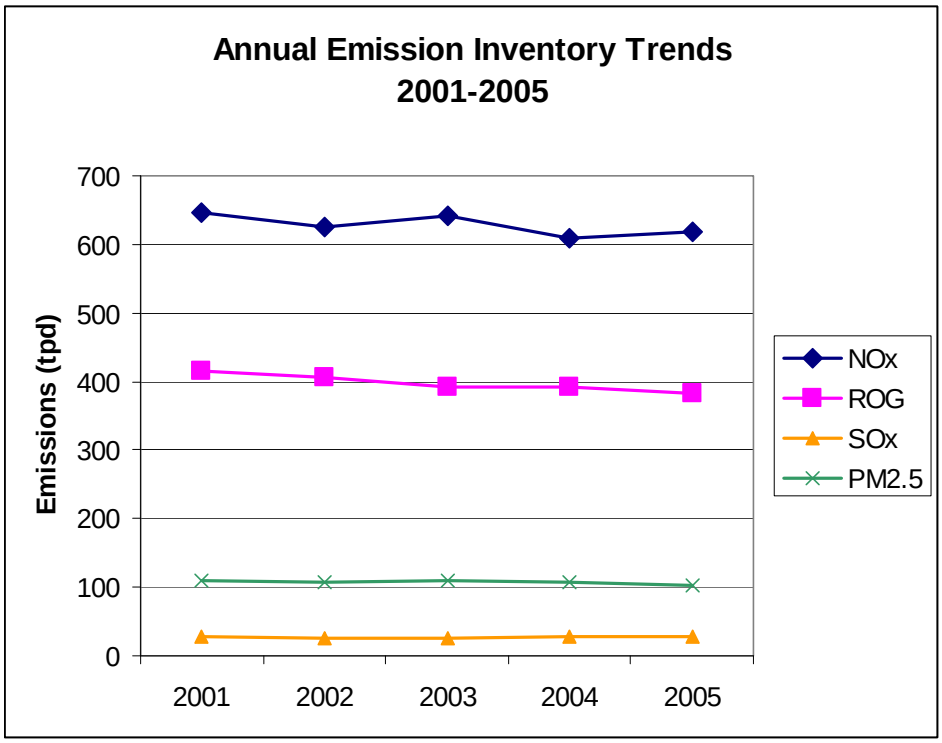


Emission Trends

At the same time that ambient concentrations have been declining, the emissions of pollutants that contribute to the different components of PM2.5 have been decreasing. Figure 18 illustrates the recent emission trends in the San Joaquin Valley air basin from 2001 through 2005. The greatest decrease in emissions occurred in ROG with a decrease of 33 tpd or 8 percent. NOx also decreased slightly, with a decline of 28 tpd, or 4 percent. Direct PM2.5 emissions showed a decrease of 7 tpd, or 7 percent, while SOx emissions did not change.

The combined downward trends in PM2.5 components, precursor concentrations, and emissions all indicate that over both in the short- and long-term the ongoing control program has had substantial benefits in improving air quality and that similar emission reductions in the future should provide continuing progress towards attaining the federal PM2.5 standards.

Figure 18: PM2.5 and PM2.5 Precursor Emission Trends in the San Joaquin Valley



3. OBSERVATIONAL MODELS AND DIAGNOSTIC ANALYSES

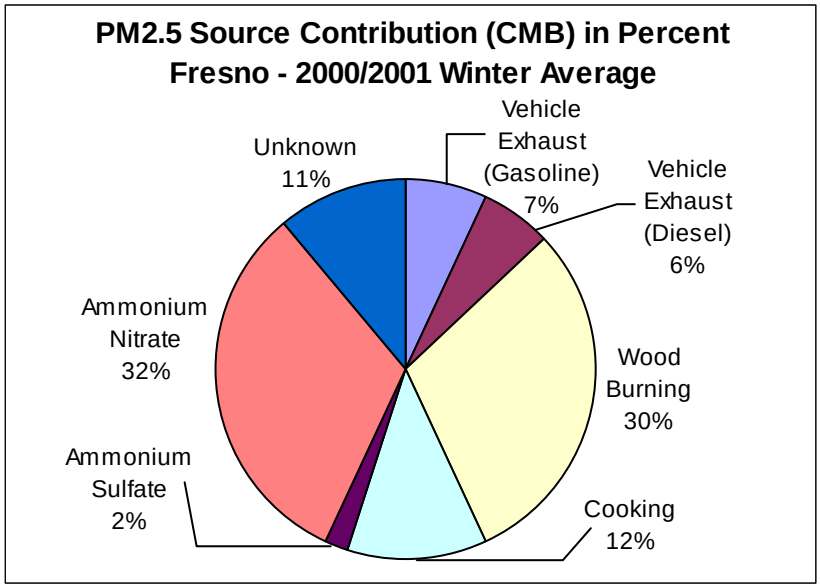
Observational models take advantage of monitored data to draw conclusions about the relative importance of different types of emissions and precursors as factors contributing to observed PM2.5 concentrations. According to U.S. EPA guidance, observational models can be used to corroborate the effects of prior control strategies, as well as identify the potential effectiveness of proposed control approaches. U.S. EPA recommends using both source apportionment (receptor models) and indicator species approaches. The two most widely applied receptor modeling approaches are multi-variate statistical models such as positive matrix factorization (PMF) and the chemical mass balance model (CMB). Receptor models are particularly useful in identifying the source contributions to directly emitted PM. This section summarizes results from prior source apportionment studies as well as both PMF and CMB applied to recent data. In addition, previous work using an indicator species approach to assess the limiting precursor in secondary nitrate formation in the San Joaquin Valley is discussed.

a. Observational Models

Prior Source Apportionment Studies

The Chemical Mass Balance (CMB), and the Positive Matrix Factorization (PMF) and UNMIX (named for its function, which is to "unmix" the concentrations of chemical species measured in the ambient air to identify the contributing sources) multivariate receptor models have been applied to PM2.5 data collected in the San Joaquin Valley. Chow, et al.[2] used the CMB source apportionment model to estimate the contribution of sources to PM2.5 in Fresno during high PM2.5 days occurring from December 15, 2000 through February 3, 2001 illustrated in Figure 19. Secondary ammonium nitrate is the most significant source, contributing 32 percent to the measured PM2.5. Residential wood combustion constitutes 30 percent of PM2.5. Vehicle emissions account for 13 percent of PM2.5, with similar contributions from gasoline (7 percent) and diesel (6 percent) fueled vehicles. Cooking accounts for 12 percent of PM2.5.

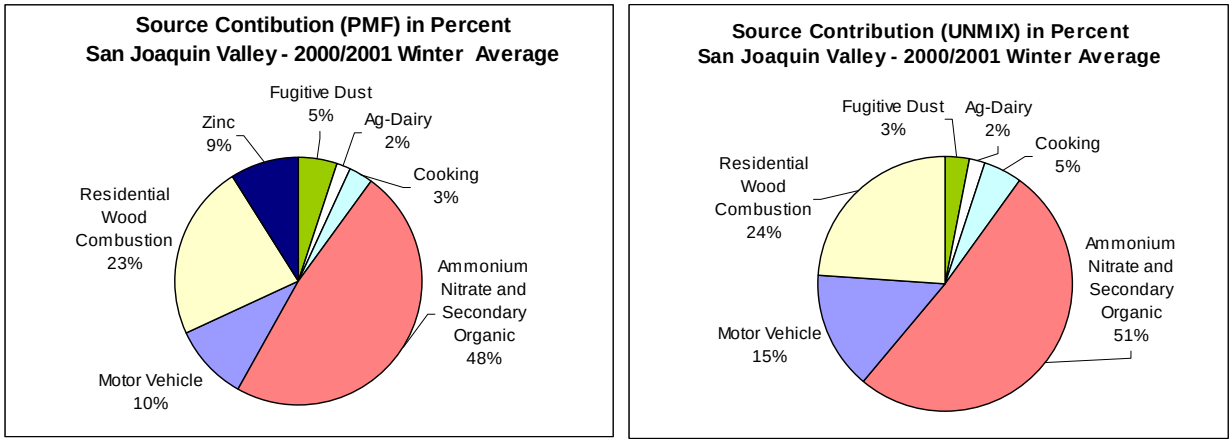
Figure 19: Source Contribution to PM2.5 Concentrations at Fresno Estimated Using the Chemical Mass Balance (CMB) Method



[2] J .C. Chow, J. G. Watson, D. H. Lowenthal, L.-W. A. Chen, B. Zelinska, L. R. Rinehart, and K. L. Magliano: Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite, Atmospheric Chemistry and Physics Discussions, 6, 10341 – 10372, 2006

Chen, et al.[3] applied the PMF and UNMIX models to chemically speciated PM2.5 measurements from 23 sites operated in the in the San Joaquin Valley during the 2000/2001 Central California PM Air Quality Study (CRPAQS) to estimate source contributions. Figure 20 illustrates the resulting source contribution throughout the Valley, estimated for the period when high PM2.5 concentrations occurred (November through January). PMF and UNMIX source contribution estimates are similar. Particles formed through chemical reactions in the atmosphere, including ammonium nitrate and secondary organic compounds are the major contributors, accounting for 48 percent (PMF) and 51 percent (UNMIX) of PM2.5. Residential wood combustion follows, with a contribution of 23 percent (PMF) and 24 percent (UNMIX). Particles directly emitted from motor vehicles account for 10 percent (PMF) and 15 percent (UNMIX) of PM2.5. In addition, the zinc component resulting from the PMF analysis is thought to be related to brake and tire wear and contributes 9 percent to PM2.5.

Figure 20: Source Contribution to PM2.5 in the San Joaquin Valley Estimated Using the Positive Matrix Factorization (PMF) and the UNMIX Models



Recent Studies

To evaluate the major PM2.5 sources and their contributions in the San Joaquin Valley using recent data, two different source apportionment techniques were applied to data collected in 2003 through 2006. The Chemical Mass Balance model (CMB) uses measured source profiles and chemical speciation data in combination to determine source contributions. A fundamental underlying assumption is that the source profiles used as input are appropriate and

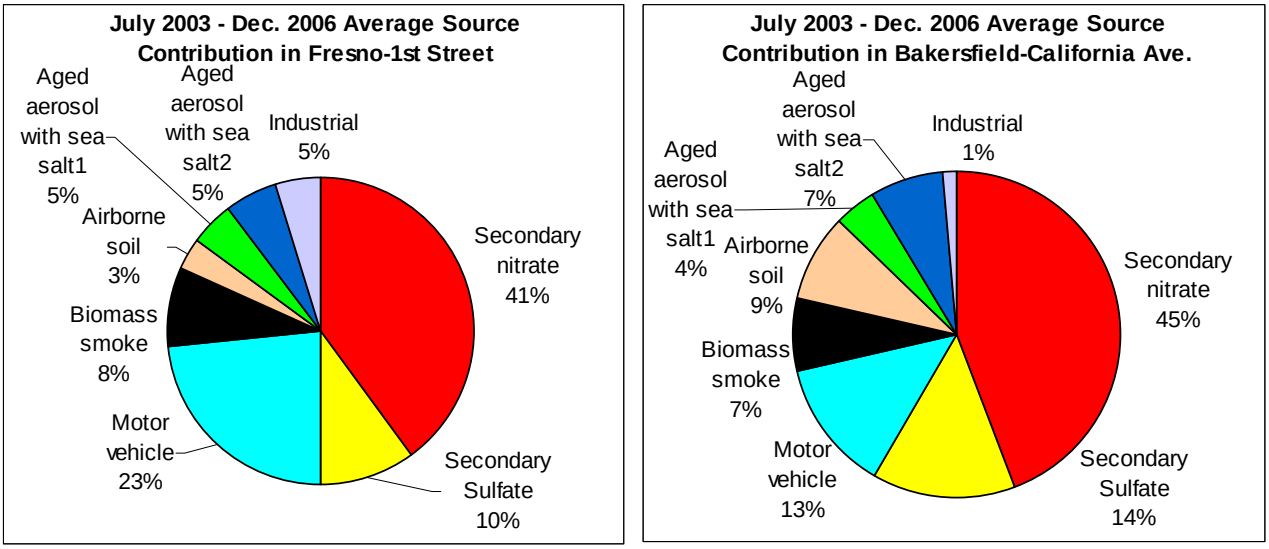
[3] L.-W. A. Chen, J. G. Watson, J. C. Chow, and K. L. Magliano: Quantifying PM2.5 Source Contributions for the San Joaquin Valley with Multivariate Receptor Models, submitted for publication, 2006.

representative for the region. In contrast, PMF does not require the input of source profiles, but rather evaluates the covariance of the chemical species to determine a set of factors, which are typically interpreted as source types. Source contributions are then calculated for each of the factors. Because the factors reflect species which vary in time in a similar manner, the factors may reflect the impacts of primary sources, as well the secondary species that have condensed on these primary particles. Since each technique has strengths and weaknesses, combined the two source apportionment techniques provide complementary results.

Positive Matrix Factorization

The PMF2 model was applied to chemically speciated PM2.5 data collected at the Fresno-First St. and Bakersfield-California Ave. Speciation Trends Network (STN) monitoring sites from July 2003 through December 2006. The average source contribution estimates illustrated in Figure 21 show ammonium nitrate is the major contributor to PM2.5 at both sites (41 percent at Fresno and 45 percent at Bakersfield). Biomass smoke contributes similar percentages at both sites (8 percent at Fresno, 7 percent at Bakersfield) as does the total aged aerosol (10 percent at Fresno, 11 percent at Bakersfield). The main differences in source contribution between the two sites include particles directly emitted from motor vehicles, which at Fresno account for 23 percent of PM2.5, the 2nd major component, while at Bakersfield account for 13 percent. Ammonium sulfate accounts for 10 percent of PM2.5 at Fresno and 14 percent at Bakersfield. Airborne soil is a minor contributor to PM2.5 at Fresno (3 percent), with a 9 percent contribution at Bakersfield.

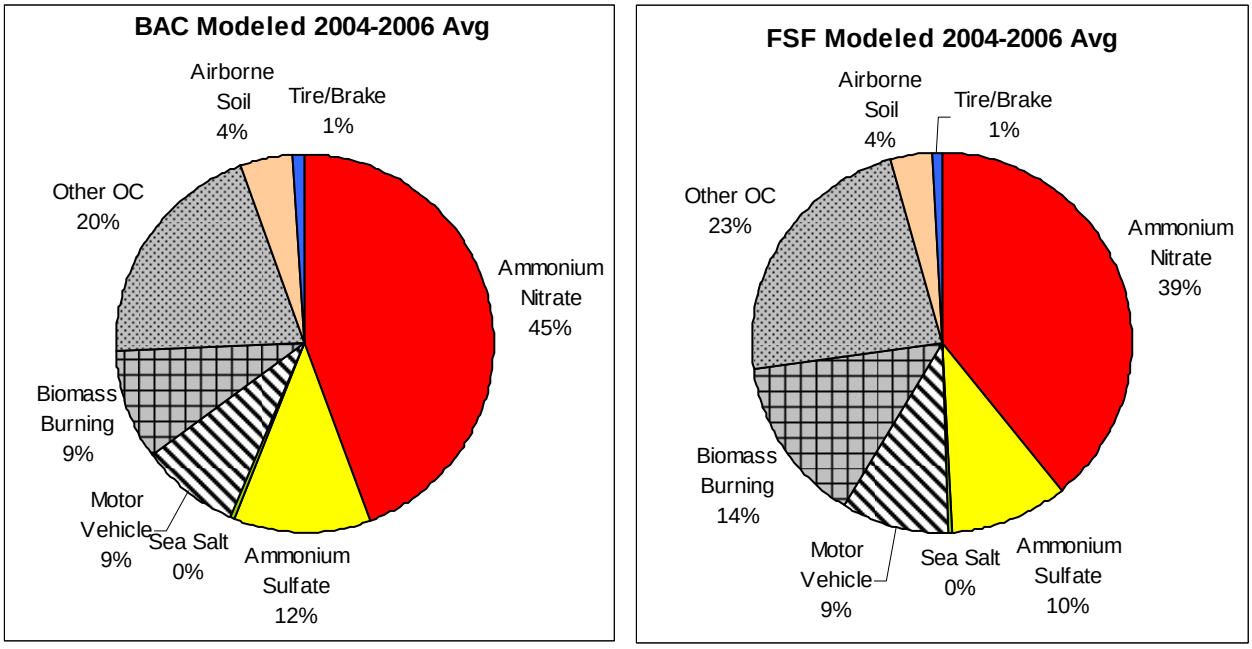
Figure 21. Average Source Contributions Estimated Using PMF2 (2003-2006)



Chemical Mass Balance Modeling

Annual average source contributions at Bakersfield-5558 California Avenue (BAC) and Fresno-1st Street (FSF) were also estimated by applying the Chemical Mass Balance (CMB 8.2) model to individual PM2.5 sample concentrations collected between January 1, 2004 and December 31, 2006 and using source profiles for PM2.5 developed during previous studies. Source contribution estimates were calculated based on the 2004-2006 annual average of the individual samples. Figure 22 shows the calculated contributions to ambient fine particulate matter made by sources included in the model. Ammonium nitrate was the most significant source contributing 44% and 39% of the PM2.5 mass at Bakersfield and Fresno, respectively. Ammonium sulfate accounted for 12% at Bakersfield and 10% at Fresno. The motor vehicle exhaust (diesel and gasoline combined) contribution was 9% at both sites. Vegetative burning, which included residential wood combustion and agricultural and prescribed burning, contributed 9% and 14%, respectively, of the PM2.5 mass. The sea salt contribution was negligible at both sites. The 'Other OC', which represents contributions from secondary organic carbon, other unidentified primary sources, and the possible positive sampling artifacts of organic carbon, accounted for 20% to 23% of the PM2.5 mass.

Figure 22. CMB Model Calculated 2004-2005 Average PM2.5 Source Contributions.



While the specific contributions vary to some extent, taken together these sources apportionment studies highlight the importance of secondary ammonium nitrate contributions to both the 24-hour and annual average concentrations. In addition, biomass burning and mobile sources were found to be significant contributors to primary PM2.5.

Diagnostic Analyses

Indicator Species Approach

As discussed in prior sections, trends in ammonium nitrate concentrations have tracked well with concurrent reductions in NOx, suggesting that NOx control is an effective approach for ensuring further reductions in ammonium nitrate. An indicator species approach provides an additional method to investigate which chemical precursor a secondary species such as ammonium nitrate is most responsive to control of. Ammonium nitrate is formed in the atmosphere through the reactions of precursor nitrogen oxides (NOx), reactive organic gases (ROG), and ammonia (NH3). The amount of each precursor in the atmosphere relative to each other determines how much ammonium nitrate is formed. The chemistry is complex, but essentially the precursor in shortest supply will limit how much ammonium nitrate is produced. Reducing emissions of this limiting precursor provides the best opportunity to cut ammonium nitrate levels. In simple terms, photochemical reactions of NOx and ROG form nitric acid (HNO3). Nitric acid then reacts with ammonia (NH3) to form ammonium nitrate. Lurmann, et al.[4] compared ammonia and nitric acid ambient concentrations measured in the San Joaquin Valley during the winter of 2000/2001, as part of CRPAQS. Figures 23 and 24 show the concentrations of nitric acid and ammonia measured at the rural Angiola site and at the urban Fresno site. At both sites ammonia concentrations are generally at least an order of magnitude higher than the nitric acid concentrations. These ammonia-rich conditions throughout the Valley indicate that, during the winter, nitric acid is the limiting precursor.

[4] F. W. Lurmann, S. G. Brown, M. C. McCarthy, and P. T. Roberts: Processes Influencing Secondary Aerosol Formation in the San Joaquin Valley during Winter, Journal of Air and Waste Management Association, 56, 1679-1693, 2006.

Figure 23: Comparison of Ammonia and Nitric Acid Concentrations Measured at Angiola during the Winter of 2000/2001 as Part of CRPAQS

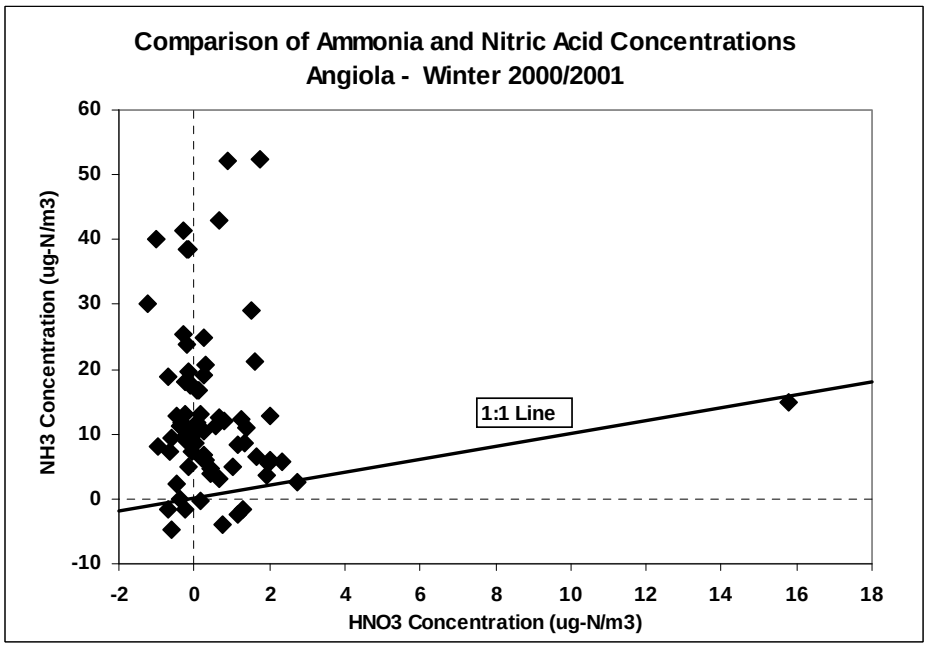
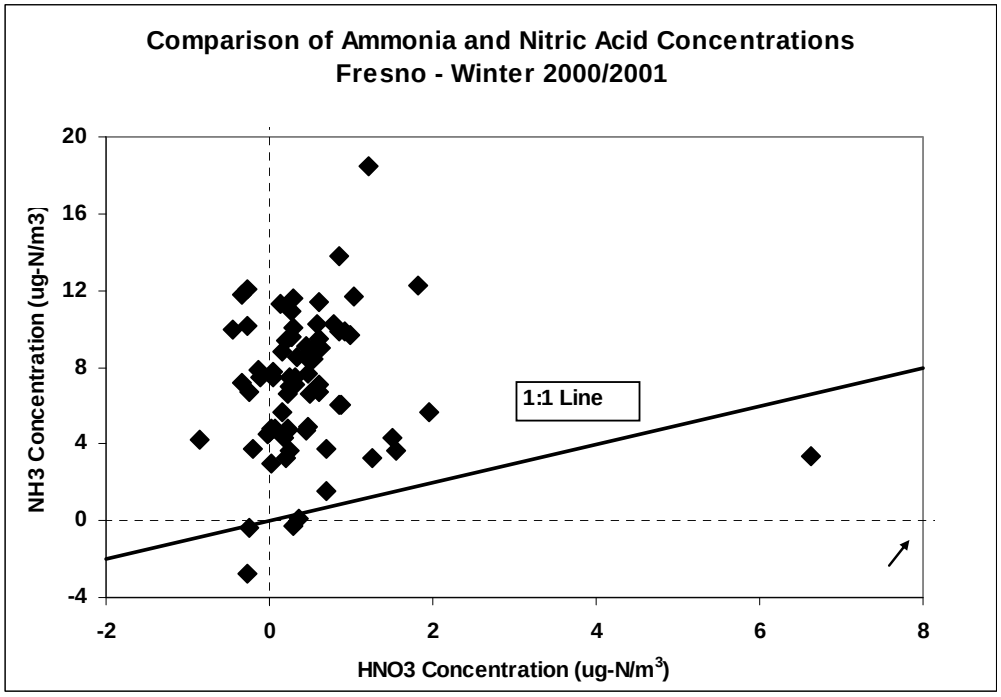


Figure 24: Comparison of Ammonia and Nitric Acid Concentrations Measured at Fresno during the Winter of 2000/2001 as Part of CRPAQS



4. AIR QUALITY MODELING

a. Rollback Modeling

In addition to the evaluation of air quality trends and the observational and diagnostic analyses, a rollback modeling analysis was conducted by the District to estimate the impacts of future emission reductions on resulting air quality. An extensive discussion of the rollback methodology and the results are provided in Chapter 3 and associated spreadsheets of the District Plan. The rollback modeling showed that Fresno and Corcoran would attain the annual PM2.5 standard with baseline emission reductions in 2014. With the addition of the ARB and District proposed control strategy, both Visalia and Bakersfield-Planz would attain in 2014 as well.

b. Grid-Based Modeling

As stipulated in the EPA Modeling Guidance, a grid-based photochemical model is necessary to perform the modeled attainment test for PM2.5 (EPA, 2007[5]). Such models offer the best available representation of important atmospheric processes and are an essential tool in analyzing the impacts of proposed emissions controls on pollutant concentrations. The EPA recommends guidelines for choosing a model for use in the attainment test. For example, the model source code should be free or low cost, modeling elements should have undergone rigorous scientific peer-review, and it should have been shown to perform well in the past for similar applications.

The Community Multiscale Air Quality Modeling System (CMAQ) has been selected for use in the $PM_{2.5}$ modeled attainment demonstration for the San Joaquin Valley Air Pollution Control District. CMAQ is a state-of-the-science "one-atmosphere" system that treats major atmospheric and land processes (e.g., advection, diffusion, gas phase chemistry, gas-particle mass transfer, nucleation, coagulation, wet and dry deposition, aqueous phase chemistry, etc.) and a range of species (e.g., anthropogenic and biogenic, primary and secondary, gaseous and particulate) in a comprehensive framework (EPA, 1999[6]; CMAS, 2007[7]).

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[5] U.S. Environmental Protection Agency. (2007) Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, $PM_{2.5}$, and Regional Haze. EPA-454/B-07-002

[6] U.S. Environmental Protection Agency (1999) Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System**.** EPA/600/R-99/030. http://www.epa.gov/asmdnerl/CMAQ/CMAQscienceDoc.html

[7] Community Modeling and Analysis System (2007) CMAQ v4.6 Operational Guidance Document. http://www.cmaq-model.org/op_guidance_4.6/manual.pdf

CMAQ was run for the year 2000 to provide the basis for the model performance evaluation. It was during 2000 that the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) took place. The study resulted in a wealth of data with which to evaluate model performance. As it is necessary to execute simulations for a model reference year and a future year to perform the recommended modeled attainment demonstration, 2005 and 2014 were also simulated. Simulations for all years were driven by the meteorological inputs for 2000, while emissions varied from year to year.

Regional air quality modeling only represents a portion of the attainment test. In order to perform the EPA-recommended Speciated Modeled Attainment Test, or SMAT, the relative response between the modeled reference and future years must be considered in conjunction with observations. This approach minimizes the uncertainties in predicting future year attainment that result from potential model bias in predicting absolute species concentrations.

Federal Reference Method (FRM) PM2.5 mass measurements provide the basis for nonattainment designations. For this reason it is recommended that the FRM data also be used to project future air quality and progress towards attainment of the health-based National Ambient Air Quality Standard (NAAQS) for PM2.5. However, given the complex physicochemical nature of PM2.5, it is necessary to consider individual species as well. While the FRM measurements give the mass of the bulk sample, a method for apportioning this bulk mass to individual PM2.5 components is a first step towards determining the best targets for emissions controls in order to reach NAAQS levels in a timely manner. Given that (1) attainment status is currently dependent upon FRM measurements and (2) concentrations of individual PM2.5 species need to be considered in order to understand the nature of and efficient ways to ameliorate the PM2.5 problem in a given region, a method has been developed to speciate bulk FRM PM2.5 mass with known FRM limitations in mind. This method is referred to as the measured **S**ulfate, **A**djusted **N**itrate, **D**erived **W**ater, **I**nferred **C**arbonaceous material and estimated acidity (**H**+) approach or “SANDWICH”. SANDWICH is based on speciated measurements from other (often co-located) samplers, such as those from the Speciated Trends Network (STN), and the known sampling environment of the FRM. The approach serves to provide mass closure, reconciliation between speciated and bulk mass concentration measurements, and the basis for a connection between observations, modeled PM2.5 concentrations, and the air quality standard.

The SMAT procedure was applied to FRM monitors operating in the San Joaquin Valley with minimal deviations from U.S. EPA’s recommended procedure. The 2006 design value was used as a basis from which to project forward to estimated future year design values for the year 2014. Speciation data for four STN (speciation) sites was used to speciate the FRM mass for all FRM sites. For those sites not collocated with STN monitors, “surrogate” speciation sites were determined based on analysis of CRPAQS data to determine which sites

had similar speciation profiles. The composition was assumed to be the same at all three Bakersfield sites (BAC, BGS, and BEP). Similarly, the percent composition at the two Fresno sites (FSF and FSH) was assumed to be the same. In addition, Stockton (SOH), Clovis (CLO), Corcoran (COP), and Modesto (MRM), were assumed to have the same speciation as one of the four speciation sites based on CRPAQS data analysis.

Quarterly average species concentrations were calculated at each STN site using the SANDWICH procedure. Modeled concentrations for the reference year (2005) and future year (2014) for each component were extracted for the FRM sites as a nine-cell average. The relative response factors were calculated for each component for each quarter. These calculations were performed using all modeled days, as we assumed that the selected FRM measurements provided a stable quarterly average value.

These quarterly species percentages were then multiplied against the base year design value for 2006 (the average FRM PM2.5 concentrations for 2004, 2005, and 2006). The quarterly observed species concentrations were then multiplied by the RRFs and summed and averaged to get a future year PM2.5 design value at each FRM site. See Table 3 for the predicted baseline and controlled 2014 PM2.5 design values. For the "controlled" 2014 emissions sensitivity scenario described above, future annual PM2.5 concentrations at all FRM sites are below the annual PM2.5 NAAQS of 15.0 $\mu g/m^3$, and, therefore, the San Joaquin Valley has passed the speciated modeled attainment test for the annual PM2.5 NAAQS.

A similar procedure to the attainment demonstration for the annual PM2.5 standard was followed for the 24-hour PM2.5 standard attainment demonstration. The exception was that only the top 25% of the measured and modeled days for each quarter were used instead of all available days. The top 25% of the days are expected to be more representative of the 24-hour design value than would all available days for a given quarter.

Table 4 shows the predicted 2014, 24-hour PM2.5 design values for the top five 2006 design value sites for the controlled emissions case. As shown, all sites in the SJV attained the 24-hour standard in 2006, and further emissions controls do not cause any monitors to become non-attainment.

Table 3. Reference and future year annual design values for SJV FRM sites

Site	Code	Speciation	2006 DV	2014 Baseline DV	2014 "Controlled" DV
Bakersfield - 5558 California	BAC	BAC	18.51	15.86	14.28
Bakersfield - 410 E Planz Road	BEP	BAC	18.86	16.26	14.70
Bakersfield - Golden State	BGS	BAC	18.64	15.98	14.39
Clovis - N Villa Avenue	CLO	FSF	16.39	14.10	12.72
Corcoran - Patterson Avenue	COP	VCS	17.24	14.75	13.27
Fresno - 1st Street	FSF	FSF	16.68	14.43	13.01
Fresno - Hamilton and Winery	FSH	FSF	17.16	14.93	13.47
Merced - 2334 M Street	MRM	M14	14.69	12.85	11.76
Modesto - 14th Street	M14	M14	14.10	12.52	11.44
Stockton - Hazelton Street	SOH	M14	12.93	11.77	10.87
Visalia - N. Church Street	VCS	VCS	18.20	16.05	14.47

Table 4. Reference and future year 24-hour design values for SJV FRM sites

Site	Code	Speciation	2006 DV	2014 "Controlled" DV
Bakersfield - 5558 California	BAC	BAC	62.4	46.2
Bakersfield - 410 E Planz Road	BEP	BAC	65.2	45.9
Bakersfield - Golden State	BGS	BAC	64.4	45.3
Fresno - 1st Street	FSF	FSF	58.0	41.2
Fresno - Hamilton and Winery	FSH	FSF	58.5	41.7

5. SUMMARY

In summary, the San Joaquin Valley has experienced tremendous progress in reducing PM2.5 concentrations since initial monitoring began in 1990. Between 1990 and 1998, PM2.5 annual average concentrations dropped by approximately 40 percent throughout the Basin. Since 1999, when the official regulatory monitoring program for comparison to the federal PM2.5 standard began, PM2.5 annual average concentrations have dropped a further 19 to 29 percent. While the peak annual average design value in the basin was 24.7 ug/m^3 in 2001, approximately one and a half times the level of the standard, it has dropped to 18.9 ug/m^3 in 2006. Currently, annual design values in the northern portion of the Valley are below the standard. In addition, based on 2004-2006 data, the San Joaquin Valley attains the federal 24-hour standard of 65 ug/m^3. Although concentrations remain the highest in the central and southern portions of the

Valley, the rate of decrease in PM2.5 in response to ongoing control programs has been significant.

Unlike ozone, PM2.5 consists of many different components. Analysis of the trends in different components of PM2.5 has shown that over the last six years, decreases in carbonaceous aerosols and ammonium nitrate have had the greatest contribution to declining PM2.5 mass trends, with carbonaceous aerosol concentrations dropping by 16 to 37 percent and ammonium nitrate concentrations dropping by 23 to 24 percent. During this same time period, ambient NOx concentrations, a precursor to ammonium nitrate, decreased by 15 percent, while NOx emissions dropped by 4 percent. Looking back to the late 1980s, both ammonium nitrate and ammonium sulfate have declined significantly, along with concurrent declines in ambient NO_2 and SO_2 concentrations and NOx and SOx emissions. These significant trends in declining PM2.5 concentrations, ambient precursor concentrations, and associated emissions all suggest that a continuing focus on further NOx reductions, as well as sources which contribute to carbonaceous aerosols will provide significant further progress in attaining the annual PM2.5 standard.

In order to estimate the impact of further emission reductions on future PM2.5 concentrations, both linear rollback and grid-based aerosol modeling were conducted. PM2.5 annual average concentrations in 2014 based on emission reductions achieved from both the ongoing control program, as well as new State and local measures, were estimated with both methods. Substantial further emission reductions for all key pollutants will occur between 2005 and 2014.

Based on the grid-based modeling, several sites in the District would be expected to attain the annual standard in 2014 with baseline emission reductions. With the addition of the new State and local measures focusing on NOx, carbon, and directly-emitted combustion emissions, the sites with the most severe problems – Visalia and Bakersfield – would also attain in 2014 with a maximum predicted design value of 14.7 in Bakersfield. The linear rollback modeling showed similar results, providing a consistent assessment of attainment prospects. It also appears that 2014 is the earliest feasible attainment date. This is due to consideration of the following factors: 1) baseline emission reductions that occur during the period up to 2014 are not sufficient alone to provide for attainment at all sites, 2) the additional emission reductions that will result from the State Strategy will not phase in prior to 2014 due to the extraordinarily complex and innovative nature of developing and implementing these new measures, and 3) the San Joaquin Valley has experienced periods of slower air quality progress due to the influence of meteorology, suggesting that the full timeframe up to 2014 will be needed to ensure attainment.

Therefore, considering all of the information available, the weight-of-evidence analyses provide a consistent assessment that the San Joaquin Valley will attain

the annual average PM2.5 standard throughout the District in 2014. This is due to the following considerations:

- The significant progress that has already occurred, a 6 ug/m3 drop in annual average design value between 2001 and 2006, which represents two-thirds of the progress needed to attain the annual standard by 2014;

- The positive response of ammonium nitrate, ammonium sulfate, and carbon concentrations to past reductions in NOx, SOx, and primary PM2.5 emissions;

- The substantial future emission reductions that will occur due to both baseline commitments as well as new measures from NOx, and primary PM2.5 emissions that have worked in the past;

- Linear rollback modeling which indicates attainment in 2014; and,

- Grid-based aerosol modeling which also indicates attainment in 2014 at all sites in the District.