Staff Report

ARB Review of
San Joaquin Valley PM2.5
State Implementation Plan

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California Environmental Protection Agency
Air Resources Board

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EXECUTIVE SUMMARY

As part of the attainment demonstration, the SJV 2015 PM2.5 Plan specifically identifies the: 1) most expeditious date of when the Valley will attain the standards, 2) relative efficacy of precursor emission reductions, 3) amount of emissions needed to attain, and 4) control strategy. The weight of evidence analysis provides a set of complementary analyses that supplement the required model based attainment demonstration. Because all methods have 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.

Analyses conducted by ARB and District staff, along with findings from the California Regional Particulate Air Quality Study (CRPAQS) provide the supplemental information supporting the attainment demonstration. CRPAQS was a public/private partnership designed to advance our understanding of the nature of PM2.5 in the Valley and guide development of effective control strategies. The study included monitoring at over 100 sites as well as data analysis and modeling, results of which have been published in over 60 papers and presented at national and international conferences.

Studies such as CRPAQS provide valuable information that supports the SIP process in a number of ways. First, these studies provide additional observational data that help to provide a more detailed understanding of the nature of the PM2.5 problem in the San Joaquin Valley. This data also is used to update the fundamental algorithms contained within air quality models, thereby enhancing their ability to simulate observed air quality conditions. Finally, they provide an improved basis for model applications used in the preparation of SIPs and a more robust platform for evaluating the response to emission controls and predicting future air quality.

In 2006, U.S. EPA tightened the 24-hour PM2.5 standard to 35 $\mu g/m^3$ and in 2012, the annual standard to 12 $\mu g/m^3$. The District adopted the 2012 PM2.5 Plan addressing the 35 $\mu g/m^3$ 24-hour standard and U.S. EPA proposed approval of the Moderate area requirements in this Plan in 2015. The SIP for the 12 $\mu g/m^3$ annual standard will be due to U.S. EPA in 2016.

What are the key sources of the PM2.5 problem in the Valley?

The geography of the San Joaquin Valley, along with weather patterns influence the accumulation, formation, and dispersion of PM2.5. As a result, PM2.5 concentrations are generally higher in the central and southern portions of the Valley, with highest values in the urban areas of and around Fresno and Bakersfield. Concentrations are highest during the winter months of November through February. During the winter of 2013/2014, a persistent high-pressure weather system over Northern California caused the atmosphere to become stagnant, which in conjunction with nearly two months without rain, resulted in episodes of high PM2.5 concentrations lasting for several weeks. These elevated wintertime PM2.5 concentrations also resulted in higher annual average concentrations.

Ammonium nitrate and carbon compounds (organic and elemental carbon) are the largest chemical constituents, comprising, on an annual average basis, 70 to 80 percent of the PM2.5 mass and about 90 percent of winter peak day PM2.5 mass. Geological material (dust) and ammonium sulfate are smaller contributors.

Source apportionment studies confirm the importance of ammonium nitrate contributions to PM2.5 and also identify motor vehicle exhaust and biomass burning as significant contributors. Sources of biomass burning include residential wood combustion, agricultural and prescribed burning, and cooking.

Ammonium nitrate is formed in the atmosphere from reactions of gaseous precursors. Emissions of nitrogen oxides (NOx) from mobile sources and stationary combustion sources react with ammonia which is primarily emitted from livestock operations and fertilizer application. Heavy duty diesel vehicles account for approximately 50 percent of annual average NOx emissions, followed by farm and off-road equipment, other vehicles, trains, and stationary combustion sources. The stagnant, cold, and damp conditions that occur during the winter promote the formation and accumulation of ammonium nitrate. Elevated concentrations can be found at both urban and rural sites.

In contrast, organic carbon is highest in urban areas due to emissions from residential wood combustion, commercial cooking operations, and mobile source tailpipe emissions which are largest in urban areas. Due to the localized urban increment from these activities, which adds to the more regional ammonium nitrate concentrations, the highest PM2.5 concentrations in the Valley usually occur at urban sites in the winter.

What is the effectiveness of controlling different PM2.5 precursors?

In addition to directly emitted PM2.5 there are multiple precursor pollutants that lead to PM2.5 formation (NOx, sulfur oxides (SOx), volatile organic compounds (VOCs), and ammonia).

Given the large contribution of ammonium nitrate to high PM2.5 concentrations, a number of different studies and analyses were evaluated to understand the role of VOCs and ammonia in ammonium nitrate formation in the San Joaquin Valley. The amount of ammonium nitrate produced depends upon the relative atmospheric abundance of its precursors. It is therefore important to understand which precursor controls are most effective in reducing ammonium nitrate concentrations. In simple terms, the precursor in shortest supply will limit how much ammonium nitrate is produced. This is known as the limiting precursor and controls of this precursor will have the most significant benefits in reducing PM2.5 concentrations.

The precursor assessment for the 2015 PM2.5 plan included evaluation of emissions inventories, monitoring studies, and photochemical modeling analyses of ammonium nitrate sensitivity to precursor emission reductions. While emissions inventory and monitoring data can indicate the relative abundance of the different precursors, photochemical models provide a quantitative approach to simulate the effects that emission reductions in each of gaseous precursors would have on the predicted ammonium nitrate concentrations.

Evaluation of emissions inventory data concluded that the ammonia-rich conditions throughout the Valley demonstrate that NOx rather than ammonia is the limiting precursor during wintertime PM2.5 episodes as well as on an annual average basis. Data of monitoring conducted during wintertime PM2.5 episodes, further corroborate this finding. In addition, photochemical modeling studies found that while large reductions in NOx led to commensurate reductions in ammonium nitrate, comparable reductions in ammonia were much less effective. Precursor sensitivity modeling conducted for the 2012 PM2.5 Plan showed that on a per ton basis, reductions in NOx are approximately nine times more effective than reductions in ammonia. Finally, evaluation of ambient air quality trends show that reductions in NOx emissions, gaseous NOx concentrations, and particulate nitrate all track each other well.

Evaluation of monitoring studies also provided some evidence that VOCs could be important at times, however, these studies were not conclusive. Therefore photochemical modeling studies are more appropriate to assess the overall impact of VOC controls. These modeling studies found that at current NOx levels, further VOC emission reductions produce essentially no benefit, and in some instances may actually lead to an increase in ammonium nitrate concentrations. Findings from these prior studies were supported by precursor sensitivity modeling conducted for the 2012 PM2.5 SIP, which indicated a very small disbenefit from reductions in VOCs.

Based on the weight of evidence presented from historical studies, coupled with the modeled precursor sensitivity analyses conducted as part of the 2012 PM2.5 Plan, ammonia controls provide only a very small benefit in reducing PM2.5 levels, and VOC controls can result in a disbenefit. However, directly emitted PM2.5, NOx and SOx controls have been documented to result in PM2.5 air quality improvement and are therefore the focus of the control strategy in the San Joaquin Valley.

What progress has the prior control approach achieved in reducing PM2.5 concentrations?

The implemented control strategy reducing directly emitted PM2.5, NOx, and SOx emissions has resulted in measurable PM2.5 air quality improvements. Over the last dozen years, the Valley has experienced progress in reducing both annual average and 24-hour PM2.5 concentrations. Between 2001 and 2013, annual average design values declined between 30 and 35 percent at individual monitoring locations. During this same time period, 24-hour PM2.5 design values in the Valley have also decreased between approximately 30 and 45 percent. In addition, the number of days exceeding the 24-hour standard decreased by about 60 to 80 percent.

Even though the drought related meteorological conditions caused significant increases in 2013 PM2.5 concentrations, all sites in the Valley still attained the 24-hour standard of 65 µg/m3 and almost half of the sites attained the annual standard of 15 µg/m^3.

Additional evaluations provide further insight into the annual and 24-hour PM2.5 progress that has been observed. For example, as the fraction of days recording PM2.5 levels above the 24-hour standard of 65 µg/m^3 has decreased, there has been a corresponding increase in the fraction of days below the level of the annual standard of 15 µg/m^3. Average concentrations during the winter months have decreased, and under similar meteorological conditions, peak 24-hour concentrations during the 2013/2014 episodes are 30 to 40 percent lower than they were during the 2000/2001 CRPAQS episode due to the impact of implemented emission controls.

Programs aimed at reducing NOx emissions have played an important role in reducing PM2.5 ammonium nitrate concentrations. Between 2004 and 2012, Valley-wide NOx emissions decreased by 41 percent, with a commensurate reduction of about 37 percent in measured PM2.5 nitrate at the Bakersfield and Fresno monitoring sites. Based on the SJV 2015 PM2.5 Plan attainment demonstration, the 38 percent in NOx emission reductions expected from the control strategy between 2012 and 2020, are projected to decrease PM2.5 nitrate by 17 percent at the Bakersfield site and 25 percent at the Fresno site.

Control measures reducing directly emitted PM2.5 have also led to measurable reductions in PM2.5 concentrations. Between 2004 and 2012, Valley-wide PM2.5 emissions from combustion sources decreased by 30 percent, with a concomitant reduction of 15 percent in measured carbonaceous PM2.5 at the Bakersfield site and 20 percent at Fresno site. Based on the SJV 2015 PM2.5 Plan attainment demonstration, the 28 percent reduction in PM2.5 carbon emission expected from the control strategy implementation between 2012 and 2020 is projected to decrease carbonaceous PM2.5 by 22 percent at the Bakersfield and Fresno monitoring sites.

When will the Valley attain the PM2.5 standard with the proposed control strategy?

The U.S. EPA approved air quality modeling for the 2008 PM2.5 SIP provided the basis to predict future PM2.5 concentrations at each monitoring site in the San Joaquin Valley. The attainment demonstration uses the fundamental chemistry and associated response of different PM2.5 constituents to emission controls reflected in the modeling in the 2008 PM2.5 SIP. This modeling science is coupled with 2013 design values and PM2.5 chemical composition reflecting drought impacts, along with emission reductions expected in 2020 (for the annual standard demonstration) and in 2018 (for the 24-hour demonstration).

To assess the representativeness of the 2008 SIP modeling for capturing the dynamics and response to emission reductions for the updated attainment demonstration, ARB staff evaluated both the meteorological characteristics, as well as the chemical composition used in the two modeling efforts. The types of meteorological conditions conducive to PM2.5 formation in 2013/2014 were similar to the 2000/2001 meteorological conditions simulated in the 2008 SIP. These factors include the presence of persistent ridges that result in warm air aloft and strong stability with limited mixing, cool morning temperatures, and low wind speeds. Although the persistence of these meteorological conditions in 2013/2014 resulted in an increased number of days with high concentrations, the underlying meteorological factors driving elevated PM2.5 concentrations were similar to 2000/2001. In addition, the PM2.5 chemical composition used in the 2008 PM2.5 modeling was very similar to 2013, indicating common atmospheric chemistry regimes. Therefore, the 2008 PM2.5 SIP modeling response to emission reduction, applied to 2013 design values, provides a suitable basis for the updated attainment demonstration.

The magnitude of emission reductions required for attainment is consistent with past response of Valley PM2.5 to NOx and directly emitted PM2.5 reductions. The implementation of new reductions from California's on-going emission control programs will provide the majority of the emission reductions needed to attain the annual PM2.5 standard throughout the San Joaquin Valley in 2020. Between 2012 and 2020, implementation of these control programs will reduce NOx emissions by 38 percent. The NO_x reductions result from ongoing implementation of both new vehicle standards for passenger and heavy-duty diesel vehicles and equipment, as well as rules accelerating the turnover of legacy diesel fleets. Implementation of stringent requirements for new off-road engines and in-use off road equipment lead to further NO_x reductions, along with District rules addressing stationary source NO_x emissions.

In addition, directly emitted PM2.5 emissions in aggregate will be decreasing by eight percent as a result of ongoing implementation of diesel on- and off-road equipment measures as well as the District control measures curtailing agricultural and residential wood burning, along with additional reductions from enhancements to the District's commercial charbroiling rule slated for adoption in 2016.

All of these measures provide the necessary control strategy to ensure the entire Valley is in attainment of the 65 ug/m^3 24-hour PM2.5 standard by 2018 and the 15 ug/m^3 annual PM2.5 standard by 2020.

What is the impact of 2014 PM2.5 air quality data?

The drought-related meteorological conditions that affected PM2.5 concentrations in the San Joaquin Valley during 2013 continued into 2014. Although complete data for 2014 is not yet available, this section provides a preliminary assessment of 2014 air quality data in relation to the attainment demonstration.

Despite the ongoing persistence of the drought, air quality conditions in 2014 generally improved at most locations, particularly in the northern and central portions of the Valley. This is an indication that although drought conditions are continuing, progress is resuming as a result of ongoing emission reductions. However, because 2014 design values will reflect the impact of multiple years of drought, a comparison to the 2013 design values used in the attainment demonstration is expected to be mixed, with some locations recording design values that are slightly lower, and other locations recording design values that are slightly higher. Based on an assessment of the PM2.5 levels predicted for 2020 as well as ongoing trends and analyses, consideration of 2014 design values is expected to remain consistent with the current attainment demonstration. However, ARB and the District will continue to monitor the impacts of the drought and its relationship to future PM2.5 attainment needs.

1. INTRODUCTION

To address the 1997 annual PM2.5 standard of 15 µg/m^3 and 24-hour standard of 65 µg/m^3, the District adopted the 2008 PM2.5 Plan. The Plan demonstrated attainment by April 2015. U.S. EPA approved this Plan in 2011 (76 FR 41338; 76 FR 69896).

The 2015 PM2.5 Plan specifically identifies the: 1) most expeditious date of when the Valley will attain the standard, 2) relative efficacy of precursor emission reductions, 3) amount of emissions needed to attain, and 4) attainment strategy. The Weight of Evidence (WOE) analysis provides a set of complementary analyses that supplement the required modeled attainment demonstration.

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 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 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. Following U.S. EPA guidance, future year modeled annual average design values that fall between 14.5 and 15.5 ug/m^3 need to be accompanied by a WOE demonstration to determine whether attainment will occur. This range in model based 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 evaluations. 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 that supports the attainment demonstration for the 1997 annual and 24-hour PM2.5 standards in the San Joaquin Valley.

2. PM2.5 STANDARDS AND HEALTH EFFECTS

PM2.5 is a complex mixture of particles and liquid droplets that vary in size and chemical composition. As a subset of PM10, particles with diameters up to 10 micrometers, PM2.5 comprises particles with diameters up to 2.5 micrometers. PM2.5 contains a diverse set of substances including elements such as carbon and metals, compounds such as nitrates, sulfates, and organic materials, and complex mixtures such as diesel exhaust and soil or dust. Some of the particles are directly emitted into the atmosphere. Other particles, referred to as secondary particles, result when gases are transformed into particles through physical and chemical processes in the atmosphere.

Numerous health effects studies have linked exposure to PM2.5 to increased severity of asthma attacks, development of chronic bronchitis, decreased lung function in children, increased respiratory and cardiovascular hospitalizations, and even premature death in people with existing cardiac or respiratory disease. In addition, California has identified particulate exhaust from diesel engines as a toxic air contaminant – suspected to cause cancer, other serious illnesses, and premature death. Those most sensitive to PM2.5 pollution include people with existing respiratory and cardiac problems, children, and older adults.

Ambient air quality standards establish the levels above which PM2.5 may cause adverse health effects. In 1997, U.S. EPA adopted the first set of PM2.5 air quality standards, an annual standard of 15 µg/m^3 and a 24-hour standard of 65 µg/m^3. In 2006, they tightened the 24-hour standard to 35 µg/m^3, and in 2012, they tightened the annual standard to 12 µg/m^3.

The District adopted the 2008 PM2.5 Plan to address the 1997 PM2.5 standards. U.S. EPA approved the 2008 PM2.5 Plan in 2011 (76 FR 41338; 76 FR 69896). As previously mentioned, meteorological conditions associated with the current drought resulted in elevated PM2.5 levels in the Valley during the winter of 2013/2014 that affected annual and 24-hour PM2.5 concentrations. As a result, the SJV will not meet the attainment deadline in the 2008 PM2.5 Plan. In March 2015, U.S. EPA reclassified the SJV as a serious nonattainment area with a December 31, 2015 attainment deadline (80 FR 1482) and required a new SIP to address the 1997 PM2.5 standards.

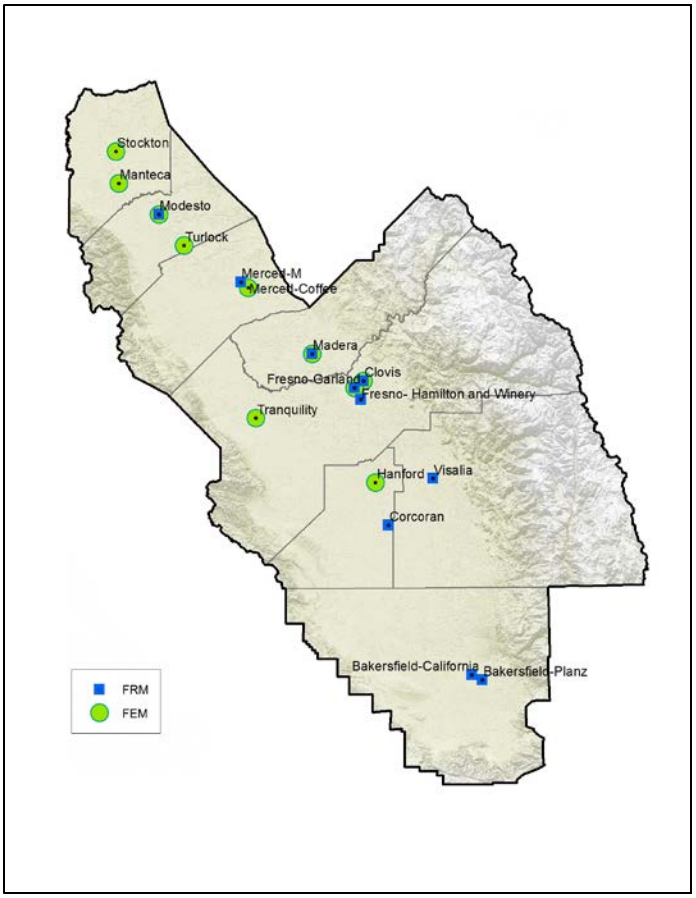
The District also adopted the 2012 PM2.5 Plan addressing the 35 µg/m^3 24-hour standard. U.S. EPA recently proposed approval of this SIP as meeting moderate area requirements. The SIP for the 12 µg/m^3 annual PM2.5 standard is due to U.S. EPA in 2016.

3. MONITORING IN THE SAN JOAQUIN VALLEY

a. Established monitoring network

An extensive network of PM2.5 monitors throughout the SJV provides data to assess compliance with ambient air quality standards and to study the nature of ambient PM2.5. Many sites include multiple monitoring instruments running in parallel. Currently ten sites operate Federal Reference Monitors (FRMs), which provide regulatory data that are used to assess compliance with the federal PM2.5 standards. Additional monitors provide hourly PM2.5 measurements, a subset of which (ten) are Federal Equivalent Monitors (FEM), which can also be used to assess compliance with the standards. The FRM and FEM monitoring sites are shown in Figure 1. The locations of these monitors are designed to capture population exposure. In addition, data collected at these monitors serve to report air quality conditions to the public, and support forecasting for the District’s agricultural and residential burning curtailment programs. Finally, four sites have chemical speciation monitors. The speciation monitors collect samples that are further analyzed in the laboratory to determine the chemical make-up of PM2.5.

Figure 1. San Joaquin Valley PM2.5 monitoring network (FRMs and FEMs).



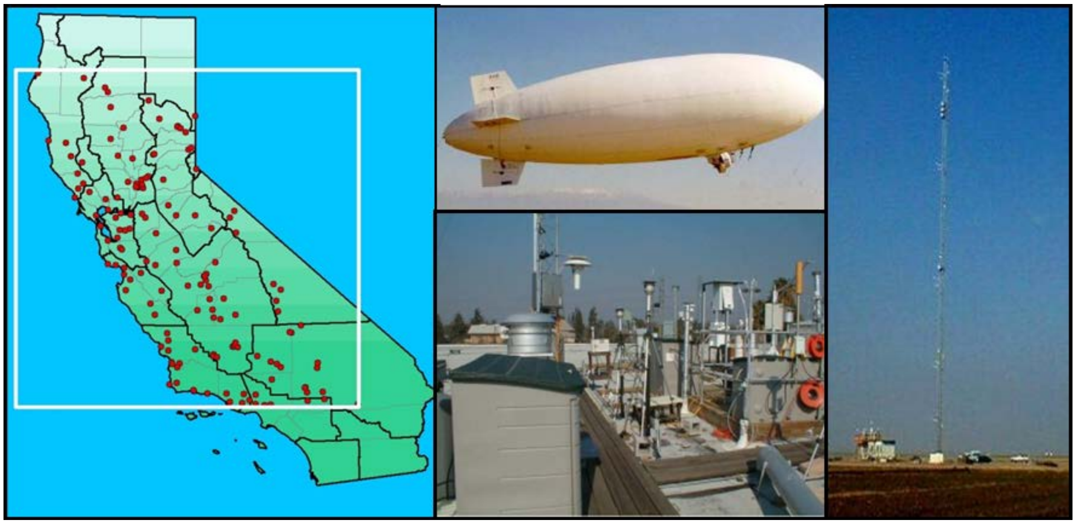
b. Extensive field studies

The San Joaquin Valley is one of the most studied areas in the world with an extensive number of publications in peer-reviewed international scientific/technical journals and other major reports. Since 1970, close to 20 major field studies have been conducted in the Valley and surrounding areas that have elucidated various aspects of the nature and causes of ozone and particulate matter. A comprehensive listing of publications (reports and peer-reviewed journal articles) is provided in Appendix A1.

The first major study specifically focused on particulate matter was the Integrated Monitoring Study in 1995 (IMS-95), which was the pilot study for the subsequent California Regional Particulate Air Quality Study (CRPAQS) in 2000 (Solomon and Magliano, 1998). IMS-95 formed the technical basis for the SJV 2003 PM10 Plan that was approved by the U.S. EPA in 2004 (71 FR 63642), and the Valley was subsequently re-designated as attainment in 2008 (73 FR 66759). CRPAQS was a key component of the technical foundation for the SJV 2008 PM2.5 Plan that U.S. EPA approved in 2011 (76 FR 41338; 76 FR 69896). CRPAQS findings remain relevant to the development of the current PM2.5 Plan.

CRPAQS was a public/private partnership designed to advance the understanding of the nature of PM2.5 in the Valley and guide development of effective control strategies. The study included monitoring at over 100 sites (Figure 2) as well as data analysis and modeling, results of which have been published in over 60 papers and presented at national and international conferences. The field campaign was carried out between December 1999 and February 2001. CRPAQS improved our understanding of the spatial and temporal distribution of PM2.5 in the Valley, its chemical composition, transport and transformation processes, and contributing sources. More details on CRPAQS can be found at the following link: http://www.arb.ca.gov/airways/ccaqs.htm.

Figure 2. CRPAQS monitoring program.



Findings from CRPAQS and other studies have been integrated into the conceptual model of PM2.5 in the San Joaquin Valley. The conceptual model provides the scientific foundation for the WOE analysis supporting the annual and 24-hour PM2.5 standards attainment demonstration. Specific findings are integrated into the various WOE analysis sections of this document.

Further field studies relevant to PM2.5 include the California portion of the Arctic Research of the Composition of the Troposphere (ARCTAS-CARB) which took place in 2008 (Jacob, et al., 2010), and Research at the Nexus of Air Quality and Climate (CalNex2010) conducted in 2010 (www.esrl.noaa.gov/csd/calnex/). The monitoring operations for both studies occurred during the early to mid-summer and extended over Southern California and the Central Valley. A synthesis of policy relevant findings has been published (http://www.esrl.noaa.gov/csd/projects/calnex/synthesisreport.pdf) . Another PM2.5 relevant field study, the San Joaquin Valley portion of the Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) was conducted from mid-January through mid-February 2013 (http://www-air.larc.nasa.gov/missions/discover-aq/discover-aq.html). Data analysis is currently in progress.

4. NATURE AND EXTENT OF THE PM2.5 PROBLEM

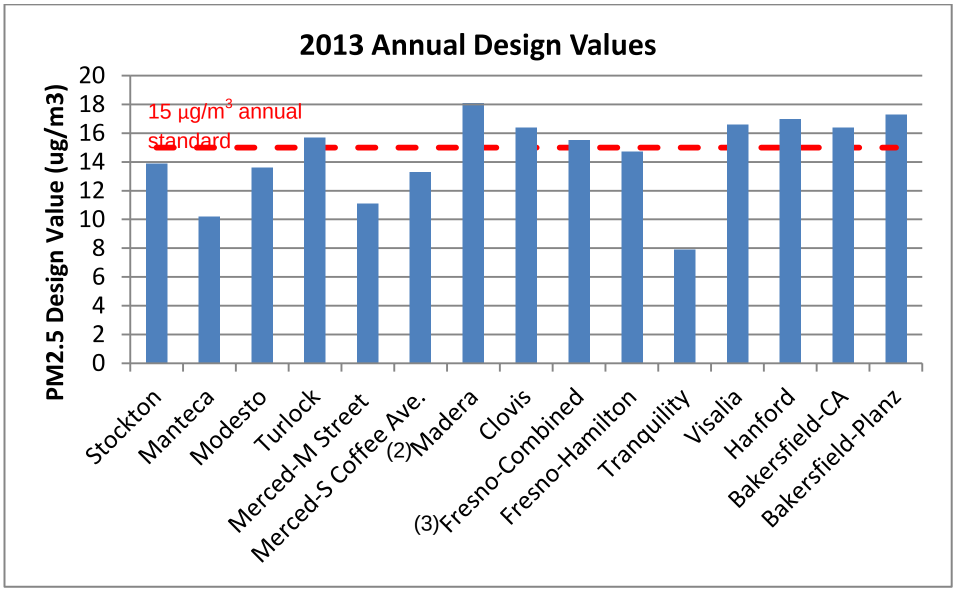
a. Current air quality

The geography of the San Joaquin Valley, along with large-scale regional and local weather patterns, influence the accumulation, formation and, dispersion of air pollutants. Covering nearly 25,000 square miles, the Valley is a lowland area bordered by the Sierra Nevada Mountains to the east, the Pacific Coast range to the west, and the Tehachapi Mountains to the south. The mountains act as air flow barriers, with the resulting stagnant conditions favoring the accumulation of pollutants. To the north, the Valley borders the Sacramento Valley and Delta lowland, which allows for some level of pollutant dispersion. As a result of geography and meteorology, PM2.5 concentrations are generally higher in the southern and central portions of the Valley.

To determine attainment for the annual PM2.5 standards, the corresponding design value at each monitoring site must be calculated following U.S. EPA protocols. The annual design value represents a three year average of the annual average PM2.5 concentrations measured at the site. If the annual design value is equal to or below 15.0 $\mu g/m^3$, the site attains the standard. Meteorological conditions related to the prevalent drought lead to elevated PM2.5 concentrations in the SJV during the 2013/2014 winter. These elevated wintertime concentrations affected both 24-hour and annual average concentrations.

Figure 3 shows the 2013 annual PM2.5 design values throughout the San Joaquin Valley(1). Although meteorological conditions associated with the drought lead to higher annual PM2.5 concentrations in 2013, seven sites remain below the standard. Sites above the standard are focused in the central and southern Valley(2).

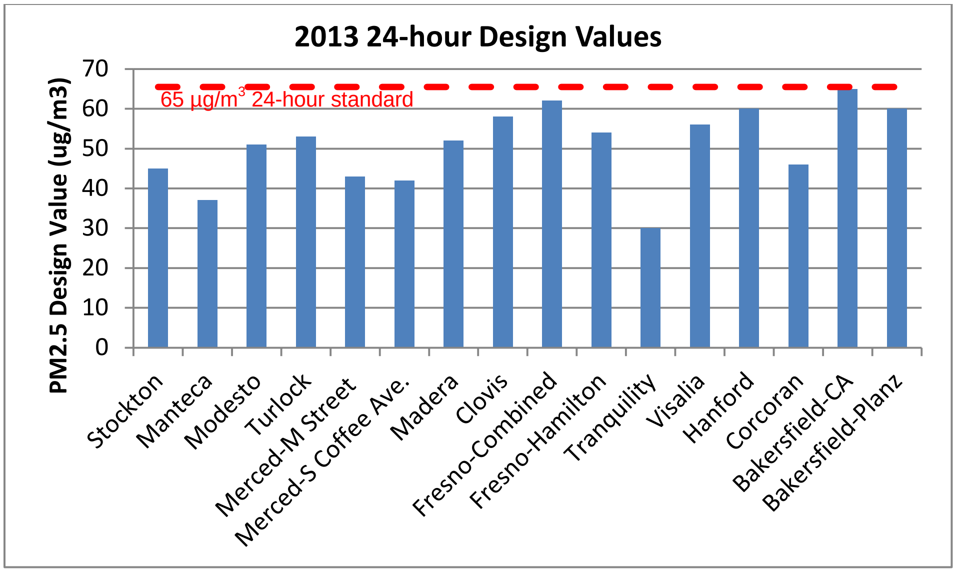
Figure 3. 2013 annual PM2.5 design values



(1) Comparisons of PM2.5 concentrations recorded at collocated or closely located FRM and FEM monitors have shown that FEM monitors record higher concentrations (e.g. the monitors in Merced).
(2) The representativeness of the Madera design value is further discussed in Appendix A2.
(3) Fresno Combined includes partial data from the old Fresno 1st and new Fresno-Garland sites.

The 24-hour PM2.5 design value represents a three-year average of the 98th percentile of the measured PM2.5 concentrations. Depending on a site's 24-hour PM2.5 data collection schedule, the 98th percentile usually corresponds to a value between the 2nd and the 8th highest value. If the design value is equal to or below 65 µg/m^3, the site attains the standard. Based on 2013 24-hour design values, all sites in the Valley attain the standard (Figure 4).

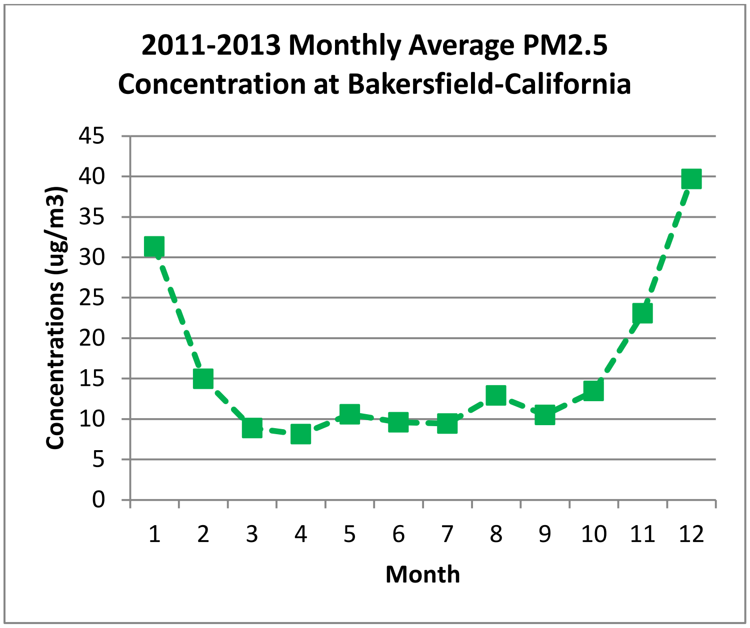
Figure 4. 2013 24-hour PM2.5 design values



b. Seasonal variability

PM2.5 concentrations in the San Joaquin Valley exhibit a strong seasonal pattern, with highest concentrations occurring from November through February (Figure 5). During the winter, PM2.5 builds up over several days or weeks. These PM2.5 episodes are caused by increased activity in some emission sources and by meteorological conditions that are conducive to the build-up and formation of PM2.5. During the winter, high-pressure weather systems over California can cause the atmosphere to become stagnant for extended periods leading to temperature inversions. Under normal conditions, temperature decreases with altitude, allowing free upward air flow dispersing emissions and pollutants. In contrast, a temperature inversion positions a layer of warmer air above cooler air, impeding upward flow of emissions and air pollutants. Often the inversion layer is lower than the mountains surrounding the Valley, trapping emissions and pollutants in the Valley. Winter month PM2.5 concentrations drive the annual average concentrations.

Figure 5. Seasonal variation in PM2.5 concentration at Bakersfield-California.



c. Chemical composition

Examination of the chemical make-up of PM2.5 provides another important element in understanding the nature of PM2.5 in the Valley and specifically identifying contributing sources. The pie charts in Figure 6 show the current chemical components that contribute to PM2.5 levels on an annual average basis at urban sites in the southern (Bakersfield), central (Fresno), and northern (Modesto) regions of the Valley. Figure 7 shows the chemical components contributing to peak day PM2.5 levels at the same sites. While the relative percentages vary, in all cases the major components are ammonium nitrate and organic material (organic carbon).

Ammonium nitrate is the largest contributor to PM2.5 levels, constituting about 40 percent of annual PM2.5 levels at the three sites. On peak PM2.5 days, the ammonium nitrate contribution is higher, approximately 50 to 65 percent. Ammonium nitrate is formed in the atmosphere from chemical reactions of NOx and ammonia. Sources emitting NOx include motor vehicles and stationary combustion sources. The largest sources of ammonia are livestock operations and fertilizer application. The stagnant, cold, and damp conditions that occur during the winter promote the formation and accumulation of ammonium nitrate. Additional information on ammonium nitrate formation can be found in section 5.

The organic matter component contributor of PM2.5 levels is largest in the central and northern portions of the Valley. On an annual and peak day basis, organic matter constitutes about 30 percent of PM2.5 at Modesto and Fresno compared to less than about 20 percent at Bakersfield. Activities such as residential wood combustion, cooking, biomass burning, and direct tailpipe emissions from mobile sources contribute to the PM2.5 level organic matter component.

Ammonium sulfate contributes approximately ten percent of annual PM2.5 levels at each of the three sites. On peak days, the ammonium sulfate contribution is lower, about five percent. Ammonium sulfate is also formed in the atmosphere from SOx emitted from combustion sources and ammonia from sources like livestock operations and fertilizer application.

Geological material or dust contributes approximately 15 percent to the annual PM2.5 levels at Bakersfield, while at Fresno and Modesto it contributes about 5 percent. The geological material contribution to peak day PM2.5 levels is less than half of the contribution to annual PM2.5 levels. Geological material is directly emitted PM2.5 and comes from dust suspended into the air by vehicle travel on roads, soil from agricultural activities, and other dust producing activities such as construction.

Elemental carbon contributes less than five percent to the annual as well as the peak day PM2.5 levels at the three sites. Elemental carbon is directly emitted PM2.5 and comes from mobile and stationary combustion sources, with significant contributions from diesel sources.

Figure 6. Three-year annual average PM2.5 chemical composition

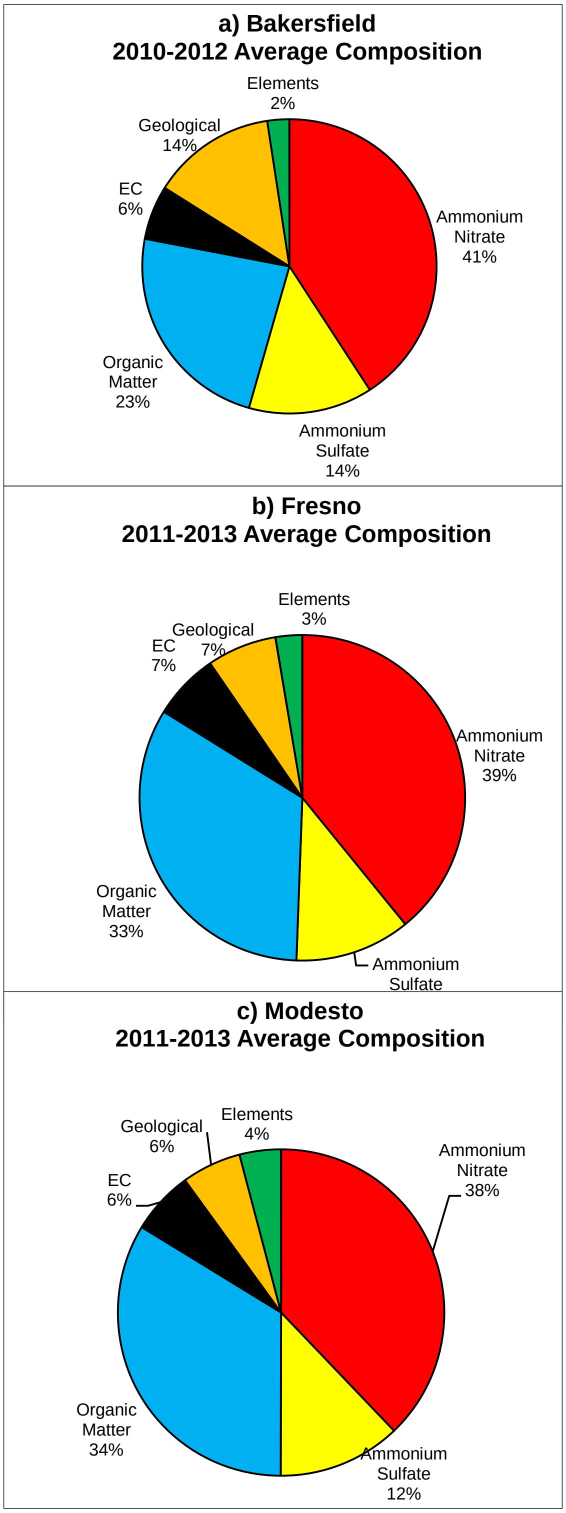
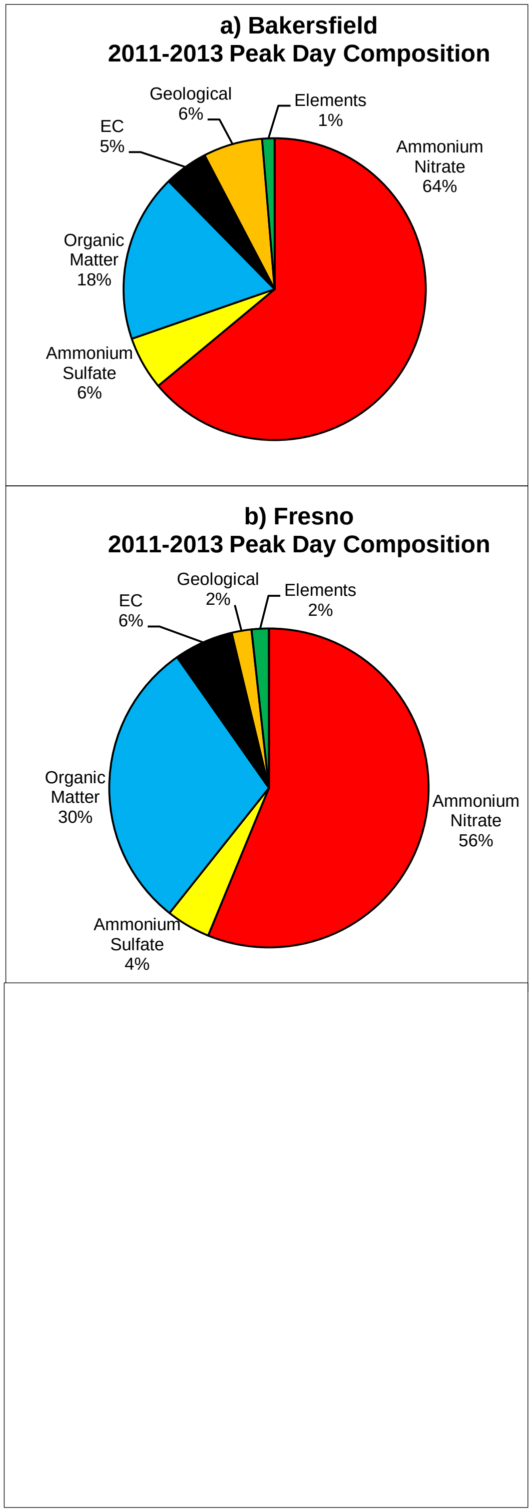


Figure 7. Three-year average high day PM2.5 chemical composition



5. SECONDARY AMMONIUM NITRATE FORMATION

a. Chemistry

As discussed previously, the cooler temperatures and higher humidity of the winter months are conducive to ammonium nitrate formation through a complex process involving NOx, ammonia, and VOCs. This occurs both at the surface and aloft, via both daytime and nighttime chemistry. Understanding the interactions amongst these precursors is needed to design an appropriate and effective approach to reduce ammonium nitrate.

During the day, NO_2 is oxidized to nitric acid (HNO_3). This daytime pathway also involves sunlight, VOCs, and background ozone:

$$NO \xrightarrow{O_3} NO_2 \xrightarrow{OH} HNO_3$$

Main oxidant is OH
Requires high sunlight, VOC rich environment

During the night, nitric acid is formed through oxidation of NO_2 (via N_2O_5) by background ozone:

$$\begin{tikzcd} NO \arrow[r, "O_3"] & NO_2 \arrow[r, "O_3"] \arrow[rr, bend right] & NO_3 \arrow[r] & N_2O_5 \arrow[r, "H_2O"] & 2\,HNO_3 \end{tikzcd}$$

Main Oxidant is Ozone (O_3)
Favors low sunlight intensity,
wet conditions

The nitric acid formed from these reactions then combines with ammonia (NH_3) to form ammonium nitrate (NH_4NO_3):

$$HNO_3 + NH_3 \longleftrightarrow NH_4NO_3$$

Since the chemistry of NOx to nitric acid formation involves multiple steps and also depends on the availability of oxidants, only a portion of the NOx emitted ultimately forms ammonium nitrate. An early photochemical modeling study applying a box model to a typical winter episode in the San Joaquin Valley found that approximately 33 percent of the molecules of emitted NOx were converted to ammonium nitrate (Stockwell et. al. 2000). A subsequent study that modeled the January 4-6, 1996 episode in the San Joaquin Valley with the University California Davis/California Institute of Technology (UCD-CIT) photochemical transport model found that on average, only 13 to 18 percent of the emitted NOx (expressed as NO_2) was converted to ammonium nitrate (Kleeman et. al. 2005). The fraction of NOx converted varied by location, with urban regions converting little NOx to ammonium nitrate, while in remote areas up to 70 percent NOx was converted.

NOx emissions mostly originate from urban traffic and transportation corridors, while ammonia is primarily generated from livestock operations and fertilizer applications.

Analysis of CRPAQS measurements suggest that, on average, daytime production of nitric acid in the San Joaquin Valley is relatively slow, and that nighttime production is the more dominant pathway (Lurmann et al. 2006). Although daytime mixing is limited, NOx and ammonia emitted during the day can be mixed upward where nighttime interactions can occur more regionally to form ammonium nitrate. Based on analyses conducted to characterize the atmospheric transport and dispersion processes during the winter CRPAQS episodes, MacDonald et al. (2006) found that the ammonium nitrate that is formed aloft during the night is subsequently entrained into the daytime boundary layer. This was observed through a rapid rise in hourly ammonium nitrate concentrations which coincided with the growth of the surface mixed layer (Watson and Chow 2002). These mechanisms help explain the more regional distribution of ammonium nitrate that is observed throughout the Valley.

b. Limiting precursor concept

The amount of ammonium nitrate produced will depend on the relative atmospheric abundance of its precursors – VOCs, NOx, and ammonia (NH_3). It is therefore important to understand which precursor controls are most effective in reducing ammonium nitrate concentrations. In simple terms, the precursor in shortest supply will limit how much ammonium nitrate is produced. This is known as the “limiting” precursor. The following figures provide an illustration of this concept. As shown in Figure 8, each molecule of ammonia pairs with one NOx molecule to produce one molecule of ammonium nitrate. In this example, there are more ammonia molecules than NOx, and therefore not all of the ammonia participates in forming ammonium nitrate, i.e. there is “excess” ammonia. Figure 9 illustrates the impact of reducing NOx. Here, a reduction in NOx, the less abundant precursor, leads to a commensurate reduction in ammonium nitrate. In contrast, Figure 10 illustrates that a larger reduction in the more abundant precursor, ammonia, results in no reduction in ammonium nitrate, as the ammonia reduced did not participate in ammonium nitrate production.

Figure 8. Ammonium nitrate formation.

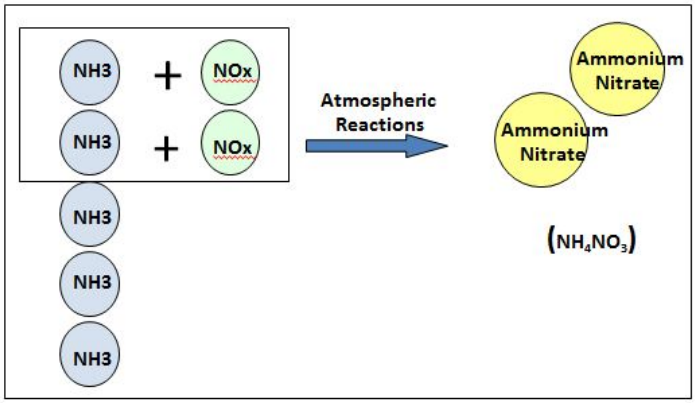


Figure 9. Reducing the less abundant precursor is more effective in reducing ammonium nitrate.

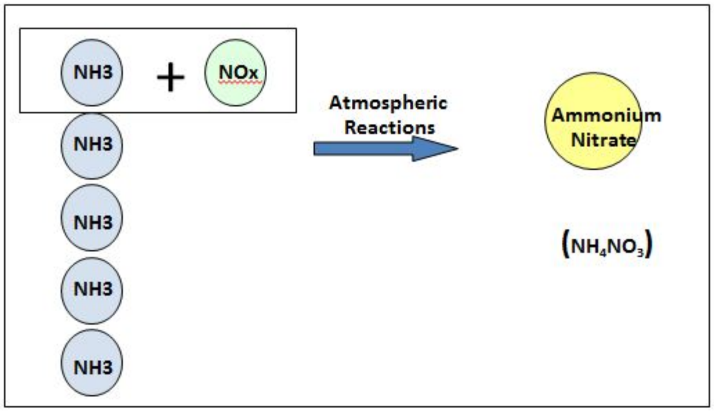
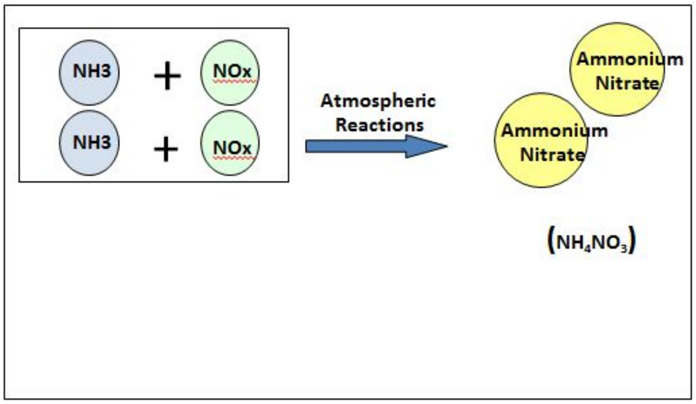


Figure 10. Reducing the more abundant precursor is less effective in reducing ammonium nitrate.



The following sections describe the current state of the science regarding the role of ammonia, VOCs, and NOx in ammonium nitrate formation and identify the most effective precursors for control.

c. Role of ammonia in ammonium nitrate formation

A number of different studies and analyses were evaluated to understand the role of ammonia in ammonium nitrate formation in the San Joaquin Valley. These included: a) comparison of the magnitude of the NOx and ammonia emissions inventories, b) ambient measurements of ammonia, nitric acid, and particulate ammonium; and c) photochemical modeling analyses of ammonium nitrate sensitivity to precursor emission reductions. While evaluation of emissions inventory and ambient data can provide indications of the relative abundance of different precursors, photochemical models provide a tool to quantitatively evaluate the impact of reducing precursor emissions on resulting ammonium nitrate concentrations.

Emission inventory

As discussed in the limiting precursor section, the precursor in shortest supply limits the amount of ammonium nitrate formation. An evaluation of the magnitude of NOx and ammonia emissions provides a first level assessment of the relative abundance of these two precursors. Table 1 lists NOx and ammonia winter and annual average emissions in the current inventory for two years (2012 and 2020). As Figure 1 in the limiting precursor section illustrated, in simple terms it takes one molecule of NOx and one molecule of ammonia to form one molecule of ammonium nitrate. However, due to differing molecular weights, one ton of NOx contains fewer molecules than one ton of ammonia. Therefore it is most appropriate to make an emissions inventory comparison after normalizing for molecular weight.

Due to emission source test procedures, most NOx emissions are expressed in terms of nitrogen dioxide (NO_2). Since one NO_2 molecule weighs 46 universal atomic units (u) and one NH_3 molecule weighs 17 u, one ton of NH_3 has 2.7 times (46 u/17 u) the number of molecules as one ton of NO_2. Dividing the NOx emissions by 2.7 therefore provides a common basis for comparison to the ammonia emissions. On this normalized comparison basis, ammonia is significantly more abundant than NOx, particularly in the future year (Table 1). In addition, as noted in the chemistry section, only a portion on the NOx is ultimately converted to ammonium nitrate.

Table 1. Comparison of NOx and ammonia emissions in selected years a) during the winter and b) on an annual average basis.

a)

Year	**Winter NH_3 emissions (tpd)**	**Winter NOx emissions (tpd)**	**Normalized NOx emissions (tpd)**
2012	310	318	118
2020	339	198	73

b)

	Annual NH_3 emissions (tpd)	**Annual NOx emissions (tpd)**	**Normalized NOx emissions (tpd)**
2012	330	332	123
2020	358	207	77

Monitoring studies

Ambient measurements of precursor concentrations provide another method to investigate the relative abundance of each precursor and therefore which is most effective for control of ammonium nitrate. Blanchard, et al. (2000) examined two metrics using ambient data collected during the IMS-95 field program in the San Joaquin Valley. The first parameter was the excess of particulate ammonium plus gas-phase ammonia over the sum of nitric acid, particulate nitrate, and particulate sulfate. The second was the ratio of particulate to total nitrate concentrations. Both metrics indicated an excess of ammonia in most IMS-95 samples and concluded that greater reductions in aerosol nitrate would occur when nitric acid was reduced rather than ammonia.

Lurmann, et al. (2006) also compared ammonia and nitric acid ambient concentrations measured in the San Joaquin Valley during the winter of 2000/2001 as part of CRPAQS. Figures 11 and 12 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 rather than ammonia is the limiting precursor.

Figure 11. Comparison of ammonia and nitric acid concentrations measured at Angiola during the winter of 2000/2001 as part of CRPAQS.

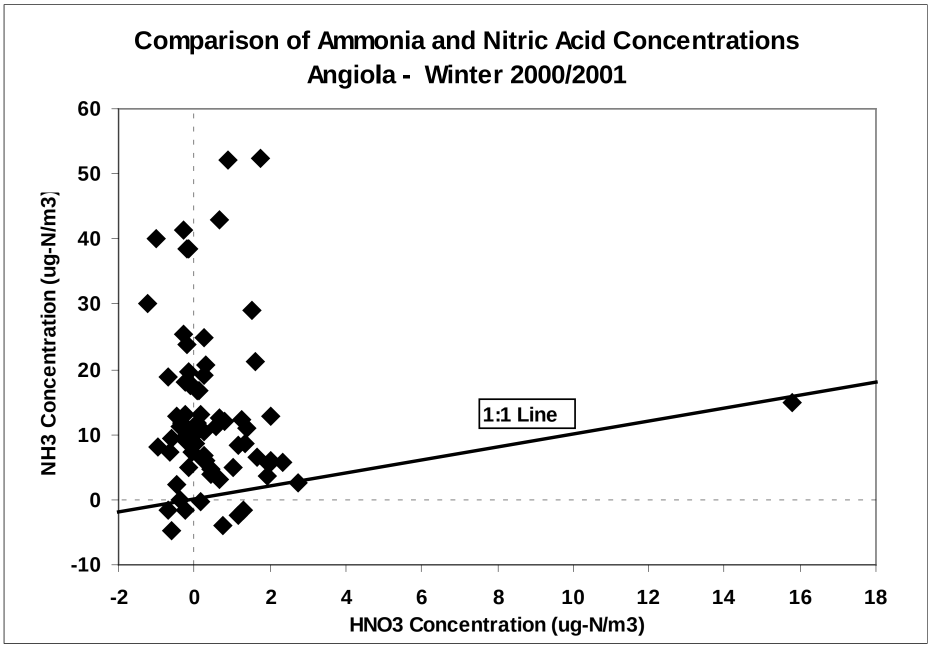
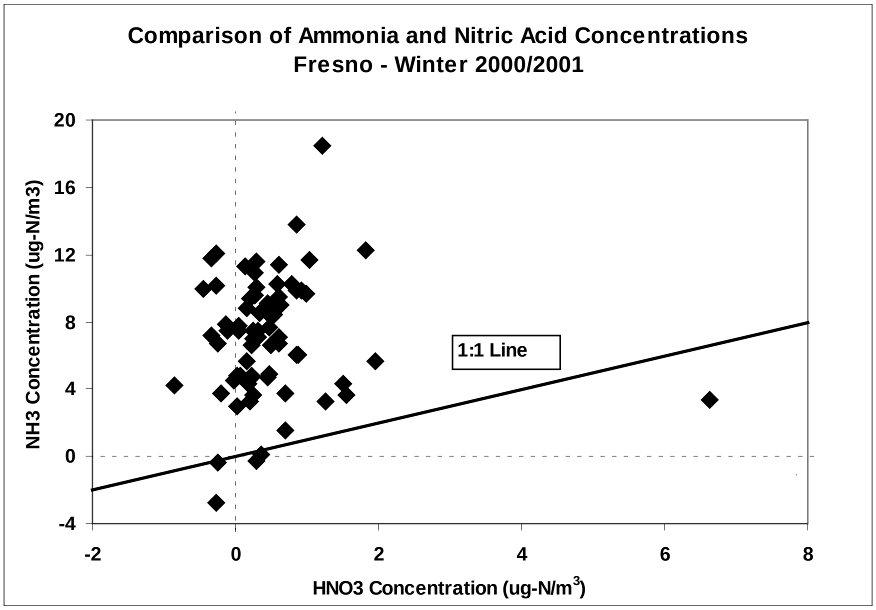
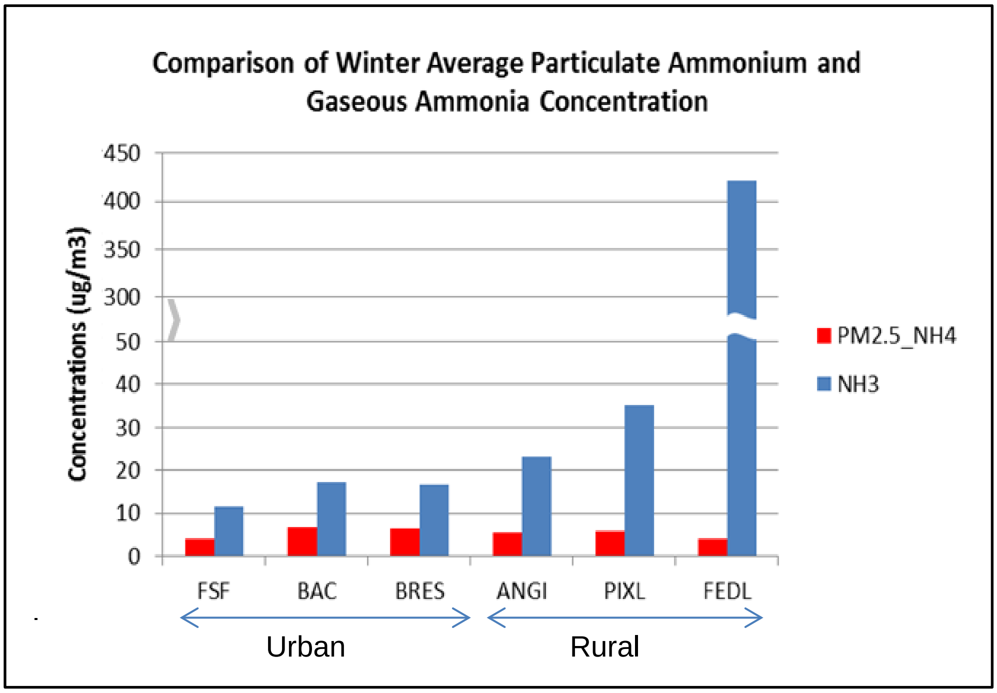


Figure 12. Comparison of ammonia and nitric acid concentrations measured at Fresno during the winter of 2000/2001 as part of CRPAQS.



The amount of gaseous ammonia (NH3) compared to particulate ammonium (NH4) provides another indicator of how much of the ammonia is converted to ammonium nitrate and therefore whether there is excess ammonia available. These measurements were collected at a larger number of sites during CRPAQS. Figure 13 shows the concentrations of particulate ammonium and gaseous ammonia at three urban sites (Fresno-1st, Bakersfield-California, and Bakersfield-residential), and three rural sites (Angiola, Pixley, and Feedlot) measured during the 2000/2001 winter CRPAQS episode. Overall, the levels of particulate ammonium at all sites are comparable, consistent with a regional formation mechanism of ammonium nitrate. Although ammonia concentrations are higher at the rural sites, especially at the Feedlot site, there is still a large amount of ammonia at each site beyond the amount that reacted with nitric acid to form ammonium nitrate. Again, these ammonia rich conditions indicate that nitric acid, rather than ammonia is the limiting precursor.

Figure 13. Comparison of particulate ammonium and gaseous ammonia concentrations measured throughout the SJV during the winter of 2000/2001 as part of CRPAQS.

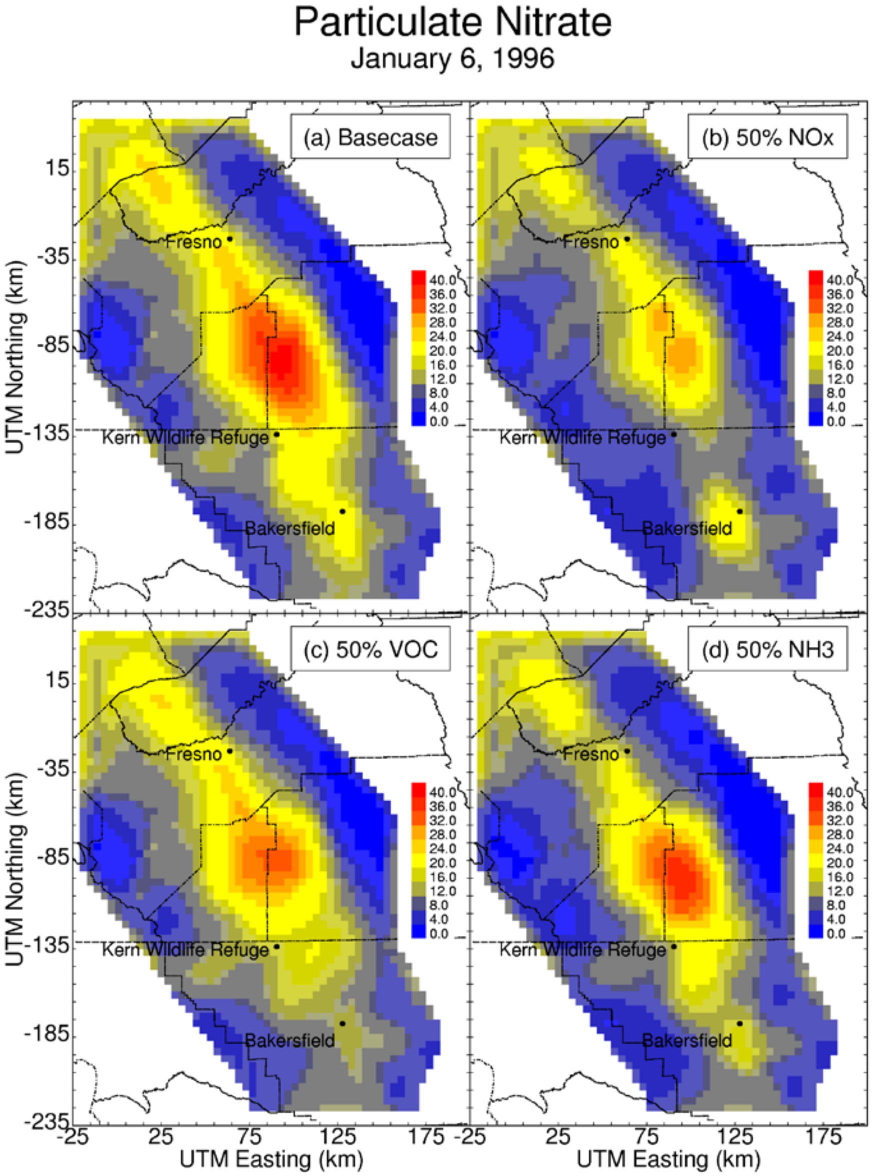


Photochemical modeling

In contrast to the previous analyses, photochemical models provide a quantitative approach to simulate the effects that emission reductions in each of the gaseous precursors would have on the predicted ammonium nitrate concentrations. A number of modeling studies have been conducted by ARB staff and academic researchers to evaluate precursor sensitivity.

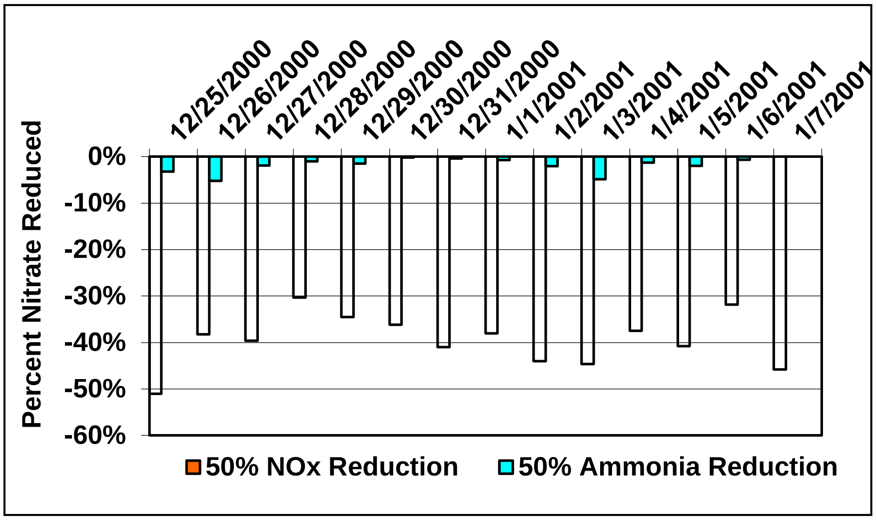
An investigation of precursor limitations for the January 4-6, 1996 PM2.5 episode measured in San Joaquin Valley as part of the IMS-95 field study used the UCD-CIT model. This sensitivity analysis revealed that NOx controls were the most effective control strategy to reduce PM2.5 ammonium nitrate concentrations (Kleeman, et al. 2005). In this study, a 50 percent reduction in NOx emissions resulted in a 25 percent reduction in total nitrate, while a 50 percent reduction in ammonia emissions resulted in a 10 percent reduction in total nitrate. The results of this analysis are shown graphically across the entire San Joaquin Valley in Figure 14.

Figure 14. Particulate nitrate reductions in response to 50 percent reductions in precursor emissions on January 6, 1996.



In 2006, ARB staff modeled air quality during the three week winter CRPAQS episode using U.S. EPA’s Community Multiscale Air Quality (CMAQ) model with California-specific modifications and corrections (Liang et al. 2006). Figure 15 illustrates the effects that reducing the emissions of ammonia and NOx have on ammonium nitrate levels. This modeling indicated that reducing ammonia emissions by 50 percent reduced ammonium nitrate by less than 5 percent. On the other hand, reducing NOx emission by 50 percent reduced ammonium nitrate concentrations by approximately 35 percent. This analysis, therefore, indicated that reducing NOx emissions was the most beneficial control strategy to reduce ammonium nitrate.

Figure 15. Percent ammonium nitrate reduction in response to 50 percent reduction in NOx or ammonia emission reductions at Fresno during the winter of 2000/2001.



In another study based on sensitivity analyses using CMAQ-Madrid simulations of the December 2000 CRPAQS episode, Pun et al. (2009) found that a 50 percent reduction in NOx emissions reduced ammonium nitrate by approximately 50 percent at rural sites and between 30-45 percent at Bakersfield. As shown in Figure 16, a 50 percent reduction in ammonia emissions did not have a significant effect on ammonium nitrate concentrations at urban sites. At the rural site of Angiola, ammonium nitrate concentrations decreased between 10 and 25 percent. However, such reductions in ammonium nitrate occurred only towards the end of the episode, when PM2.5 concentrations at the rural site measured approximately 80 µg/m3 and concentrations at the urban site recorded over 110 µg/m3 (Figure 9). At the end of the episode, PM2.5 concentrations at Bakersfield peaked at 155 µg/m3 (January 5, 2001). For the most part, the San Joaquin Valley does not currently reach those PM2.5 concentration levels. Figure 17 shows a comparison of PM2.5 concentrations during the CRPAQS and the 2013/2014 PM2.5 episodes from November 1 through February 5 when the highest PM2.5 concentrations were recorded in the last 10 years. In addition, Pun et al. noted that under wintertime conditions, nitric acid concentrations in the SJV were small and therefore ammonium nitrate formation was generally limited by the availability of nitric acid rather than ammonia.

Figure 16. Time series with daily observations, base case simulation results and results from the sensitivity cases of (a) nitrate and (b) PM2.5 at Angiola (left) and Bakersfield (right). (Source: Pun et al., 2009, excerpt from Figure 2, pg. 406).

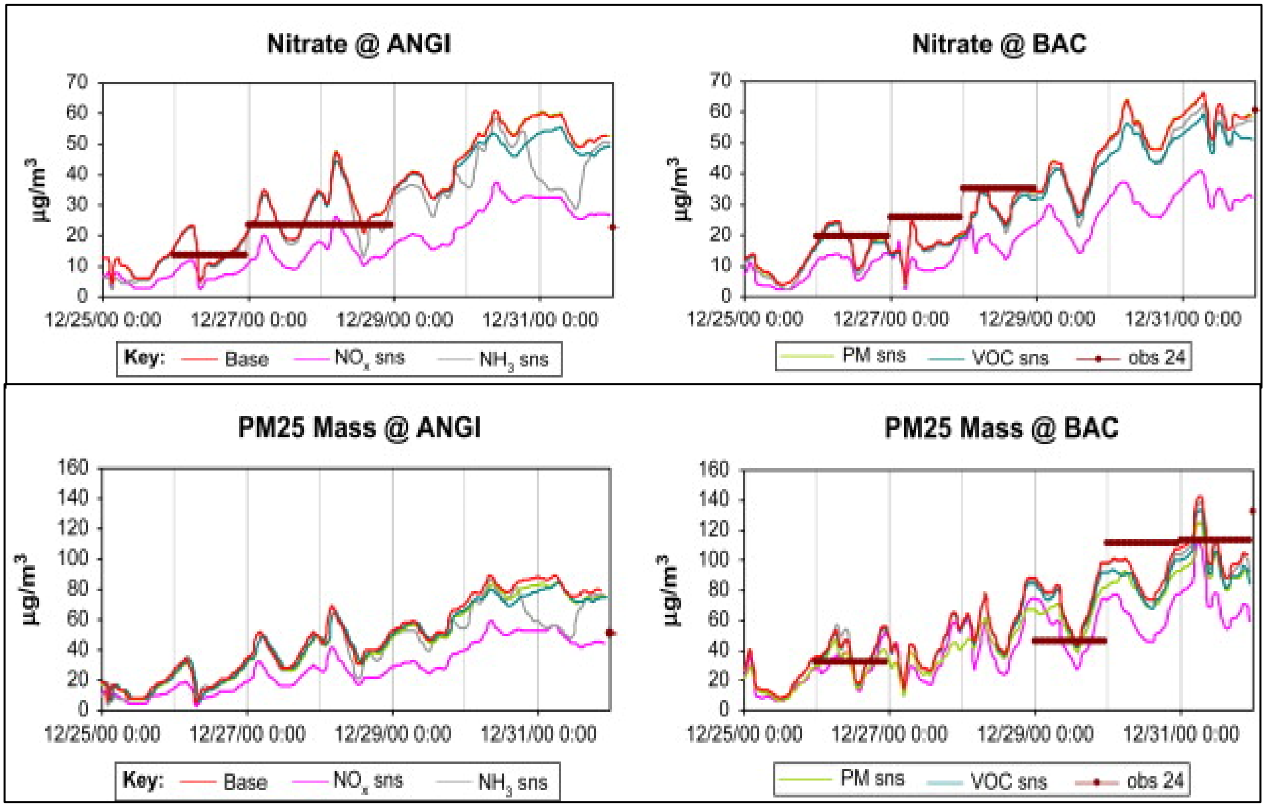
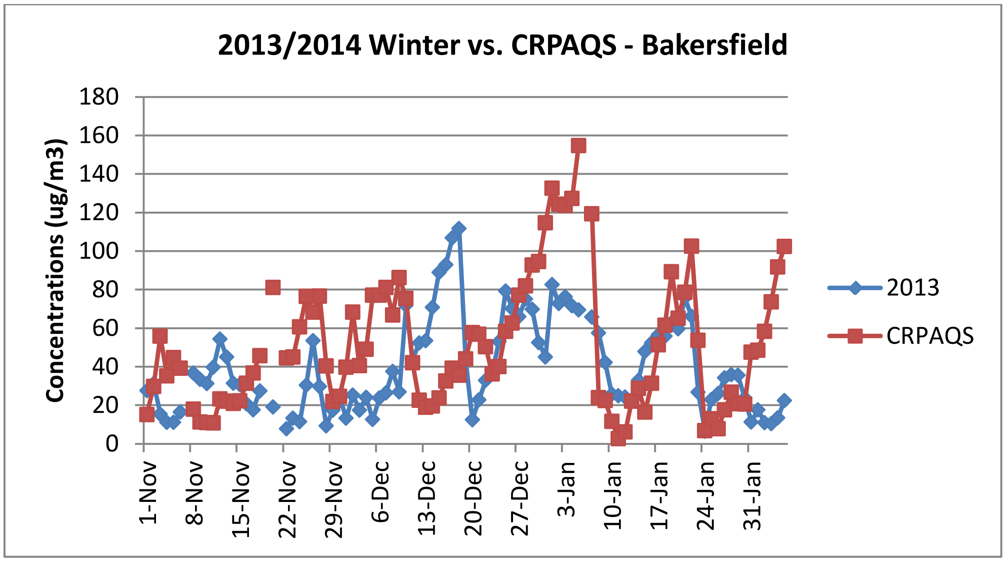


Figure 17. Comparison of PM2.5 concentrations at Bakersfield during the 2000/2001 CRPAQS winter episode and the winters of 2013/2014.



In 2012, as part of the emission control strategy development for the San Joaquin Valley PM2.5 Plan for the federal 35 µg/m^3 24-hour standard, ARB staff conducted modeling using CMAQ to simulate the response of PM2.5 concentrations to reductions in PM2.5 precursors in 2019 throughout the Valley (SJV 2012 PM2.5 Plan; Chen, et al. 2014). Simulations were run during the first and fourth quarters (January–March and October-December) of 2019. In the San Joaquin Valley, high PM2.5 values in the first and fourth quarters drive the annual average concentrations to be over the annual PM2.5 standard.

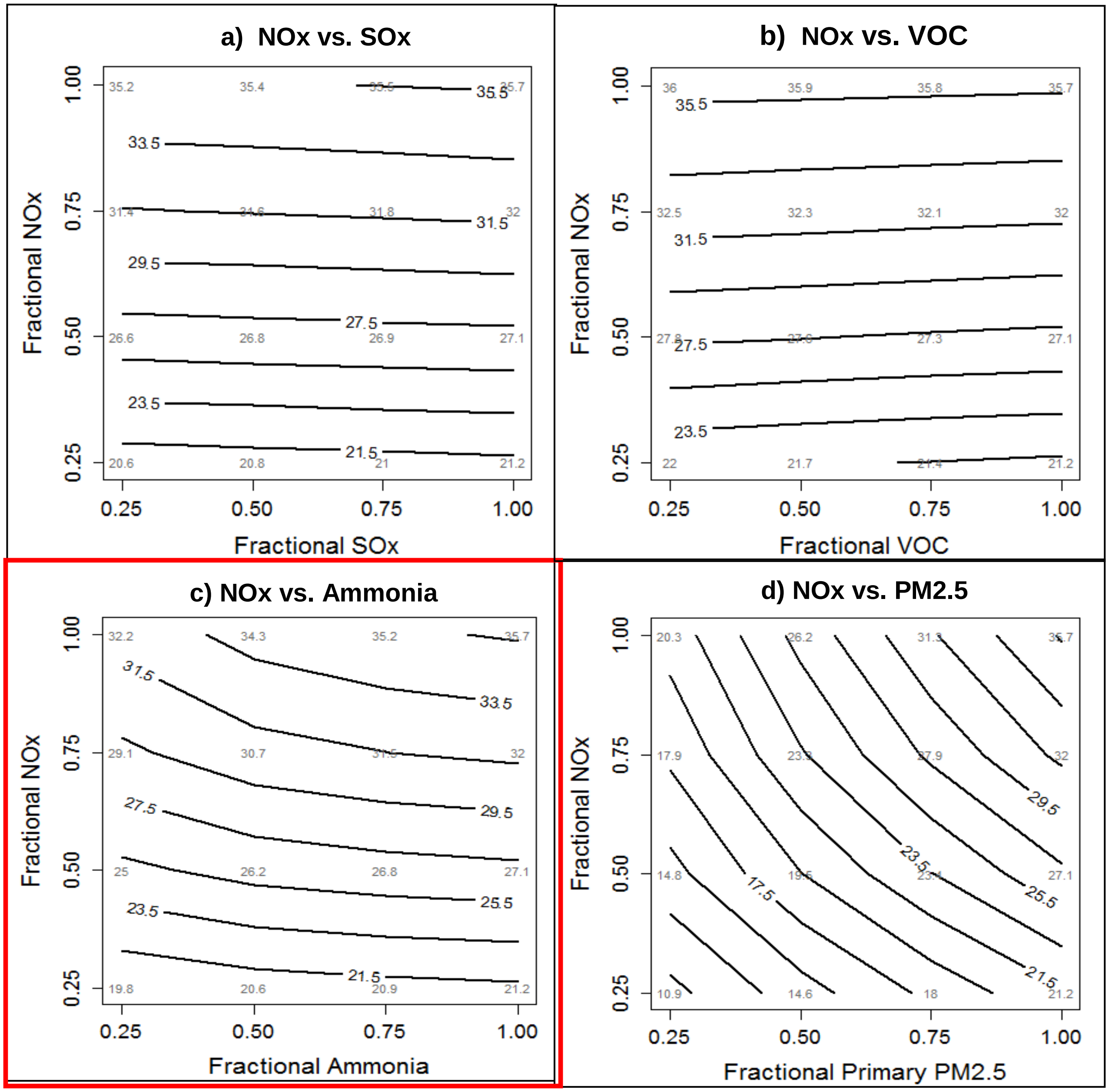
Per the analysis above, Table 2 compares the modeled effect on the 2019 24-hour PM2.5 design value obtained at each monitoring site from a 25 percent reduction in the specified precursor. The information is normalized to reflect the reduction in design value per ton of each precursor reduced. Consistently, direct PM2.5 reductions have the most benefit, followed by NOx reductions. Reductions in ammonia and SOx provide much smaller benefits. While on an annual average basis, SOx emission reductions are quite effective in reducing PM2.5 concentrations, during the winter they are less effective since ammonium sulfate is more prevalent during the non-winter months. Reductions in VOCs result in small disbenefits at most sites. On a relative basis, Valley-wide reductions in ammonia are approximately nine times less effective than NOx and over 35 times less effective than PM2.5.

Table 2. Modeled PM2.5 air quality benefit per ton of valley-wide precursor emission reductions.

Monitoring Site	**Reduction in 2019 PM2.5 Design Value (µg/m^3 per ton reduction)**				
	PM2.5	**NOx**	**NH_3**	**SOx**	**VOC**
Bakersfield-California	0.34	0.08	0.008	0.08	-0.001
Bakersfield-Planz	0.29	0.08	0.009	0.08	-0.001
Visalia	0.27	0.07	0.005	0.04	-0.001
Corcoran	0.25	0.09	0.010	0.04	-0.003
Fresno-1st	0.31	0.06	0.008	0.04	0.000
Fresno-Hamilton	0.28	0.06	0.007	0.05	0.001
Clovis	0.25	0.07	0.008	0.04	0.000
Modesto	0.19	0.04	0.006	0.08	0.000
Merced	0.19	0.05	0.005	0.05	0.000
Stockton	0.14	0.03	0.007	0.09	0.000

Figure 18 shows the results of modeling sensitivity runs plotted on isopleth diagrams for Bakersfield-California site for all precursors relative to NOx. These diagrams reflect the change in the 2019 24-hour PM2.5 design value relative to reduction in precursor emissions. The diagrams illustrate that because ammonia emission are much more abundant than NOx emission, the atmosphere is more responsive to reductions in NOx emissions as compared to ammonia. Controlling NOx emissions in turn have significant benefits at reducing PM2.5 levels as ammonium nitrate is a large component.

Figure 18. Bakersfield–California Isopleth Diagrams



a) NOx vs. SOx

b) NOx vs. VOC

c) NOx vs. Ammonia

d) NOx vs. PM2.5

Chen et al. (2014) reported that in the San Joaquin Valley, 2019 24-hour PM2.5 design values showed strong responses to emission reductions in directly emitted PM2.5 and NOx. At Bakersfield-California, a 50 percent reduction in PM2.5 emissions and NOx emissions decreased the 2019 24-hour PM2.5 design value by 27 percent and 24 percent, respectively. In contrast, a 50 percent reduction in ammonia emissions decreased the design value by approximately 4 percent. In further detail, a 50 percent reduction in NOx emissions resulted in an approximate 42 percent drop in nitrate concentrations at Bakersfield, comparable to the reductions reported by Pun et al. (2009). Reductions in SOx emissions had a minor effect on the PM2.5 24-hour design values, since ammonium sulfate is a minor component of winter-time PM2.5 levels. VOC reductions slightly increased PM2.5 concentrations. The authors noted similar responses to PM2.5 precursors at Fresno. On average, at the other seven monitoring sites in the San Joaquin Valley, a 50 percent reduction in NOx emissions lowered PM2.5 approximately 23 percent, while a 50 percent reduction in ammonia emissions lowered PM2.5 by 5 percent. The authors conclude these results demonstrate that in the San Joaquin Valley in 2019, ammonium nitrate formation will be generally limited by nitric acid rather than ammonia.

Due to the highest PM2.5 concentrations occurring in Kern County, ARB staff conducted specific model sensitivity runs to evaluate the benefits of emission reductions focused on the nonattainment sub-area as part of the SJV 2012 PM2.5 Plan. The Kern County sensitivity runs demonstrated that one ton per day of PM2.5 reductions provided a 1 $\mu g/m^3$ improvement in the Bakersfield-California 2019 24-hour PM2.5 design value; one ton per day of NOx reductions provided for a 0.12 $\mu g/m^3$ improvement while one ton per day of ammonia reductions provided for a 0.02 $\mu g/m^3$ improvement and one ton per day of VOC reductions had no effect.

These modeling results, along with the findings from past modeling and monitoring studies continue to highlight that reductions in directly emitted PM2.5 emissions provide the most benefit, followed by NOx emissions in reducing PM2.5 concentrations and making progress towards attainment. Ammonia emission reductions are approximately an order of magnitude less effective. VOC emission reductions do not provide air quality benefits. Taken together, the emission inventory, monitoring data, and precursor sensitivity analyses all indicate that in the San Joaquin Valley, NOx, rather than ammonia is the limiting precursor for ammonium nitrate formation.

d. Role of VOC in ammonium nitrate formation

A number of studies have also been examined regarding the role of VOCs in ammonium nitrate formation. These include both monitoring studies conducted as part of CRPAQS, as well as studies that used differing types of air quality modeling to quantitatively assess the expected change in ammonium nitrate to hypothetical VOC reductions.

Monitoring studies

As previously mentioned, there are two primary pathways through which ammonium nitrate can form. During the day, NO_2 is oxidized to nitric acid. Nitric acid then reacts with ammonia to form ammonium nitrate. This daytime nitric acid formation pathway involves sunlight, VOCs, and background ozone. During the night, nitric acid is formed through oxidation of NO_2 (via N_2O_5) by background ozone, which then also reacts with ammonia to form ammonium nitrate. Studies by Pun et al. (1998, 2004) suggested that the daytime pathway may be important and therefore the formation of ammonium nitrate would be sensitive to changes in VOC emissions. However, other studies (Lurmann et al., 2006), suggest that on average, daytime production of nitric acid in the San Joaquin Valley is relatively slow and that nighttime production of ammonium nitrate aloft, which then mixes to the surface after sunrise could explain the observed homogeneous patterns of ammonium nitrate in the Valley. Ying et al. (2009) also theorized that the ozone concentration aloft in the San Joaquin Valley is predominantly due to the regional background and does not vary significantly with surface-level VOC emissions. Therefore, nighttime ammonium nitrate formation in the San Joaquin Valley would not be sensitive to VOC reductions.

While the monitoring studies cited above provide evidence that the VOC pathway may be important at times, these studies do not provide quantitative information about the overall role of and cannot be used to evaluate the benefits of, VOC controls. Rather, modeling studies are more appropriate to assess the overall impact of precursor controls.

Photochemical modeling

Staff reviewed the results of six modeling studies containing information on the significance of VOC controls in reducing ammonium nitrate in the San Joaquin Valley. While the results of the earliest studies were mixed, later studies provide generally consistent results regarding the role of VOCs. In assessing the potential benefits of VOC controls it is important that significance be interpreted in the context of California's overall control program with its strong focus on NOx control to achieve benefits for both PM2.5 and ozone.

Two early studies used simplified box modeling to explore the sensitivity of ammonium nitrate to VOC and NOx reductions. One of the two studies simulated a typical winter episode (Stockwell et al., 2000) and found that decreases in VOC emissions had little effect. The second study (Pun and Seigneur, 2001) simulated winter conditions during the 1996 IMS-95 pilot study around the Fresno area. The study found that ammonium nitrate formation decreased with VOC emission reductions, but increased with NOx reductions. Pun and Seigneur (2001) theorized that reducing NOx could lead to higher concentrations of the hydroxyl radical (OH) and increase the overall rate of nitrate production, despite the reductions in NOx. However, the box modeling approach used had a number of limitations, including lack of transport into/out of the box, robust vertical transport, and use of an older chemical mechanism. In addition, the VOC emissions were increased by a factor of two to improve model performance. As such, the box modeling did not fully represent the complete scope of atmospheric variations and has limited usefulness in assessing the responsiveness to VOC controls.

Subsequent modeling sensitivity studies for the same winter episode were conducted with the UCD-CIT model, an advanced research grade modeling system (Kleeman et al., 2005). The authors concluded that NOx emission controls are more effective in reducing PM2.5 nitrate concentrations in the San Joaquin Valley. Summary study results indicate that on average, large reductions in VOC emissions (on the order of 50 percent) reduced PM2.5 nitrate concentrations by approximately 17 percent. However, to evaluate the significance and effectiveness of VOC controls in the context of control strategy design, the study's isopleths of PM2.5 nitrate response to combined NOx/VOC emission reductions provide more in-depth information.

Figures 19 (a) and 20 (a) show that, based on the shapes of the graphs, NOx controls are the most effective approach to reduce PM2.5 nitrate concentrations at Fresno and at the location with the highest modeled PM2.5 nitrate concentration (grid location - 85 km Northing, 90 km Easting) respectively. Once NOx controls are taken into consideration, VOC emission reductions produce essentially no benefit, and in some instances may actually lead to an increase in PM2.5 nitrate concentrations. For example, as illustrated in Figure 19 (a) for Fresno, after considering an approximately 70 percent reduction in NOx emissions resulting from existing and proposed controls, reductions in VOC emissions to any level would not decrease PM2.5 nitrate concentrations. Furthermore, at grid location -85 km Northing, 90 km Easting (Figure 20 (a)), any level of VOC emission reductions would actually cause an increase in nitrate concentrations. Nitrogen-containing molecules such as PAN can act as temporary sinks for nitrogen dioxide (NO_2). When VOCs are controlled, the reduced availability of certain radicals, which are generated from VOCs, reduces the amount of NO_2 that is sequestered, thereby increasing the availability of NO_2 and enhancing ammonium nitrate formation (Meng et al., 1997).

Figure 19. 24-hour average NOx/VOC particulate nitrate isopleths at Fresno for (a) all sources, (b) diesel engines, (c) catalyst equipped gasoline engines, and (d) upwind sources of nitrate. Units are µg/m^3. (Source: Kleeman et al., 2005, Figure 3 pg. 5333).

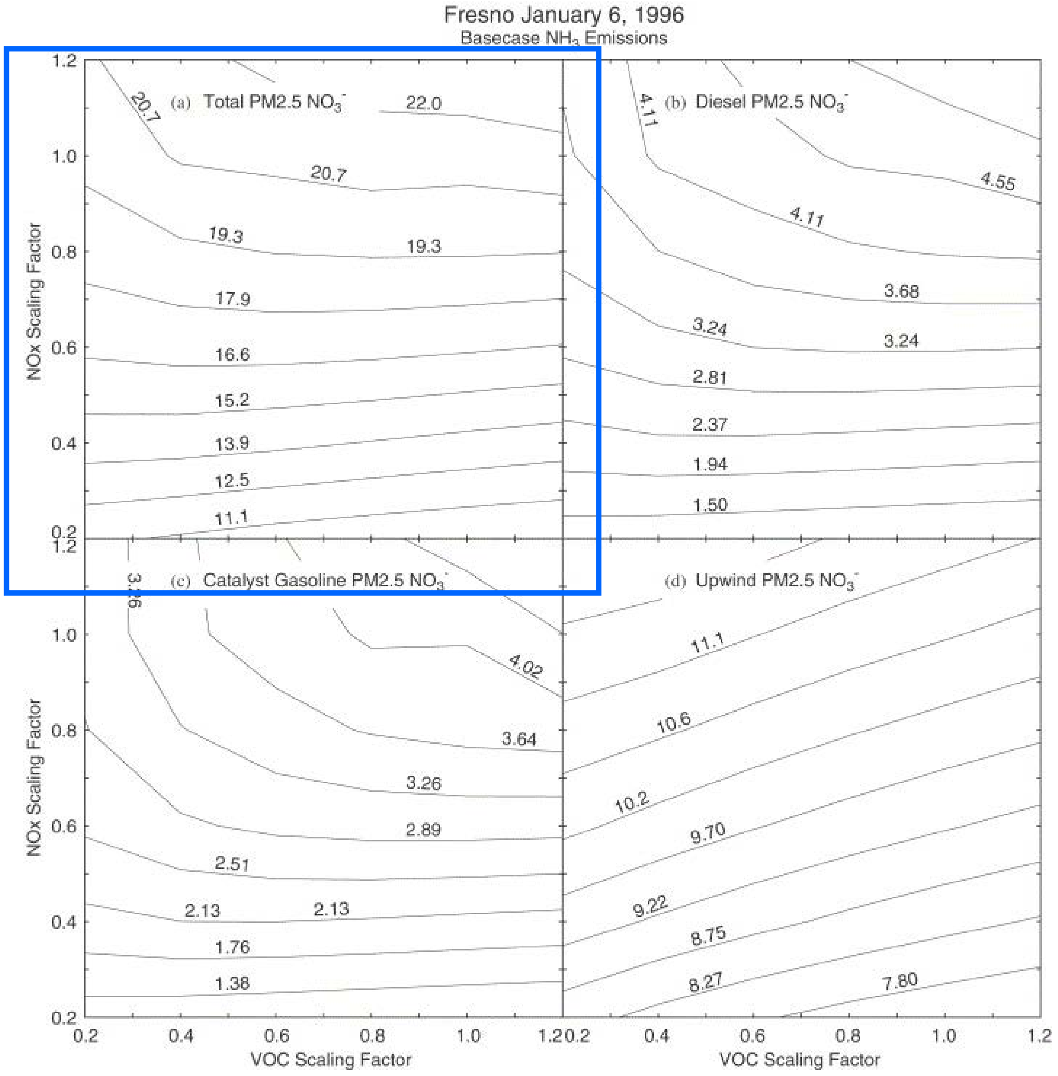
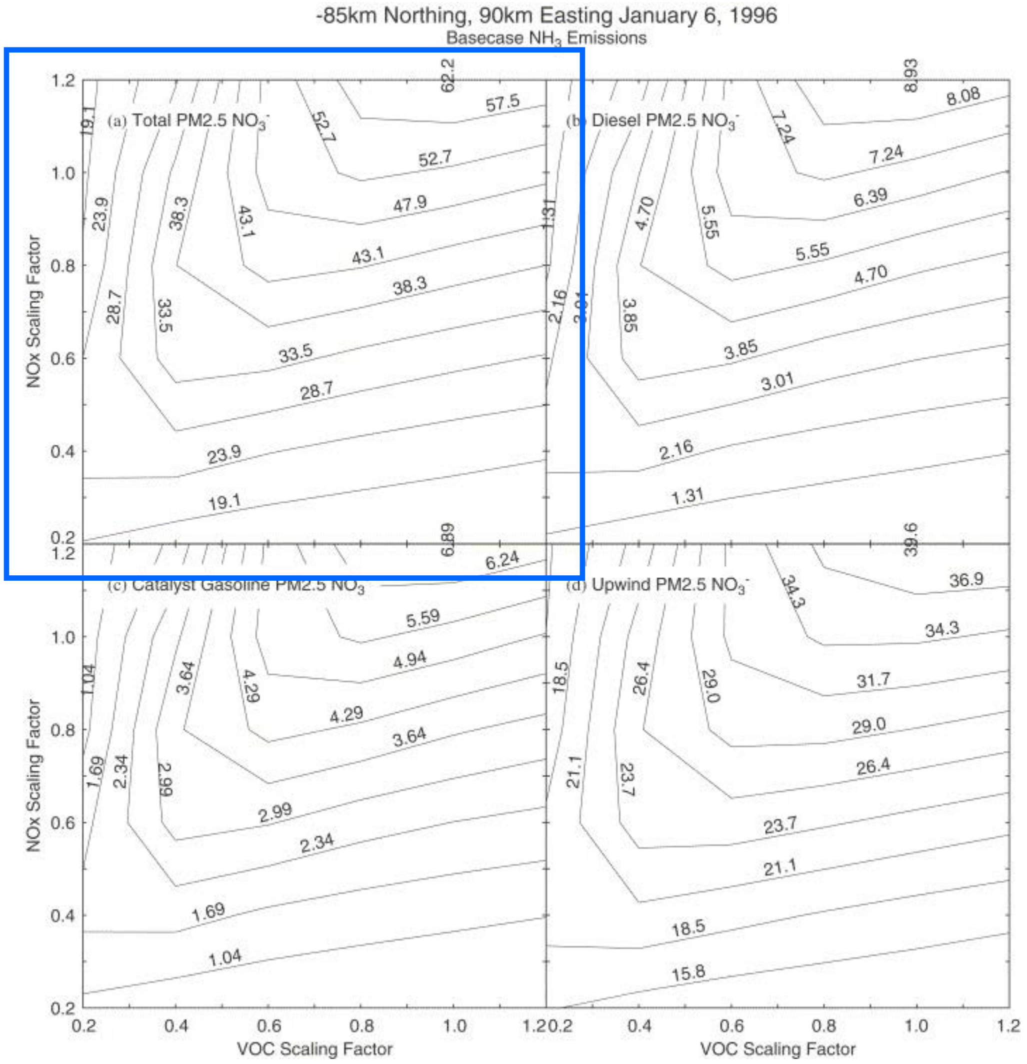


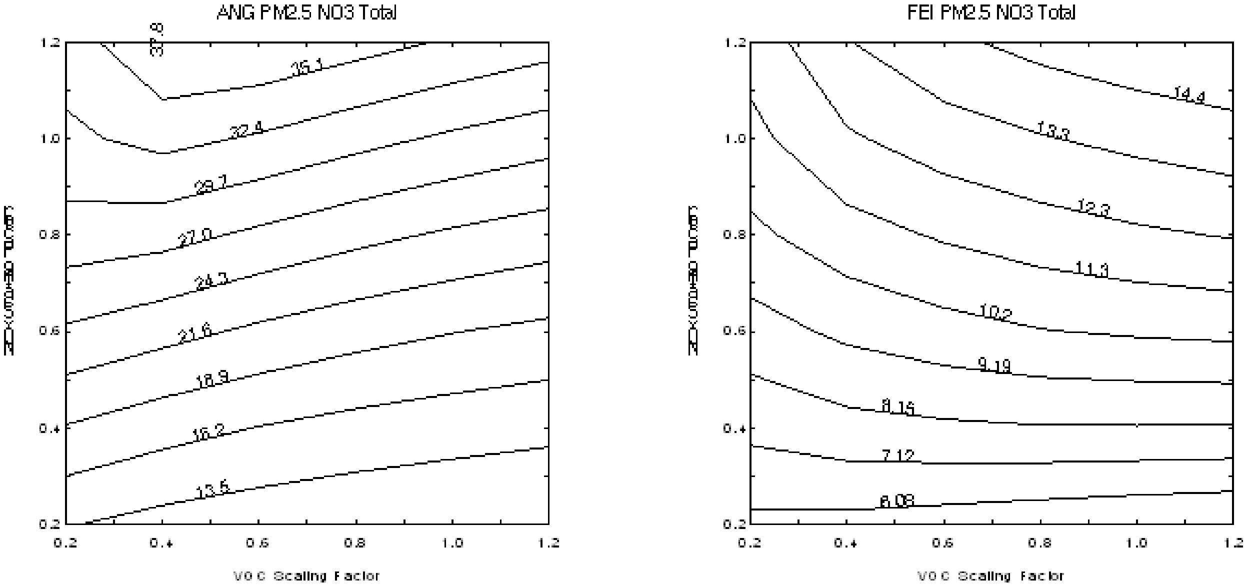
Figure 20. 24-hour average NOx/VOC particulate nitrate isopleths at grid location -85 km Northing, 90 km Easting for (a) all sources, (b) diesel engines, (c) catalyst equipped gasoline engines, and (d) upwind sources of nitrate. Units are µg/m^3. (Source: Kleeman et al., 2005, Figure 5 pg. 5335).



Three additional modeling studies investigated the two-week winter episode of 2000-2001 that occurred during the CRPAQS field study.

In the first study, preliminary data from modeling of this CRPAQS winter episode conducted using the Lagrangian form of the UCD-CIT model qualitatively confirm that NOx control is the most efficient method to reduce nitrate concentrations (Kleeman, M.J., personal communication, May 2008). Figure 21 illustrates the response of PM2.5 nitrate concentrations to NOx and VOC emission reductions at a rural (Angiola) and an urban (Fresno) site on December 31, 2000. Again, based on their shapes, these graphs show that NOx controls are the most effective approach to reduce PM2.5 nitrate concentrations. Once NOx controls are taken into consideration (approximately 70 percent reduction in NOx emissions), reductions in VOCs of up to 30 percent produce basically no benefit (Fresno). Furthermore, at some locations (Angiola) any VOC emission reductions may actually lead to an increase in PM2.5 nitrate concentrations.

Figure 21. The isopleths plot of PM2.5 nitrate with emission control of NOx and VOC at Angiola (ANG) and Fresno (FEI) after a five-day back trajectory simulation for December 31, 2000. Units are in µg/m^3. (Source: Kleeman, M.J., personal communication, May 2008).



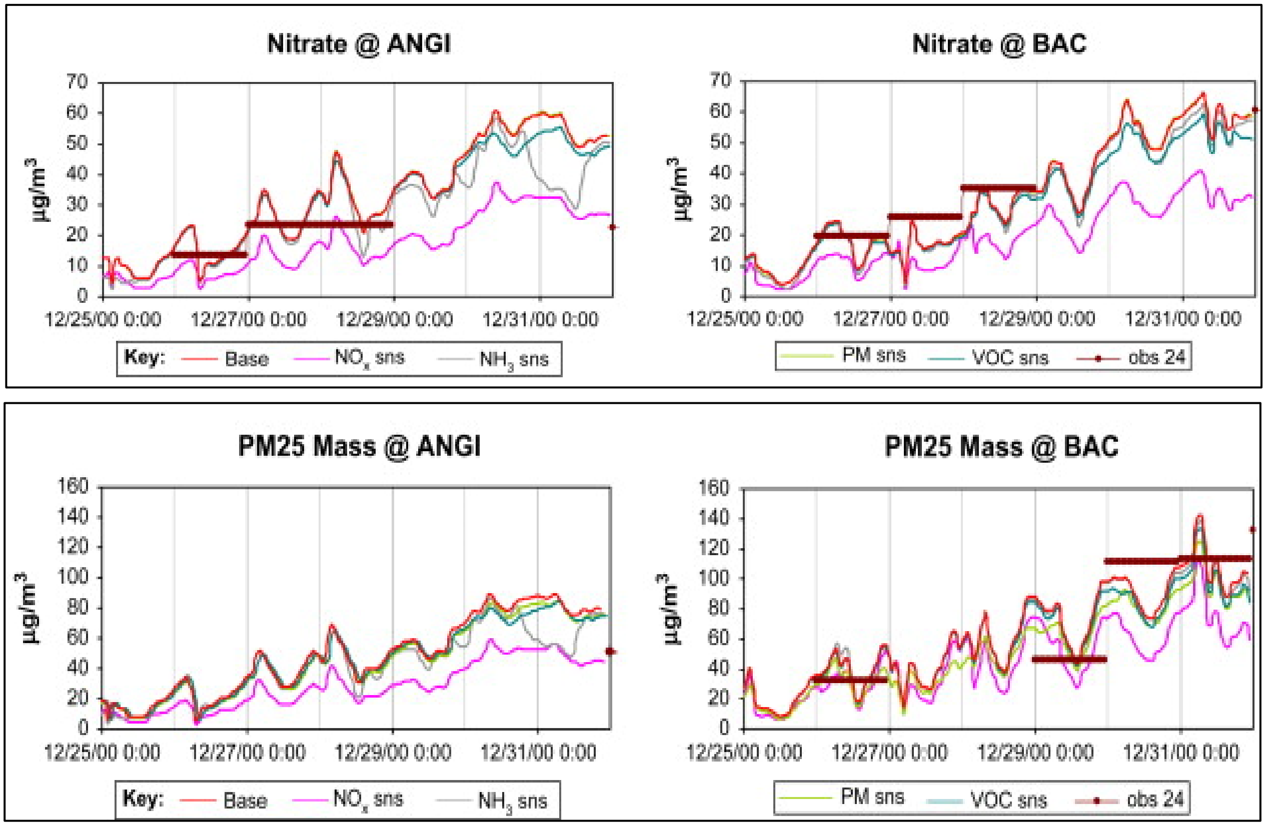
A second study conducted simulations of the two-week CRPAQS episode with the CMAQ photochemical model (Livingston, et al., 2009). The study consisted of two simulations. The first was a baseline scenario using a preliminary emissions inventory. This simulation showed that 50 percent reductions in anthropogenic VOC and NOx emissions had similar effects in reducing ammonium nitrate (about 20 percent each). A second simulation was conducted using an updated emission inventory representing a more accurate spatial distribution of total ammonia emissions (referred to as “Vehicle NH_3” scenario, per Livingston, P., personal communication, January 19, 2011). This second 50 percent VOC reduction simulation showed a much lower response to VOC controls. The response was lowered to a 12 percent reduction in ammonium nitrate, with a corresponding increase in responsiveness to NOx control of 38 percent reduction in ammonium nitrate. These results are consistent with those found by Kleeman et al., 2005.

A third study modeled one week of the CRPAQS episode using a version of CMAQ with a more advanced chemical mechanism (CMAQ-Madrid) (Pun et al, 2009). In contrast to the earlier Pun study using a simplified box modeling approach, this later work found that on average, nitrate was most sensitive to reductions in NOx emissions. While isopleths were not provided, the time evolution of nitrate and PM2.5 mass to VOC response illustrated in Figure 22 provides further details regarding the efficacy of VOC control. The response of nitrate to a 50 percent reduction in VOC emissions increased as PM2.5 levels rose during the episode. In urban areas, a 50 percent reduction in anthropogenic VOC emissions caused small reductions in nitrate, on the order of 10 percent, on the modeled days when 24-hour PM2.5 concentrations measured over 100 $\mu g/m^3$ at urban sites and above 65 $\mu g/m^3$ in rural areas.

The difference in the VOC response on the days with the higher PM2.5 concentrations as compared to those days with lower concentrations may be due to a difference in the chemical formation regime for nitrate. In general, there is sufficient background ozone to generate enough free radicals to initiate and propagate the chemistry of nitrate formation (Ying et. al, 2009). However, on days with high PM2.5 concentrations, the daytime photochemistry may have contributed to a rapid increase in nitrate, resulting in higher VOC and NOx sensitivity. It does not appear that VOCs contributed significantly to the free radical budget on the simulated days mainly because rapid increases in ozone were not observed. The effect of VOC levels on nitrate formation may also have a diurnal pattern since the hydroxyl and hydroperoxyl radical levels are high during the daytime and negligible at night. In addition, more reactive VOCs react quickly during the day and there is a minimal carry over to the next day. Therefore, it is reasonable to assume that the higher response to VOC and NOx at higher PM2.5 concentrations may be due to the nitrate formation mechanism rather than to PM2.5 accumulation due to the length of the episode.

Overall, nitrate was only responsive to a 50 percent reduction in VOCs at PM2.5 levels that are no longer reached in the San Joaquin Valley. Currently, the 24-hour PM2.5 design value in the Valley is 65 $\mu g/m^3$ recorded at Bakersfield and the rest of the Valley records 24-hour design values between 30 $\mu g/m^3$ and 63 $\mu g/m^3$. Given the current levels of PM2.5, we believe the Valley is now in a nitrate chemical formation regime that is less responsive to VOC controls.

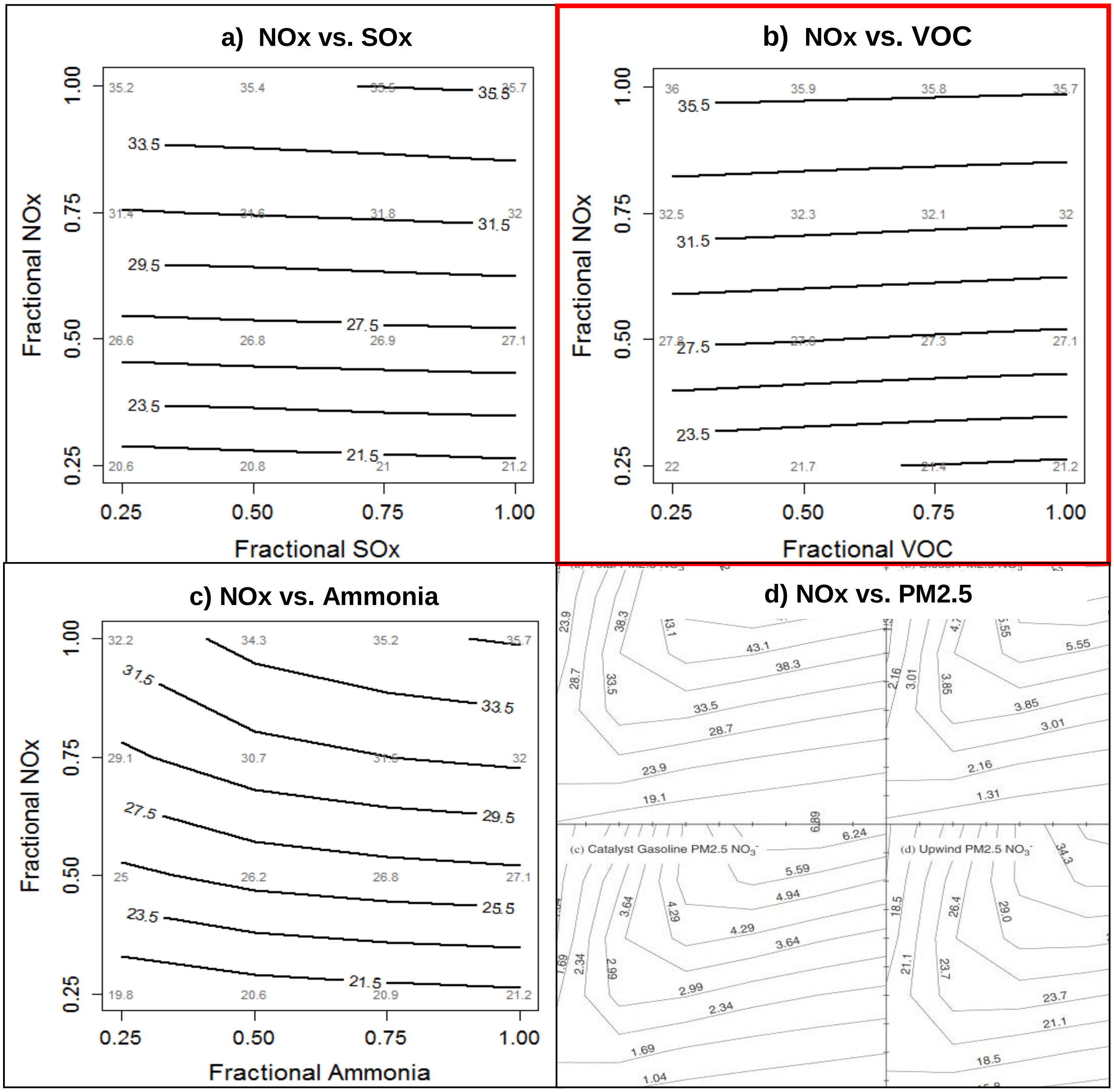
Figure 22. Time series with daily observations, base case simulation results and results from the sensitivity cases of (a) nitrate and (b) PM2.5 at Angiola (left) and Bakersfield (right). (Source: Pun et al., 2009, excerpt from Figure 2, pg. 406).



As mention earlier, in 2012, as part of the emission control strategy development for the San Joaquin Valley Plan for the federal 35 µg/m^3 24-hour standard, ARB staff conducted modeling using CMAQ to simulate the response of PM2.5 concentrations to reductions in PM2.5 precursors in 2019 throughout the Valley (SJV 2012 PM2.5 Plan; Chen et al., 2014). Table 2 provided the modeled effect on the 2019 24-hour PM2.5 design value obtained at each monitoring site from a 25 percent reduction in the specified precursor. The information is presented normalized to reflect the reduction in design value per ton of each precursor reduced. Consistently, direct PM2.5 reductions have the most benefit, followed by NOx reductions. Reductions in VOCs result in small disbenefits at most sites. Valley-wide reductions in PM2.5 are approximately four times as effective as NOx. In contrast, reductions in VOCs result in either no impact of very small disbenefits.

Figure 23 again shows the results of modeling sensitivity runs plotted on isopleth diagrams for Bakersfield-California site with NOx vs VOCs highlighted. Reductions in NOx have significant benefits in reducing PM2.5 design values. On the other hand, reducing VOCs leads to very small increases in the design value because these reductions have the effect of making more NOx available for nitric acid, and subsequent ammonium nitrate formation.

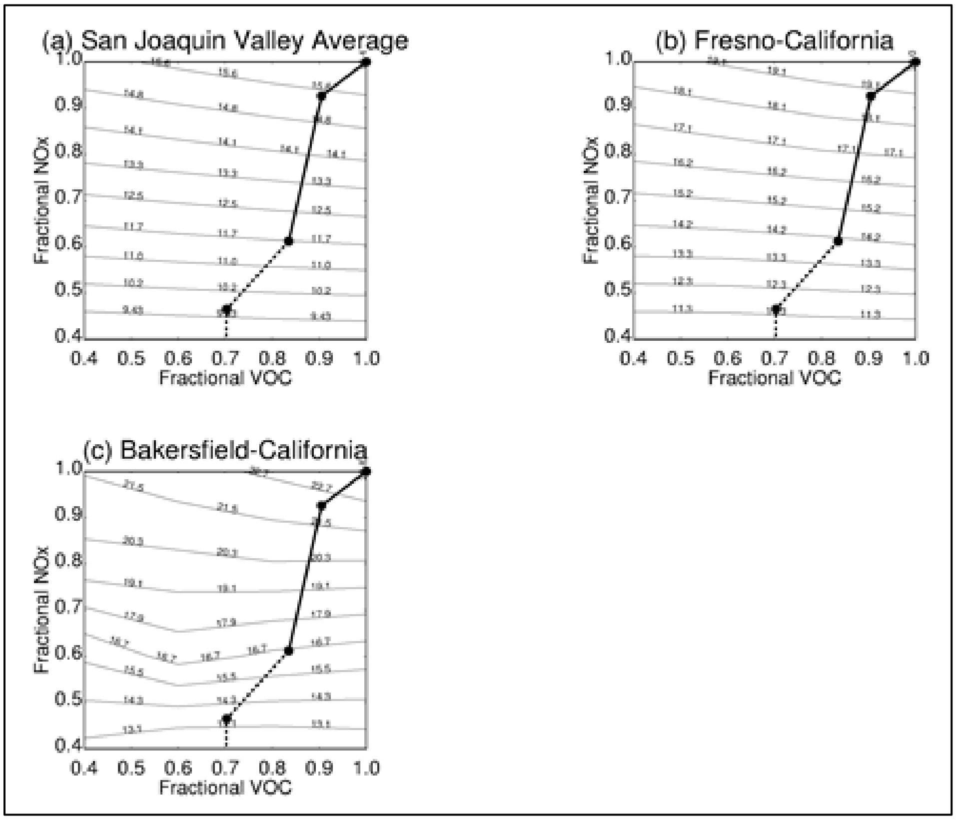
Figure 23. Bakersfield-California Isopleth Diagrams.



Chen et al. (2014) reported that at Bakersfield-California, a 50 percent reduction in anthropogenic VOC emissions in the Valley slightly increased the 2019 24-hour PM2.5 design value by 0.2 µg/m^3. At this site, VOC emission reductions lead to slightly higher ammonium nitrate concentrations and slightly lower secondary organic carbon. On average, a 50 percent VOC emission reduction had no impact on PM2.5 levels in the Valley.

In addition, Chen et al. used the UCD/CIT model to study the response of PM2.5 nitrate to NOx and VOC emission reductions during the December 15, 2000-January 7, 2001 winter period in the San Joaquin Valley. The authors generated isopleths diagrams for December 31, 2000 at Bakersfield, Fresno, and the San Joaquin Valley regional average, where 24-hour average PM2.5 nitrate concentrations are presented at various levels of NOx and VOC emission reductions. Valley-wide emission trends for 2000, 2005, 2010 and 2015 expressed as a fraction of 2000 were superimposed on the isopleth diagrams (Figure 24). Results show that at each five-year interval point, greater reductions in PM2.5 nitrate are achieved through NOx controls rather than VOC controls. The authors explain this response is reasonable, because background ozone transported into the San Joaquin Valley from the global background is the main oxidant during the winter stagnation episodes in the valley.

Figure 24. Response of 24-hour PM2.5 nitrate concentrations to NOx and VOC controls on December 31, 2000: (a) San Joaquin Valley average, (b) Fresno, and (c) Bakersfield. The solid line with dots represent estimated emissions control trend since 2000 and the dashed line represents projected emissions controls towards 2020. Dots represent emissions in 2000, 2005, 2010, and 2015. The projected 2020 emissions are less thatn 40 percent of the 2000 emissions and are therefore not shown on the graph. (Source: Chen et al., 2014, Figure 5, pg. 189).



Taken together, these air quality modeling studies indicate that in the San Joaquin Valley, NOx, rather than VOCs, is the limiting precursor for nitric acid and subsequent ammonium nitrate formation, and reductions in VOCs result in small increases in PM2.5.

6. SECONDARY ORGANIC AEROSOL FORMATION

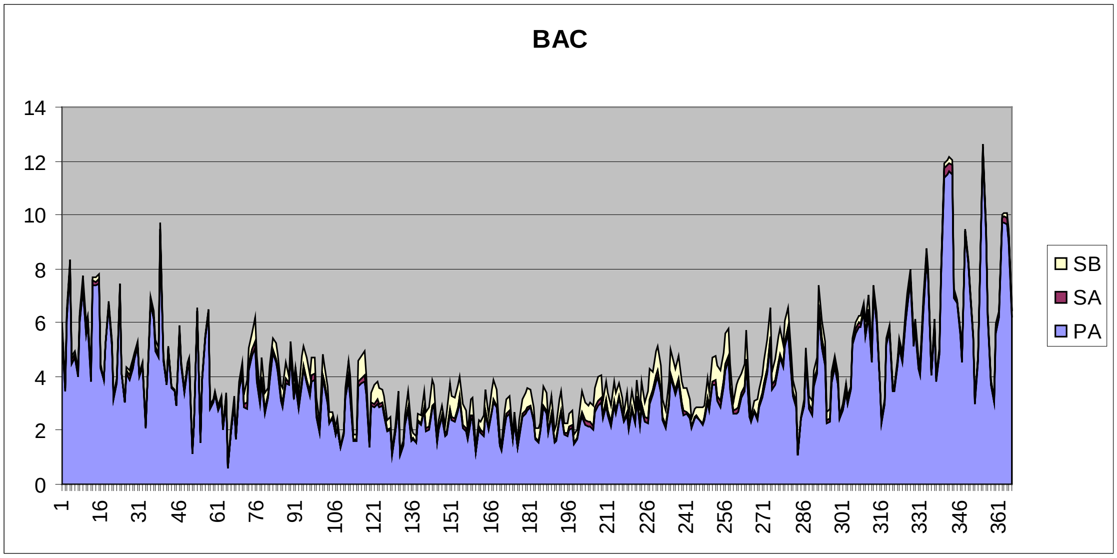
VOC emissions also have the potential to contribute to secondary organic aerosols (SOA). While these components contribute to observed PM2.5 concentrations in the San Joaquin Valley to a small degree, the weight of evidence indicates that anthropogenic VOC is not a significant contributor to PM2.5.

SOA form when intermediate molecular weight VOCs, emitted by anthropogenic and biogenic sources, react and condense in the atmosphere to become aerosols. In addition, lighter VOCs participate in the formation of atmospheric oxidants which then participate in the formation of SOA. The processes of SOA formation are complex and have not been fully characterized. The apportionment of PM2.5 organic carbon to primary and secondary components is a very active area of current research.

Using the UCD-CIT model, Chen et al. (2010) investigated the apportionment of PM2.5 organic carbon for the 2000/2001 CRPAQS episode. From the total predicted PM2.5 organic carbon in the urban Fresno and Bakersfield areas, six percent and four percent were SOA, respectively, while in the rural Angiola area, 37 percent was SOA. The major SOA precursors of secondary organic aerosol were long-chain alkanes followed by aromatic compounds. The sources of these precursors were solvent use, catalyst gasoline engines, wood smoke, non-catalyst gasoline engines, and other anthropogenic sources, in that order.

In contrast, on an annual average basis, secondary organic aerosols derived from anthropogenic VOC emissions account for only one to two percent of the annual total PM2.5 concentrations throughout the Valley. ARB air quality modeling exercises conducted as part of the SJV 2008 PM2.5 Plan attainment demonstration analysis using the CMAQ model showed that primary PM2.5 emissions are the main contributor to organic aerosols and SOA contribute to only a small extent. Furthermore, as illustrated in Figure 25, SOA are mostly formed during the summertime, when total PM2.5 concentrations are low, and are mainly derived from biogenic emission sources. On an annual average basis, SOA derived from anthropogenic VOC emissions are a small part of the organic aerosol concentrations (three to five percent).

Figure 25. Daily contributions to organic aerosol concentrations in Bakersfield in 2000 modeled with CMAQ: Primary organic aerosols (PA), secondary aerosols formed from biogenic VOC emissions (SB) and secondary aerosols formed from anthropogenic source VOC emissions (SA). Units are µg/m^3.



As part of the CRPAQS study, simulations of a wintertime episode conducted using CMAQ-Madrid, a model with an enhanced secondary organic aerosol formation mechanism, also found that organic aerosol concentrations were dominated by directly emitted (primary) emissions. The study found that, because of the dominance of primary PM2.5 organic matter, a 50 percent reduction in anthropogenic VOC emissions has limited effects on the modeled PM2.5 organic matter (Pun, et al., 2009).

These study results show that for secondary organic aerosols, further VOC reductions would have very limited effectiveness in reducing PM2.5 concentrations. VOC reductions also result in small increases in PM2.5 overall, due to the fact that they increase nitrate.

7. SECONDARY AMMONIUM SULFATE FORMATION

Sulfur oxides (SOx) emitted from stationary and mobile combustion sources mostly as sulfur dioxide (SO_2) are oxidized in the atmosphere to ultimately form sulfuric acid (H_2SO_4). Sulfuric acid then combines with ammonia to form ammonium sulfate:

$$H_2SO_4 + 2\ NH_3 \longrightarrow (NH_3)_2SO_4$$

Table 3 lists SOx and ammonia winter and annual average emissions in the current inventory for two years (2012 and 2020). As shown in the above equation, in simple terms it takes one molecule of SOx and two molecules of ammonia to form one molecule of ammonium sulfate. However, due to differing molecular weights, one ton of SOx contains fewer molecules than one ton of ammonia. Therefore it is most appropriate to make an emissions inventory comparison after normalizing for molecular weight

Since one SO_2 molecule weighs 64 u and one NH_3 molecule weighs 17 u, one ton of NH_3 has 3.8 times (64 u/17 u) the number of molecules as one ton of SO_2. As one molecule of SO_2 reacts with 2 molecules of NH_3, dividing the SO_2 emissions by 1.9 therefore provides a common basis for comparison to the ammonia emissions. On this normalized comparison basis, ammonia is approximately 80 times more abundant than SOx. Thus, SOx emissions are the limiting precursor for ammonium sulfate formation.

Table 3. Comparison of SOx and ammonia emissions in selected years a) during the winter and b) on an annual average basis.

a)

Year	Winter NH_3 emissions (tpd)	Winter SOx emissions (tpd)	Normalized SOx emissions (tpd)
2012	310	7.9	4.2
2020	339	7.7	4.1

b)

Year	Annual NH_3 emissions (tpd)	Annual SOx emissions (tpd)	Normalized SOx emissions (tpd)
2012	330	8.1	4.3
2020	358	7.8	4.1

8. EMISSION SOURCES OF ANNUAL AVERAGE PM2.5

a. Emission inventory

Emission inventories provide emission estimates for sources of directly emitted (primary) PM2.5 and of each of the gaseous precursors of secondary PM2.5 (NOx, SOx, and ammonia). Table 4 lists the main PM2.5 components and links them to their largest emission sources based on San Joaquin Valley emission inventory data for 2012, the base year for the 2015 PM2.5 Plan. VOC emission are not listed, since, as discussed in sections 5d and 6, overall, VOC emission reductions have no effect on PM2.5 concentrations in the Valley. Emission sources are listed in descending order of magnitude.

As described in section 4c, ammonium nitrate is the main PM2.5 component, contributing about 40 percent of PM2.5 levels. It is formed in the atmosphere from reactions of NOx and ammonia emissions. Heavy-duty diesel vehicles (trucks) are the largest source of NOx emissions, followed by farm equipment, off-road equipment, light-duty vehicles, trains, and residential fuel combustion. Ammonia is primarily emitted from livestock husbandry and fertilizer application. Ammonium sulfate, formed in the air from reactions of SOx and ammonia emissions, contributes about 10 to 15 percent to PM2.5 levels. SOx is mostly emitted from the manufacturing of chemicals and glass related products and fuel combustion sources in oil and industrial manufacturing processes. Organic carbon, which contributes about 20 to 35 percent to PM2.5 levels, and elemental carbon, which contributes about two to five percent of PM2.5 levels, are directly emitted, with key sources being residential fuel combustion, diesel trucks, cooking, and managed burning and disposal. Geological material contributes about five to 15 percent of the PM2.5 mass and is directly emitted from activities generating dust, such as farming operations and on-road and off-road vehicle travel, as well as wind-blown dust.

While emission inventories provide a broad overview of Valley wide and county level sources, additional methods using ambient data and source apportionment modeling provide supplemental information on the sources directly impacting individual monitoring sites. The following sections describe these analyses.

Table 4. Main emission sources of PM2.5 components.

PM2.5 Component (percent of PM2.5)	**Process**	**Emission Sources**
Ammonium nitrate (about 40 percent)	Formed in the atmosphere from the reactions of NOx and ammonia emissions	**NOx:** Heavy duty diesel vehicles account for approximately 50 percent of the 2012 annual NOx emissions. Farm equipment, off-road equipment, light, medium, and heavy duty gas trucks, trains, light duty passenger cars, and residential fuel combustion account for an additional 40 percent.
		Ammonia: Livestock husbandry and fertilizer application account for over 90 percent of the 2012 annual ammonia emissions.
Ammonium sulfate (about 5-15 percent)	Formed in the atmosphere from the reactions of SOx and ammonia emissions	**SOx:** Manufacturing of chemicals, glass, and related products, fuel combustion, and residential wood combustion account for over 80 percent of the 2012 annual SOx emissions.
Organic Carbon (about 20-35 percent)	Directly emitted from motor vehicles and combustion processes	**Combustion PM2.5**: Residential fuel combustion, diesel trucks, cooking, managed burning and disposal, farm equipment, oil and gas production, electrical utilities, aircraft, and off-road equipment account for over 75 percent of the annual combustion PM2.5 emissions.
Elemental Carbon (about 2-5 percent)	Directly emitted from motor vehicles and combustion processes	
Geological (about 5-15 percent)	Directly emitted from dust generating sources	**Dust PM2.5:** Farming operations, fugitive windblown dust, paved and unpaved road dust, construction and demolition, and mineral processes account for 100 percent of the 2012 annual dust PM2.5 emissions.

b. Source apportionment using source receptor models

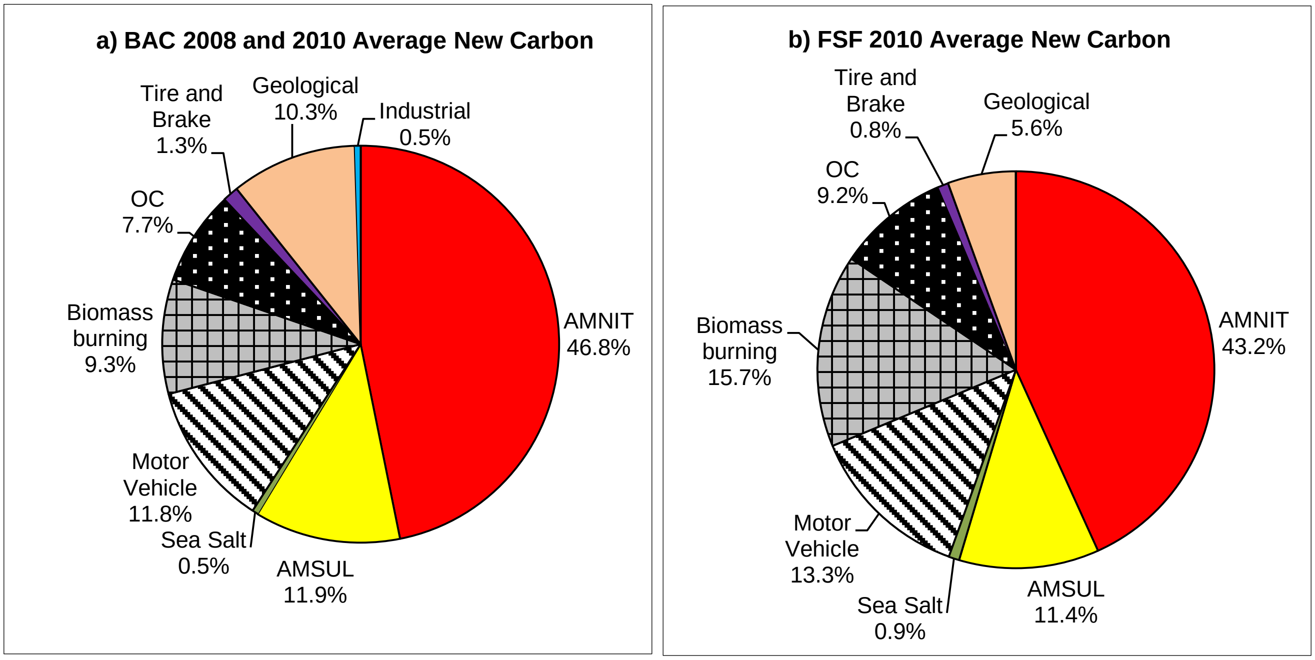
Source receptor models (also known as observational models) can be used to determine the relative importance of the different types of PM2.5 emission sources at individual monitoring sites. The Chemical Mass Balance (CMB) model statistically relates measured chemical species of ambient PM2.5 to the chemical species emitted by diverse sources. The Positive Matrix Factorization (PMF) statistical model distinguishes correlation patterns among measured PM2.5 species to identify sources.

Chemical Mass Balance Modeling

Source contributions to annual average PM2.5 concentrations at Bakersfield-California (BAC) and Fresno –1st Street (FSF) were estimated by applying the CMB model version 8.2 to individual PM2.5 samples using PM2.5 source profiles developed during previous studies. The PM2.5 samples were from between 2008 and 2010. Per U.S. EPA guidance, between 2007 and 2009, the carbon collection and analysis method was changed to improve comparability with the rural Interagency Monitoring of Protected Visual Environments (IMPROVE) PM2.5 carbon data. Since the new carbon method started operating in May 2007 at Bakersfield and in April 2009 at Fresno, the CMB analysis relied on 2008-2010 data from Bakersfield and 2010 data from Fresno. Appendix A3 describes this CMB analysis in further detail.

Figure 26 shows the calculated contributions to ambient PM2.5, on an annual average basis, from sources included in the CMB model. Ammonium nitrate, the most significant source, contributed approximately 45 percent at both Bakersfield and Fresno-1st. Biomass burning, which included residential wood combustion and agricultural, prescribed burning, and likely also cooking, contributed nine percent at Bakersfield and 16 percent at Fresno. Motor vehicle exhaust (diesel and gasoline combined) accounted for about 12 percent at both sites. Ammonium sulfate contributed approximately 12 percent and organic carbon about eight percent at both sites. Geological (dust) contributed ten percent at Bakersfield and six percent at Fresno. Contributions of the remaining sources were minor at both sites.

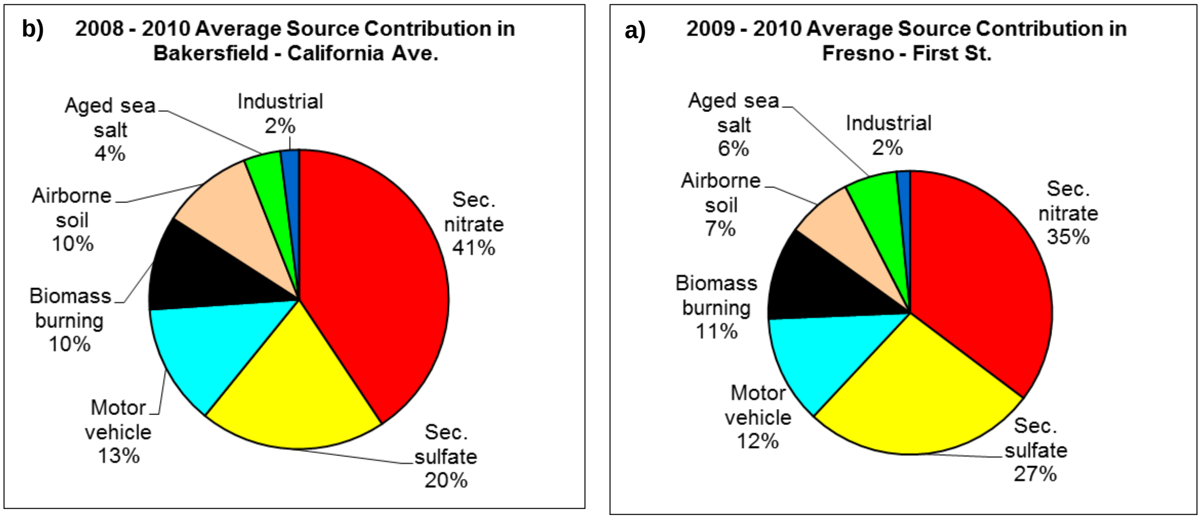
Figure 26. CMB model calculated average PM2.5 source contributions at a) Bakersfield-California (BAC) between 2008 and 2010 and b) Fresno-1st Street (FSF) in 2010.



Positive Matrix Factorization

The PMF2 model was applied to the chemically speciated PM2.5 data collected at the Bakersfield-California and Fresno-1st Street monitoring sites. Bakersfield data from 2008-2010 and Fresno-1st data from 2009-2010 were used. Appendix A4 describes this PMF analysis in further detail. The average source contributions to PM2.5 concentrations are illustrated in Figure 27. Similar to the CMB results, ammonium nitrate contributes the most at both sites, 41 percent at Bakersfield and 35 percent at Fresno-1st. At both sites, motor vehicle exhaust contributes about 12 percent and biomass burning (which includes residential wood combustion, agricultural burning, and likely also cooking) contributes approximately ten percent. Secondary ammonium sulfate accounts for 20 percent at Bakersfield and 27 percent at Fresno-1st. Airborne soil contributes ten percent at Bakersfield and seven percent at Fresno. Other sources are minor contributors.

Figure 27. Average source contributions estimated using PMF at a) Bakersfield-California (BAC) between 2008 and 2010 and b) Fresno-1st Street (FSF) between 2009 and 2010.



While the absolute magnitude of the contributions estimated by the two models vary to some extent, taken together, the CMB and PMF source apportionment studies confirm the importance of secondary ammonium nitrate contributions to PM2.5 levels on an annual average basis and during the winter. In addition, motor vehicle exhaust and biomass burning, were found to be significant contributors to PM2.5 levels. Ammonium sulfate and geological

9. PM2.5 AIR QUALITY PROGRESS

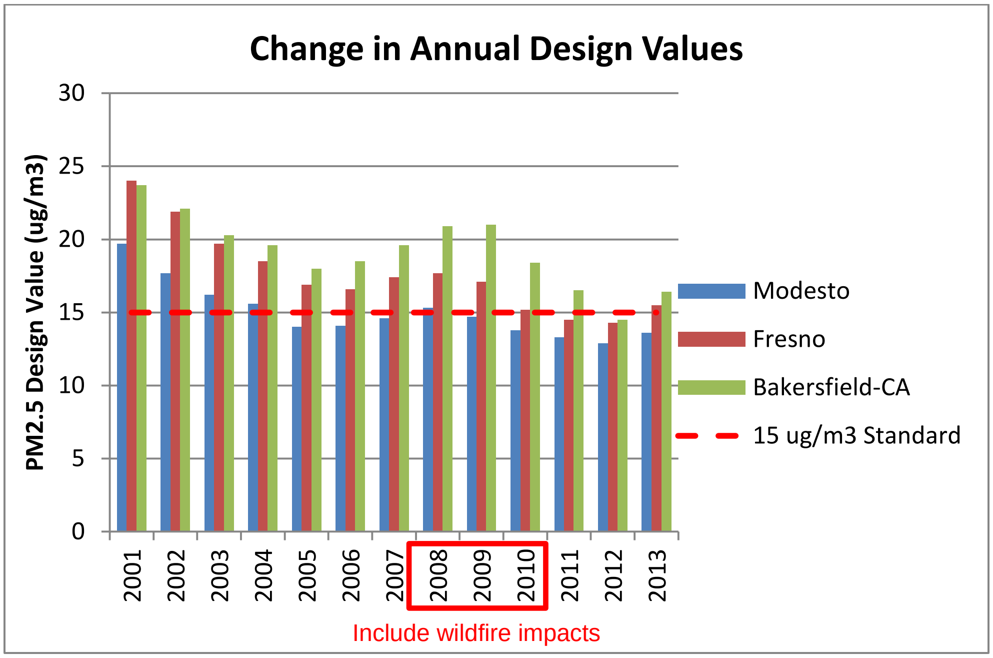
a. Annual PM2.5 trends

On an annual average basis, PM2.5 air quality has improved over the last dozen years. Figure 28, shows annual design value(1) trends at sites in the northern (e.g., Modesto), central (e.g., Fresno-1st/Garland) and southern regions (e.g., Bakersfield-California).

The Valley was nearing attainment of the annual standard through 2012, with only a few sites recording design values over the standard. However, due to meteorological conditions associated with the drought PM2.5 concentrations during the 2013/2014 winter increased, causing 2013 design values to go over the standard at more sites in the Valley.

Despite the increase in 2013, the Valley is still seeing overall progress. Between 2001 and 2013, annual design values declined between 10 and 35 percent. About half of the sites in the Valley attain the standard in 2013, with the highest remaining levels in the central and southern regions, where design values are about five to 20 percent over the standard.

Figure 28. Trend in annual PM25 design values (2001-2013) at the Bakersfield-California, Fresno-1st/Garland, and Modesto monitoring sites.



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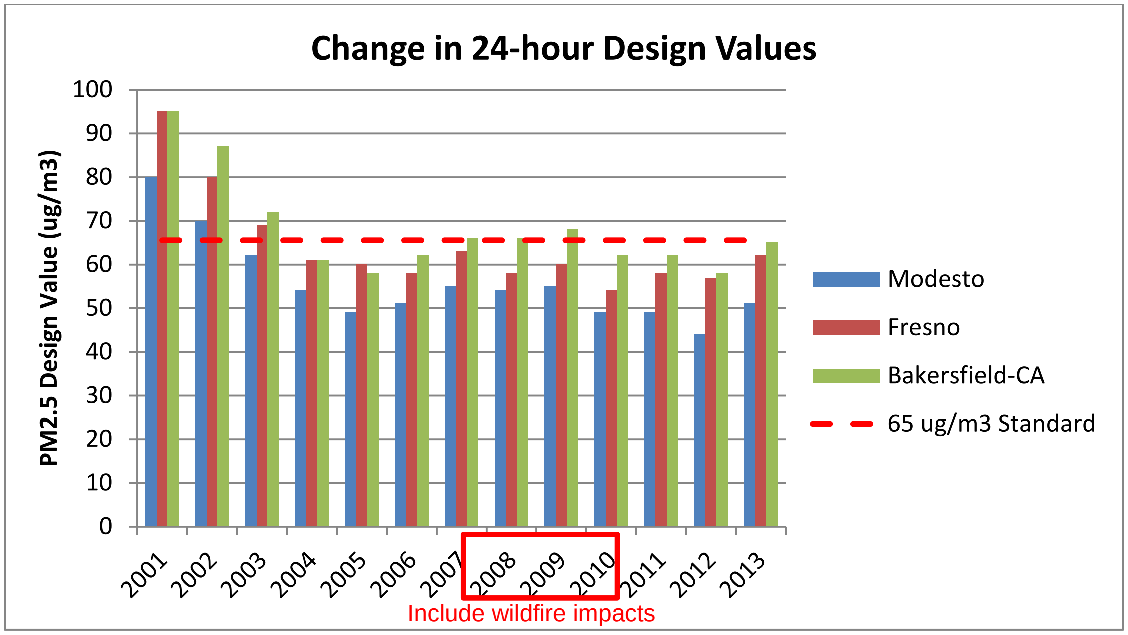
(1) The design value -- the metric used to determine compliance with the standard -- represents the average of three consecutive annual averages of the PM2.5 concentrations measured at a specific site (e.g. the 2013 PM2.5 annual design value is the average of the 2011, 2012, and 2013 annual average PM2.5 concentrations). If the annual design value is equal to or below 15.0 µg/m^3, the site meets the standard.

b. 24-Hour PM2.5 trends

As illustrated in Figure 29, over the long-term, the 24-hour PM2.5 design values also show a downward trend. The most pronounced progress occurred between 2001 and 2003. Extensive wildfires occurred during the summer of 2008 in Northern California. These wildfires impacted the 2008, 2009, and 2010 design values throughout the Valley, with greater impact in the northern Valley. Overall, between 2001 and 2013, the 24-hour PM2.5 design values in the Valley have decreased between 15 and 45 percent. In 2013, all sites in the Valley attained the standard.

Figure 29. Trend in 24-hour PM2.5 Design Values (2001-2013) at the Bakersfield-California, Fresno-Garland, and Modesto monitoring sites.



Looking at the number of days with measured PM2.5 concentrations over the 65 µg/m^3 and 35 µg/m^3 standards provides another way to assess PM2.5 impacts. Over the long term, between 1999 and 2013, the number of days exceeding the 65 µg/m^3 standard decreased by about 60 percent at the Bakersfield-California site and by about 80 percent at the Fresno-Garland site (Figure 30). Within the same period, the number of days over the 35 µg/m^3 decreased by about 30 percent at the Bakersfield-California site and by about 40 percent at the Fresno-1st site (Figure 31). The increase in the number of exceedance days in 2013 compared to 2012 was due to the severe meteorological conditions during the winter of 2013-2014 related to the drought. The Valley experienced similarly severe meteorological conditions during the 1999-2000 and 2000-2001 winters. The total number of exeedance days, however, was much higher during these earlier years, providing evidence that the emission reductions achieved in the Valley have resulted in PM2.5 air quality improvement.

Figure 30. Trend in measured days over the 24-hour standard of 65 µg/m^3 (1999-2013) at the Bakersfield-California and Fresno-1st/Garland monitoring sites.

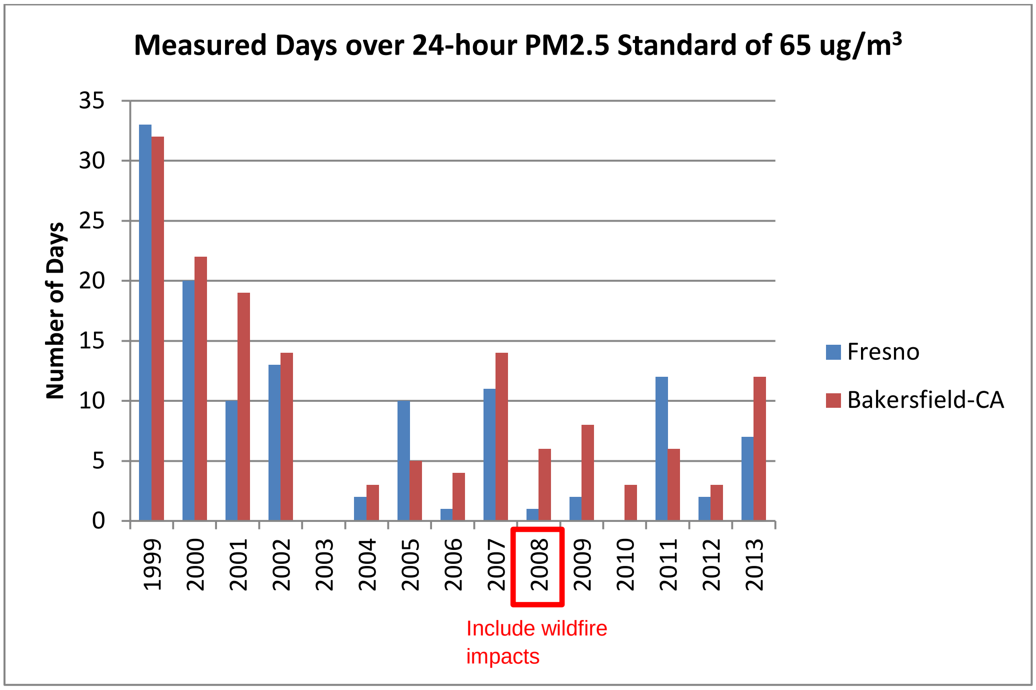
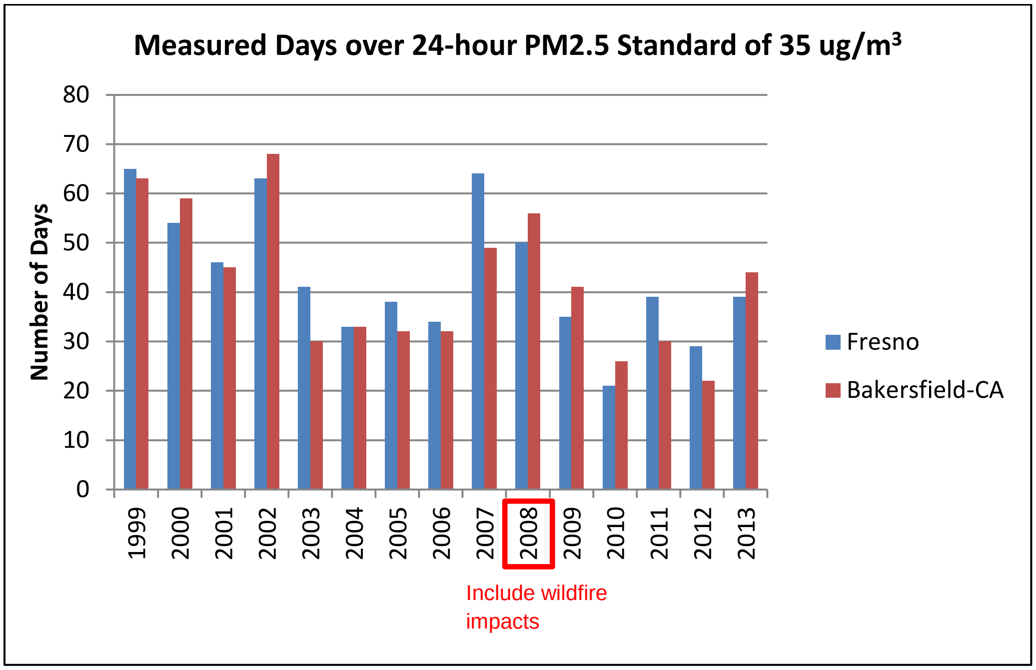


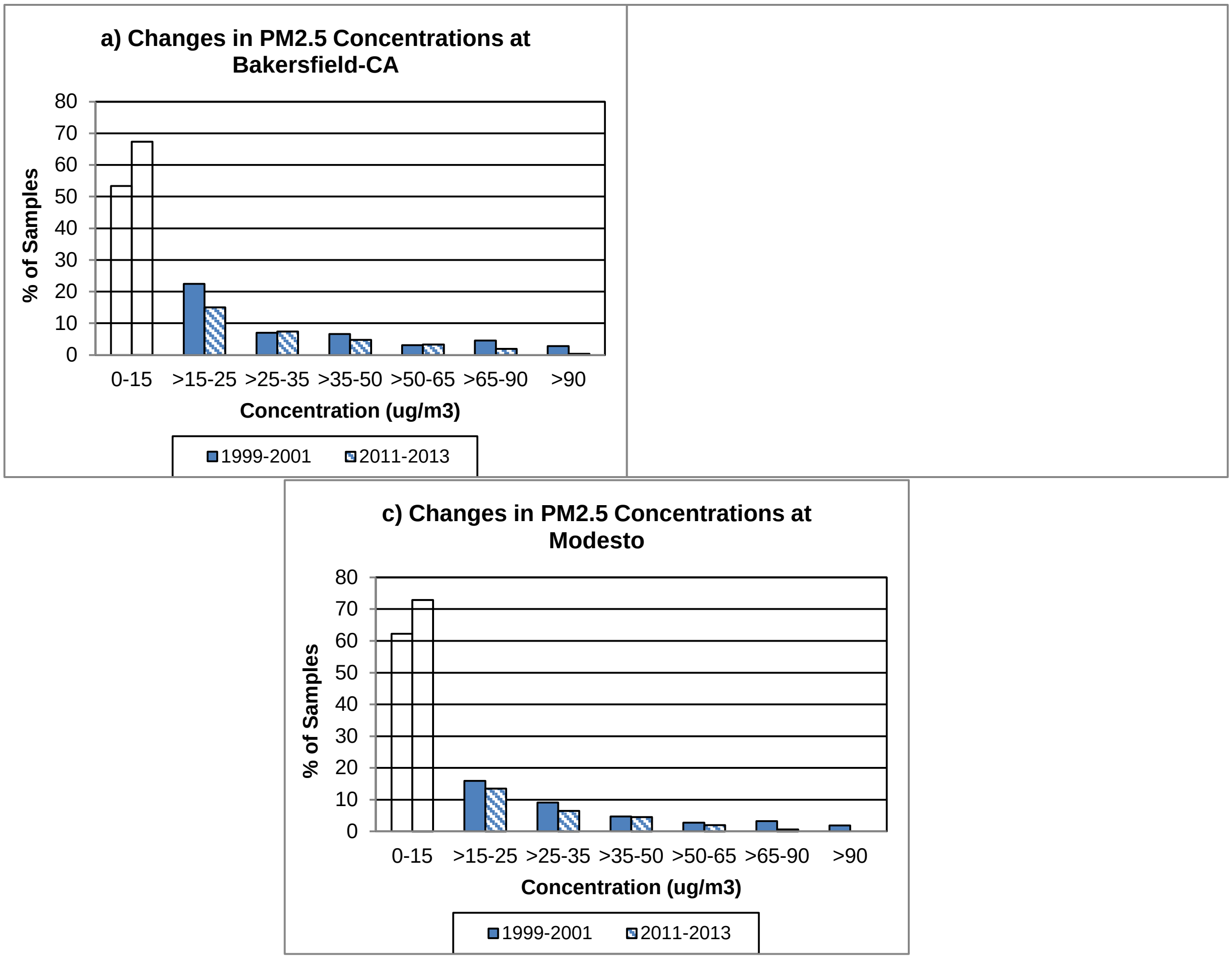
Figure 31. Trend in measured days over the 24-hour standard of 35 µg/m^3 (1999-2013) at the Bakersfield-California and Fresno-1st/Garland monitoring sites.



c. Trends in 24-hour, seasonal, and hourly PM2.5

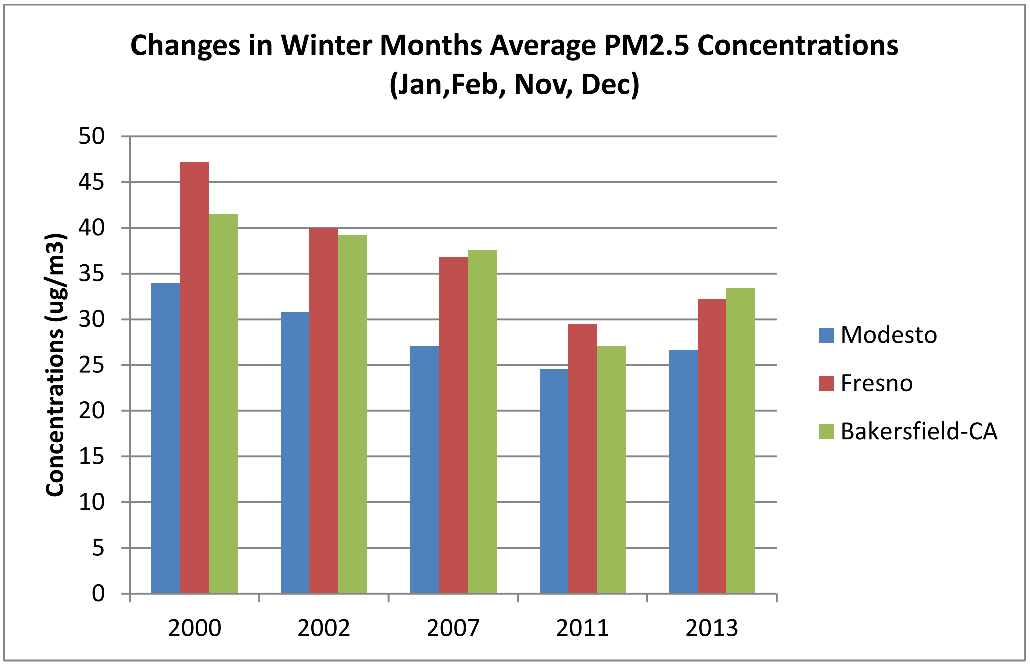
Comparing the change in the frequency distribution of 24-hour PM2.5 concentrations over the last dozen years provides another means of looking at air quality changes over the years. As illustrated in Figure 32, the fraction of days recording PM2.5 over the 24-hour standard of 65 µg/m^3 as well as the fraction of days over the 24-hour standard of 35 µg/m^3 decreased between the three-year periods of 1999-2001 and 2011-2013 at the three monitoring sites shown. The frequency of days over the 65 µg/m^3 standard at Bakersfield and at Fresno decreased from eight to two percent, and at Modesto from five to one percent. The frequency of days over the 35 µg/m^3 standard also decreased, at Bakersfield from over 15 to 10 percent, at Fresno from 20 to 10 percent, and at Modesto from close to 15 to less 10 percent. In contrast, during these same periods, the fraction of days recording concentrations at or below the annual standard increased from about 50 up to about 70 percent at Bakersfield, from 55 up to 70 percent at Fresno, and from about 60 up to about 75 percent at Modesto.

Figure 32. Change in PM2.5 concentration frequency distribution between the 1999-2001 and 2009-2013 periods at the a) Bakersfield-California, b) Fresno-1st/Garland, and c) Modesto monitoring sites.



Focusing on the winters (November through February) when meteorological conditions were most conducive to PM2.5 formation and accumulation provides further insight into PM2.5 air quality progress. These years include 2000, 2002, 2007, 2011, and 2013, which as illustrated in Figure 31, also had the highest numbers of days measuring over the 24-hour PM2.5 standard. Figure 33 illustrates the decrease in the winter average PM2.5 concentrations for these years at the Bakersfield-California, Fresno-1st, and Modesto monitoring sites. Although the severe drought conditions in 2013 resulted in winter average PM2.5 levels that were higher than 2011, 2013 PM2.5 levels were lower than those in 2000, 2002, and 2007. Overall, comparing 2000 to 2013, winter average PM2.5 concentrations decreased by about 20 percent in Bakersfield and Modesto, and about 30 percent in Fresno.

Figure 33. Changes in winter-months average (January, February, November, December) PM2.5 concentrations at the Bakersfield-California, Fresno-1st/Garland and Modesto monitoring sites among years with most PM2.5 conducive meteorology.



Progress in reducing PM2.5 levels is further evidenced by comparing daily PM2.5 concentrations during two episodes with the most similarly severe meteorological conditions. The graphs in Figures 34, 35, and 36 compare PM2.5 concentrations measured at Bakersfield, Fresno, and Modesto, respectively, between November 1, 2013 and February 5, 2014 to the PM2.5 concentrations measured during the same three months in 2000/2001 (the CRPAQS episode). Overall, the 2013/2014 air quality was better compared to 2000/2001 for all air quality statistics analyzed. Maximum 24-hour concentrations were approximately 30 to over 40 percent lower. The average concentrations during the three month period were 20 percent lower. The number of days over the 2006 24-hour standard of 35 µg/m^3 decreased by about 20 to

30 percent. Even more significant was the 25 to 70 percent decline in the number of days with concentrations over the 65 µg/m^3 standard.

Figure 34. Comparison of the 2013/2014 PM2.5 episode to the CRPAQS episode of 2000/2001 at the Bakersfield-California monitoring site.

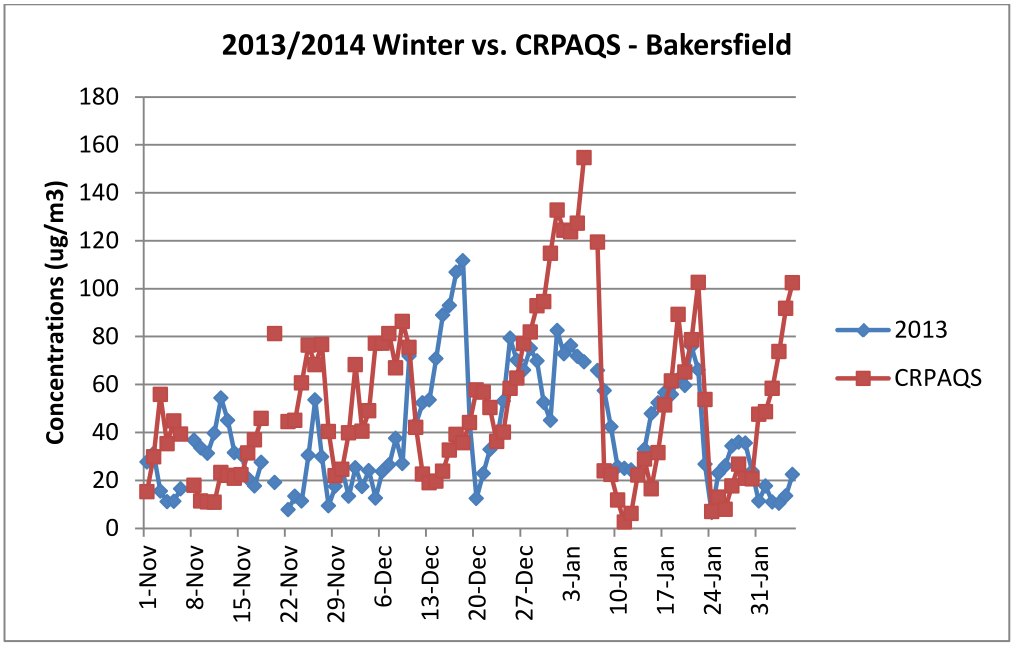


Figure 35. Comparison of the 2013/2014 PM2.5 episode to the CRPAQS episode of 2000/2001 at the Fresno 1st/Garland monitoring site.

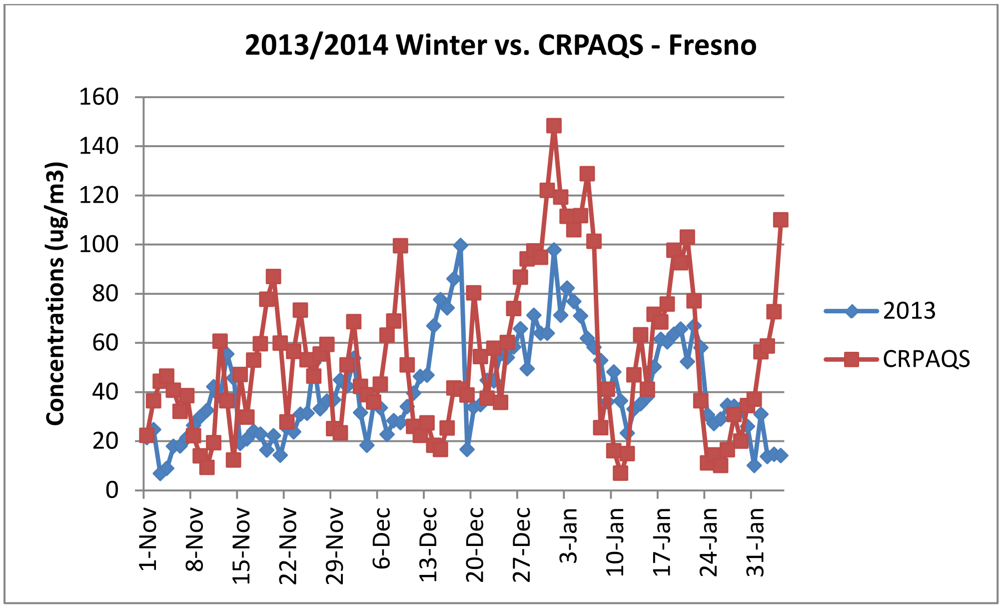
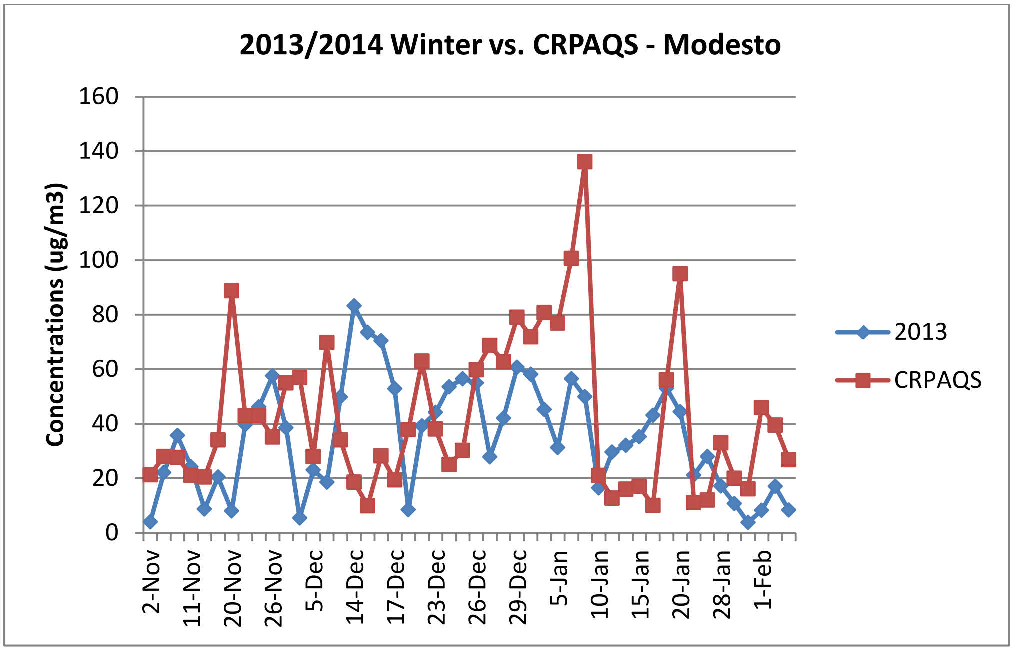
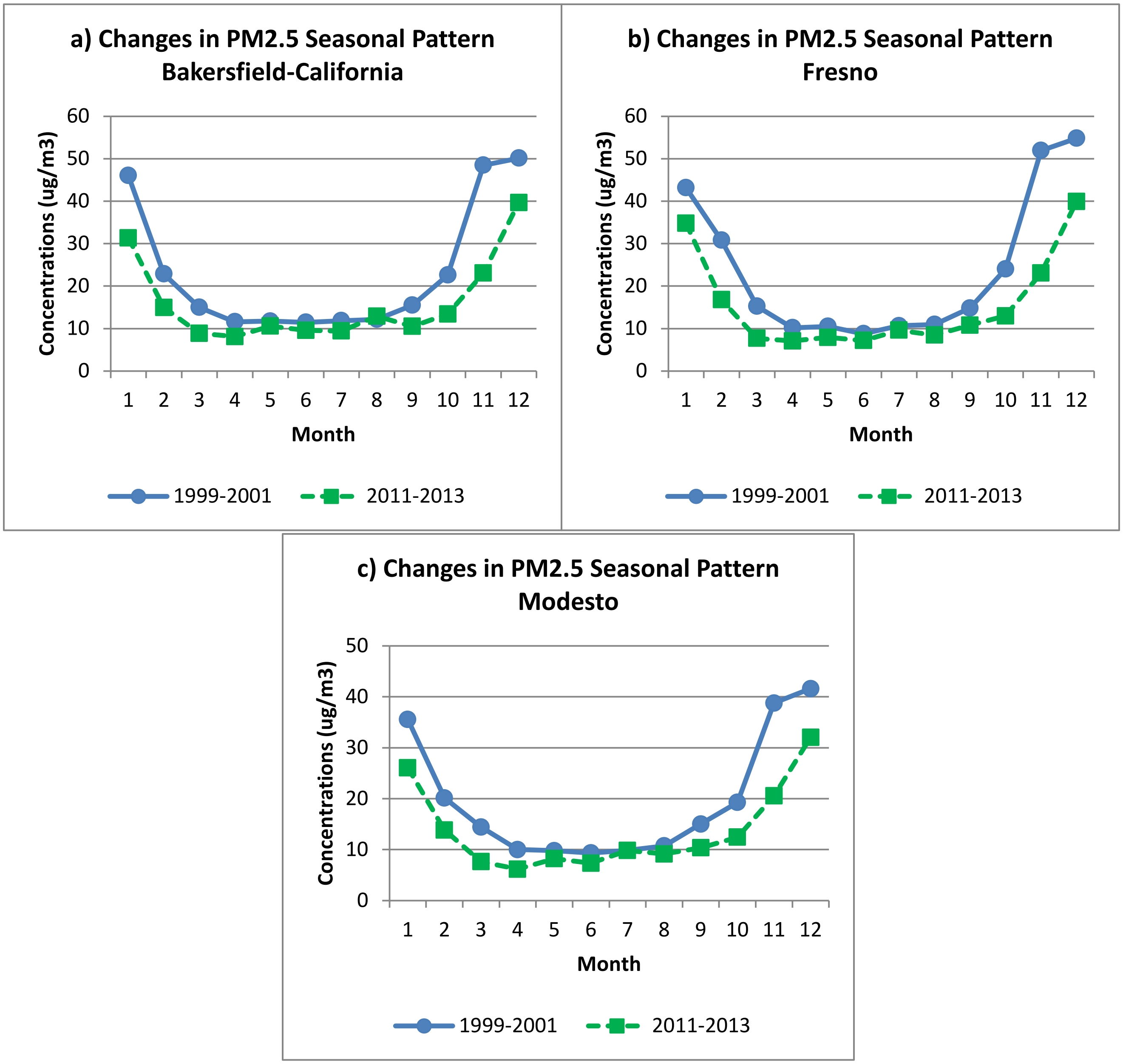


Figure 36. Comparison of the 2013/2014 PM2.5 episode to the CRPAQS episode of 2000/2001 at the Modesto monitoring site.



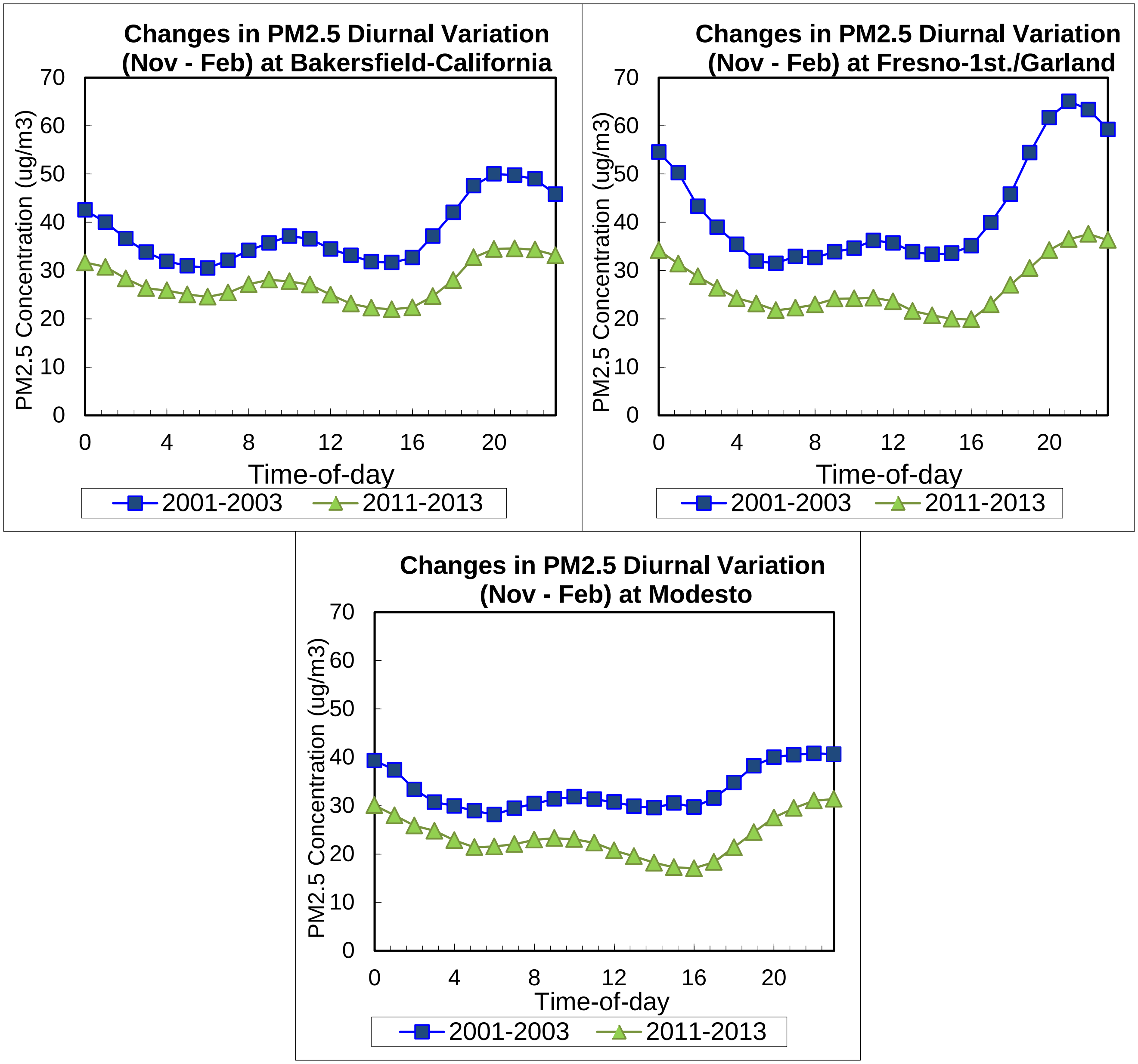
Progress in reducing PM2.5 levels is further corroborated by comparing changes in monthly average PM2.5 concentrations between 1999-2001 and 2011-2013 (Figure 37). The overall PM2.5 seasonal pattern has not changed; however the average monthly concentrations have decreased. The most significant improvements in PM2.5 have been achieved during the winter months.

Figure 37. Changes in PM2.5 monthly concentrations between the 1999-2001 and 2011-2013 three-year periods at the a) Bakersfield-California, b) Fresno-1st/Garland, and c) Modesto monitoring sites.



Comparing changes in PM2.5 diurnal patterns offers further insight. Figure 38 illustrates changes in the three-year averages of hourly PM2.5 concentrations recorded during November-February between 2001-2003 and 2011-2013 at a) Bakersfield-California, b) Fresno-1st/Garland, and c) Modesto. The overall diurnal patterns have not changed, yet hourly concentrations have decreased throughout the day. Peak daytime concentrations decreased approximately 25 to 30 percent and peak nighttime concentrations decreased approximately 20 to 40 percent.

Figure 38. Changes in the average November-February PM2.5 hourly concentrations between the 2001-2003 and 2011-2013 three-year periods at the a) Bakersfield-California, b) Fresno-1st, and c) Modesto monitoring sites.



d. Chemical composition trends

As previously discussed, PM2.5 concentrations measured at monitoring sites in the Valley have decreased from the 1999-2001 to the 2009-2012 three-year periods at Bakersfield and to the 2011-2013 period at Fresno and Modesto. Trends in individual PM2.5 chemical components, as well as emission inventory trends were evaluated to highlight the main chemical components leading to the progress in PM2.5 air quality and to evaluate the response to State and District control programs.

Speciation monitors in the SJV collect data on PM2.5 chemical composition. Figures 39, 40, and 41 illustrate the three-year average trends in the individual PM2.5 components at Bakersfield, Fresno, and Modesto. Between 2007 and 2009, the carbon collection and analysis method was changed to improve comparability with the rural IMPROVE PM2.5 carbon data. Thus, for trend analyses, the total carbon compounds mass was estimated as the difference between the measured PM2.5 mass and the inorganic components mass.

Ammonium nitrate, ammonium sulfate, and carbon compounds are the major constituents of PM2.5 levels. On an annual average basis, concentrations of these key constituents have all shown significant decreases. Ammonium nitrate concentrations in the Valley declined about 25 to 35 percent between 2004 (2002-20014 average) and 2013 (2011-2013 average). During the same time-frame, concentrations of ammonium sulfate declined about 20 to 36 percent and other, including organic and elemental carbon declined about approximately 15 percent. The most significant declines occurred between 2004 and 2005, and again between 2008 and 2011.

Figure 39. Trends in three-year average PM2.5 chemical components at Bakersfield.

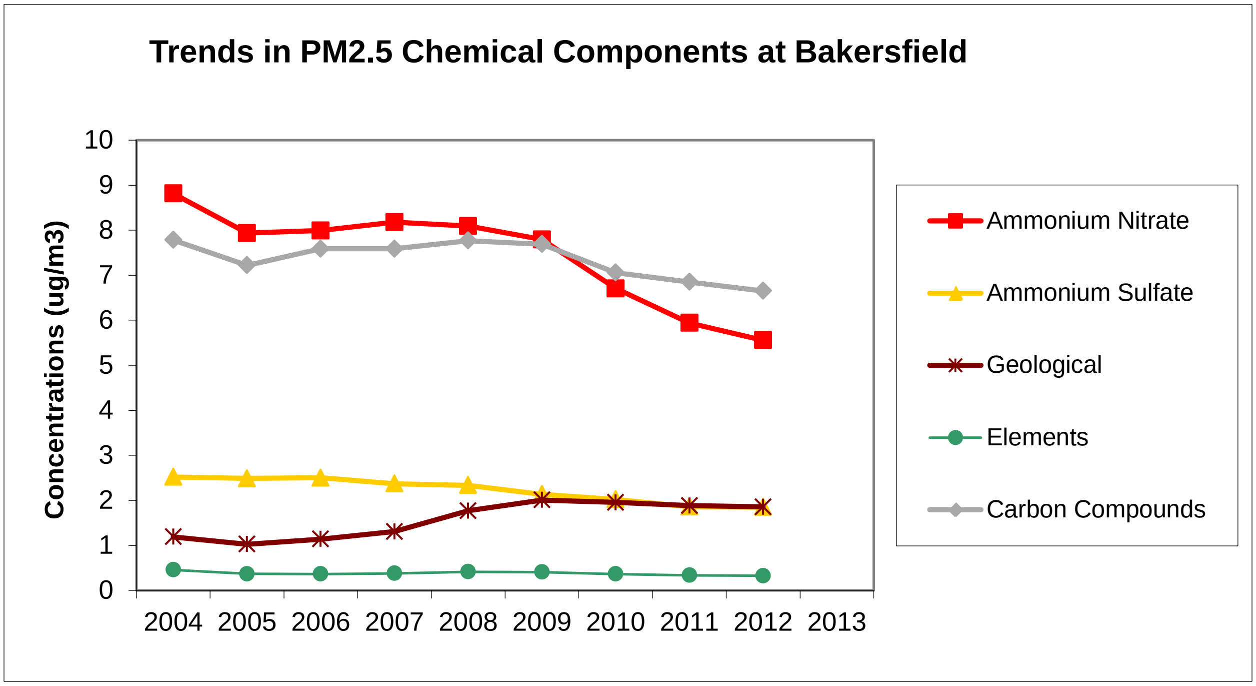


Figure 40. Trends in three-year average PM2.5 chemical components at Fresno.

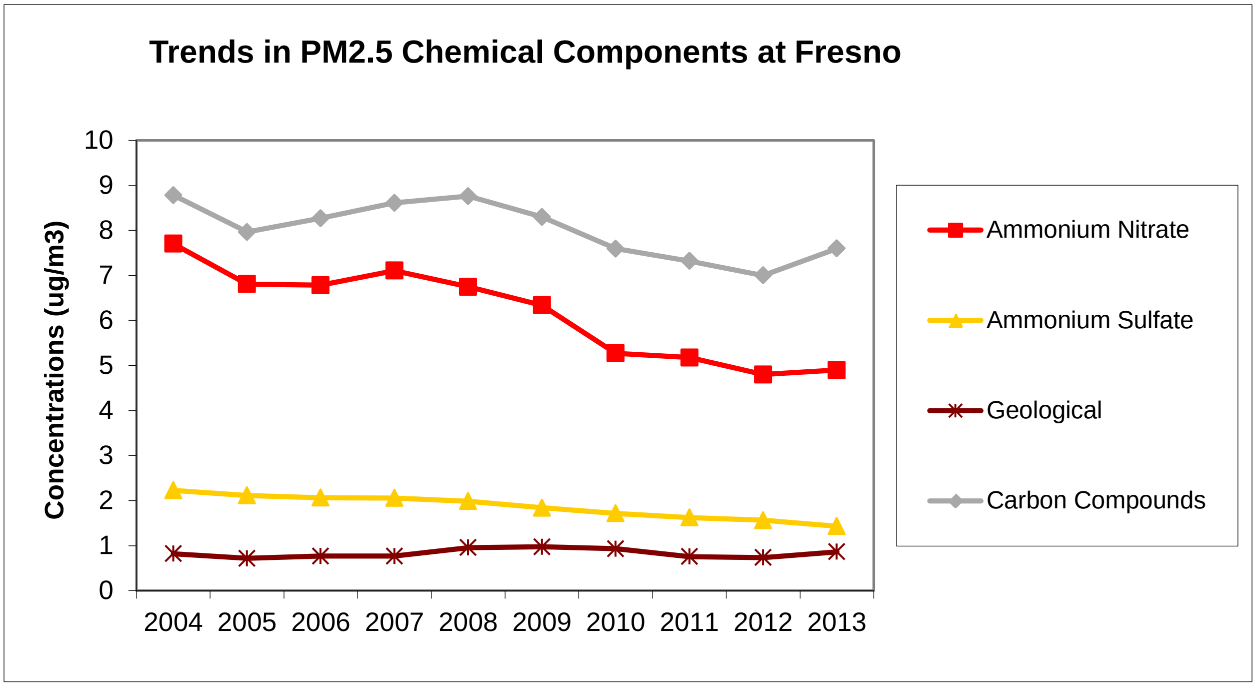
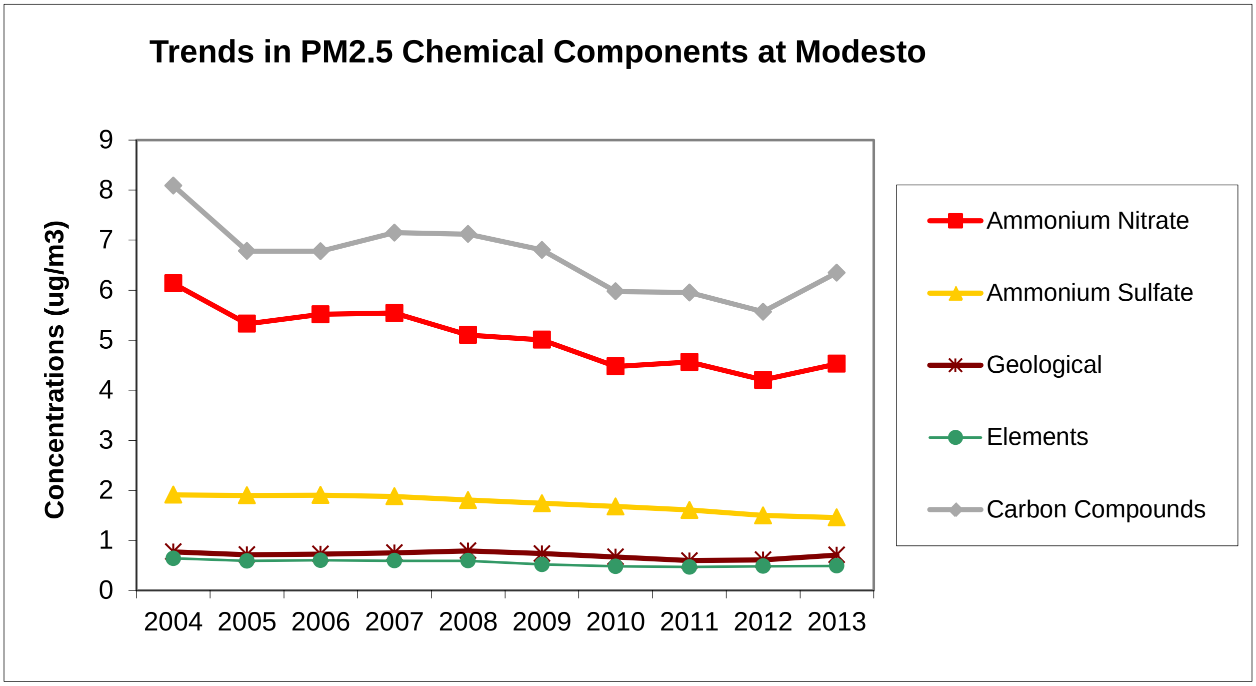


Figure 41. Trends in three-year average PM2.5 chemical components at Modesto.

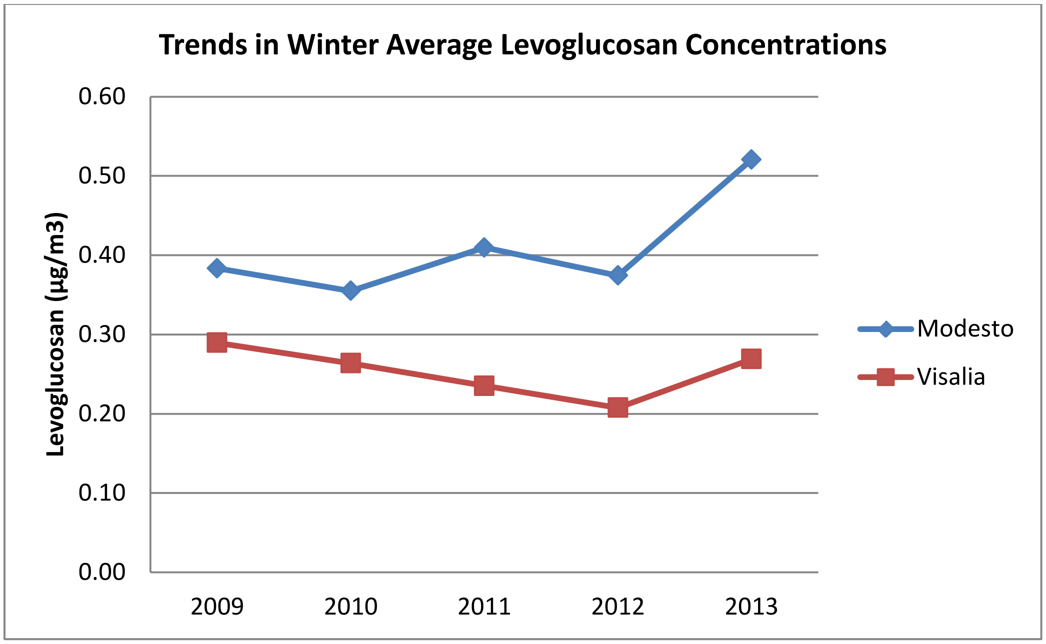


The 2015 SJV PM2.5 Plan’s Appendix A describes further analyses on PM2.5 air quality trends.

e. Trends in chemical markers of source types

Selected compounds measured in the atmosphere can serve as chemical markers for specific sources. Since 2007, ARB conducts measurements of levoglucosan, a chemical marker of wood smoke, at the Modesto and Visalia monitoring sites. Figure 42 illustrates the trends in winter time levoglucosan concentrations at these two sites. The data are presented as three-year averages (e.g., the 2009 concentration represents the 2007-2009 average concentration). Between 2009 and 2013, levoglucosan decreased by about ten percent at Visalia, with steady decrease until 2012 and a marked increase in 2013. On the other hand, levoglucosan levels at Modesto stayed approximately constant between 2009 and 2012 and increased by approximately 35 percent in 2013. The severe drought conditions led to the higher levoglucosan concentrations recorded in 2013. The District Rule 4901, which restricts residential wood-burning on days when high concentrations of PM2.5 are predicted, as well as the District's stringent smoke management program under which agricultural burning is prohibited on those same days, led to the observed reductions in levoglusoan.

Figure 42. Trends in three-year winter average levoglucosan levels at Modesto and Visalia.



f. Emission inventory trends

Reductions in PM2.5, NOx and SOx emissions are key to effectively reducing PM2.5 concentrations. Figure 43 illustrates annual emission trends in the San Joaquin Valley air basin from 2000 through 2013(1) for PM2.5 and the two key precursors.

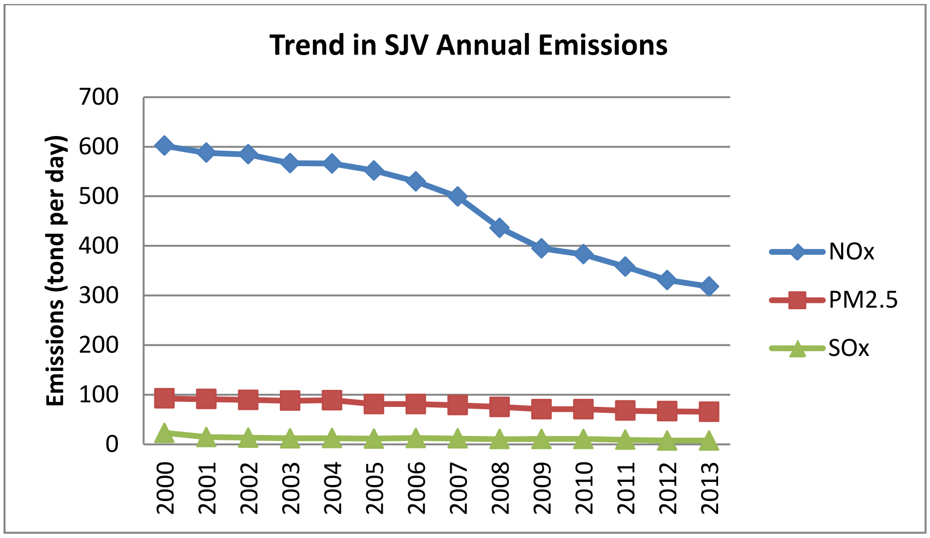
- NOx emissions have decreased by 284 tons per day (tpd) or 47 percent. Major reductions occurred in emissions from heavy-duty diesel trucks, stationary combustion sources, and other mobile sources (e.g., farm and off-road equipment, trains)

- Direct PM2.5 emissions decreased by 27 tpd or about 30 percent. Major reductions occurred in emissions from residential wood combustion, mobile sources, such as heavy-duty diesel trucks and off-road equipment, and entrained dust.

- SOx decreased by 15 tpd or about 65 percent. Major reductions occurred in emissions from stationary fuel combustion sources and industrial processes.

The combined downward trends in PM2.5 components and emissions of PM2.5, NOx, and SOx indicate that the ongoing control program has had substantial benefits in improving air quality in the SJV and that further emission reductions in the future are expected to provide continuing progress towards attaining the annual PM2.5 standard.

Figure 43. PM2.5 and PM2.5 precursor annual emission trends in the San Joaquin Valley.



(1) Historical 2000-2011 emissions are from the 2016 Ozone SIP baseline emission inventory.

10. LINKING AIR QUALITY TRENDS TO EMISSION REDUCTIONS

a. NOx control

Programs aimed at reducing NOx emissions have played an important role in reducing nitrate concentrations and, consequently, overall PM2.5 concentrations in the Valley. As discussed in section 5, previous studies have identified NOx as the limiting precursor for ammonium nitrate formation. As a result, NOx emissions and PM2.5 nitrate levels track each other over the years. Trends in estimated NOx emissions, as well as monitored ambient concentrations, are compared with trends in measured PM2.5 nitrate concentrations. As illustrated in Figure 44, between 2004 and 2012, Valley-wide NOx emissions decreased by about 41 percent, with a commensurate reduction of about 37 percent in PM2.5 nitrate concentrations at the Bakersfield and Fresno sites. Furthermore, the reductions in NOx emissions were also reflected in the corresponding reduction in the ambient gaseous NOx concentrations. Figures 45 and 46 show a strong correlation between trends in PM2.5 nitrate concentrations and ambient NOx concentrations at the Bakersfield and Fresno sites. Between 2004 and 2012, concentrations of PM2.5 nitrate decreased about 37 percent and ambient NOx decreased between 35 percent and 40 percent.

Figure 44. Comparison between trends in Valley wide annual average NOx emission and PM2.5 nitrate concentrations at Bakersfield and Fresno. Concentrations are presented as three-year averages (e.g., 2004 represents the average of 2002-2004).

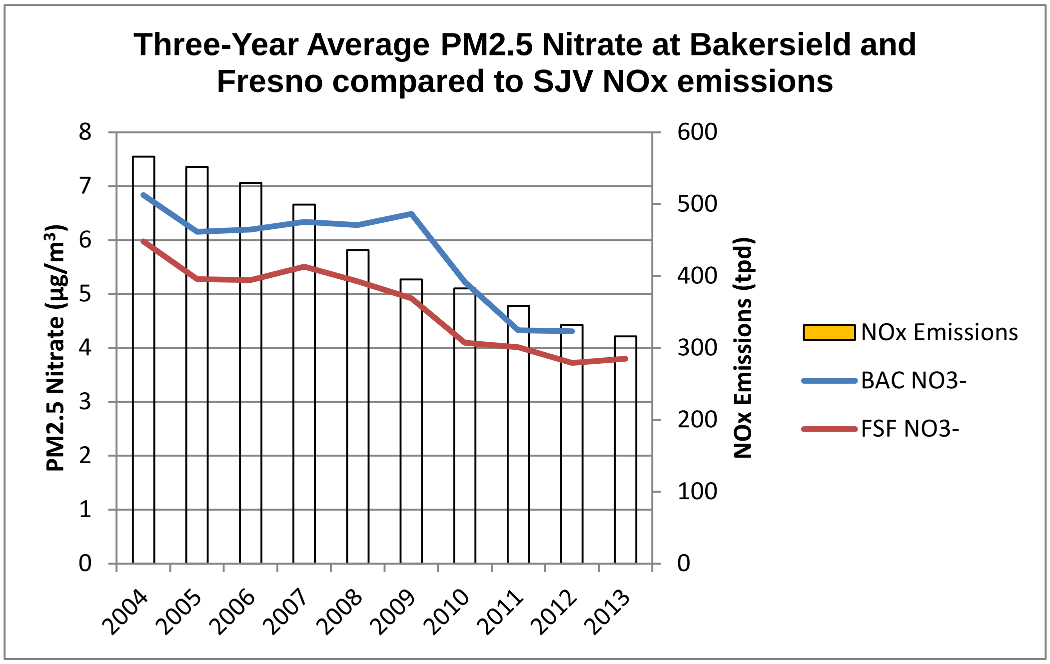


Figure 45. Comparison of trends in annual average trends in PM2.5 nitrate and NOx concentrations in Bakersfield. Concentrations are presented as three-year averages.

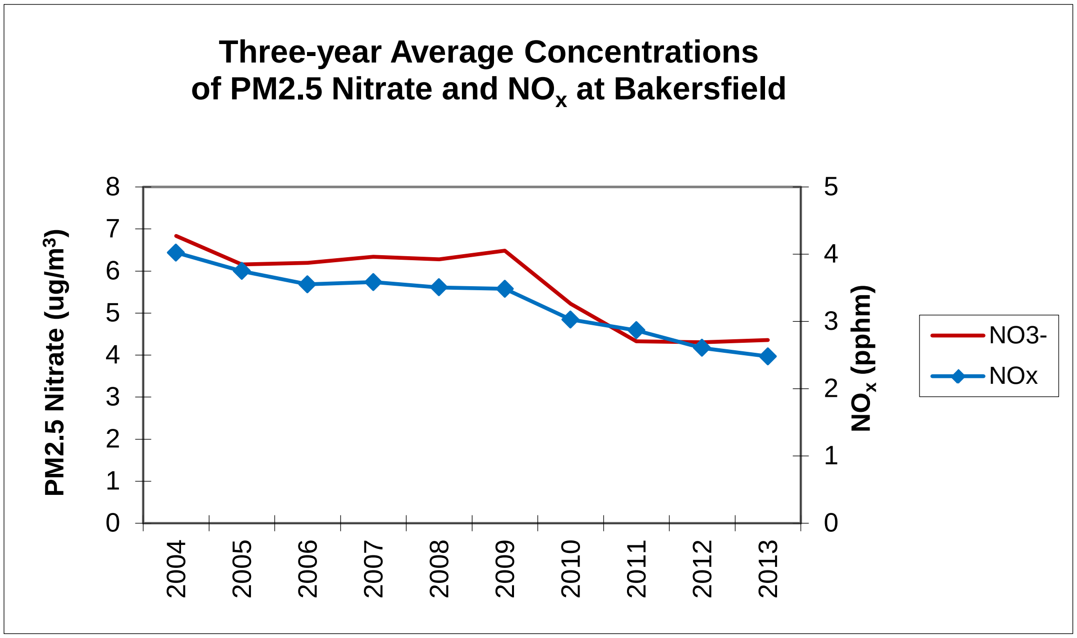
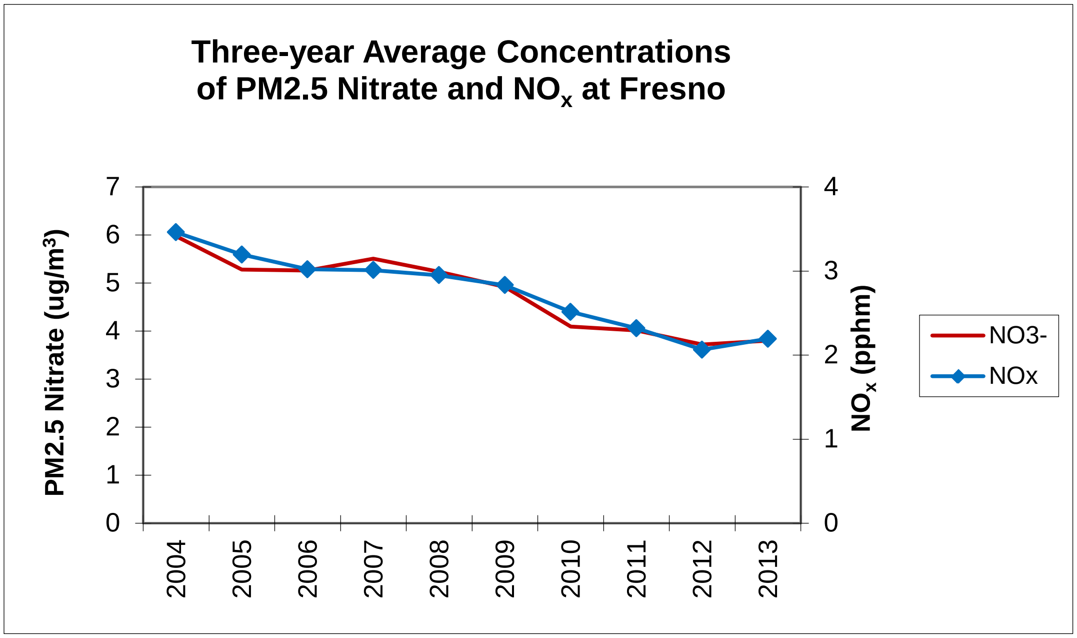


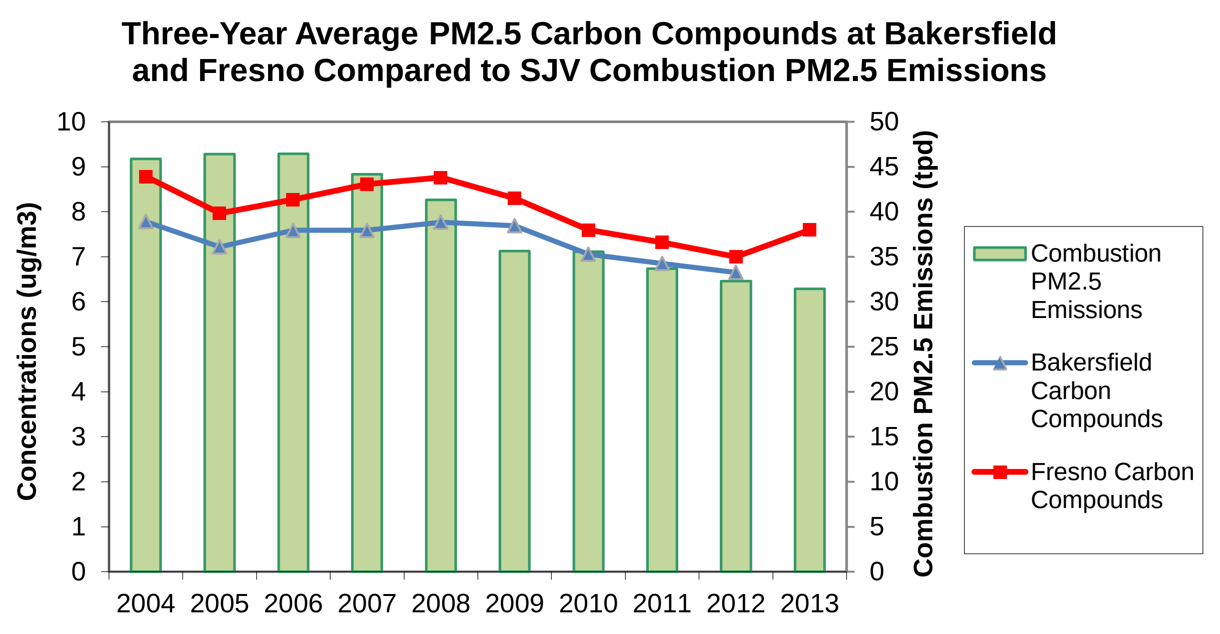
Figure 46. Comparison of trends in annual average PM2.5 nitrate and NOx concentrations in Fresno. Concentrations are presented as three-year averages.



b. Residential wood combustion controls

Programs geared at reducing PM2.5 emissions from combustion sources have played an important role in reducing overall PM2.5 concentrations in Valley. As illustrated in Figure 47, between 2004 and 2012, Valley-wide combustion PM2.5 emissions decreased by approximately 30 percent with a concomitant 15 percent reduction in measured PM2.5 carbon compounds at the Bakersfield site and 20 percent reduction at the Fresno site. The most significant declines in PM2.5 carbon compounds occurred between 2004 and 2005 and again between 2008 and 2012. The severe drought conditions in 2013 caused the observed increase in PM2.5 carbon compounds at Fresno.

Figure 47: Comparison between trends in Valley wide annual average Combustion PM2.5 emissions and concentrations of PM2.5 carbon compounds at Bakersfield and Fresno. Concentrations are presented as three-year averages (e.g., 2004 represents the 2002-2004 average).



Reductions in combustion sources include the implementation of District Rule 4901, which restricts residential wood-burning on days when high concentrations of PM2.5 are predicted. In addition, as part of the District's stringent smoke management program, agricultural burning is prohibited on those same days. Through a series of Rule 4901 amendments, the PM2.5 threshold for calling no-burn days was established in 2003 at 65 µg/m^3 and subsequently tightened to 30 µg/m^3 in 2008. Before the 2014/2015 winter, the District lowered the no-burn threshold to 20 µg/m^3 for most wood burning devices. Only the cleanest, registered, U.S. EPA certified devices are allowed to continue burning, up to a threshold of 65 µg/m^3. A grant program for the change-out of old dirty devices with cleaner woodstoves complements the no-burn program.

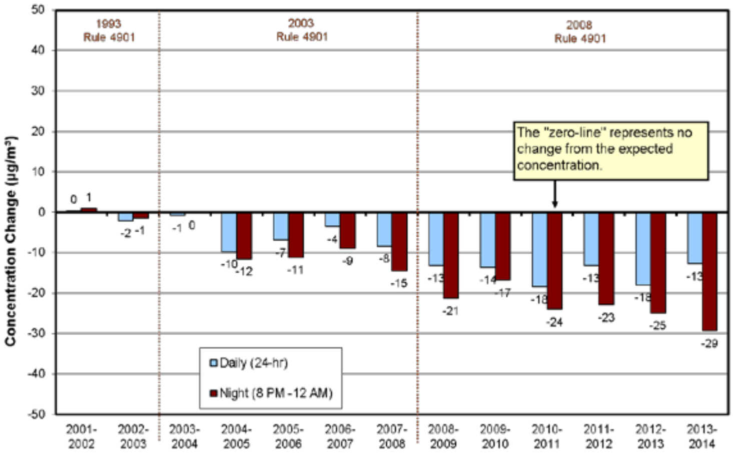
The District staff developed a statistical model to quantify PM2.5 reductions and evaluate air quality improvements attributable to the 2003 and 2008 amendments to Rule 4901. The District used generalized linear model techniques with logarithmic transformations based on the relationships between meteorology and PM2.5 concentrations that existed prior to the 2003 Rule 4901 amendments. Results from this model were used to evaluate rule effectiveness through the winter of 2013-2014.

Using daily and hourly observed PM2.5 concentrations as dependent variables with meteorological parameters such as wind speed, temperature, and stability as independent variables, statistical relationships of PM2.5 to meteorology were developed for the winters of 2001-2002 and 2002-2003. These statistical relationships made it possible to predict daily and evening PM2.5 levels in the period following the 2003 and 2008 rule amendments, which were then compared to observed PM2.5 concentrations to evaluate air quality improvements. A consistent pattern of model-predicted values being higher than what was actually observed provides statistical evidence that a control measure, e.g., wood-burning curtailments, was responsible for the changes in PM2.5 concentrations.

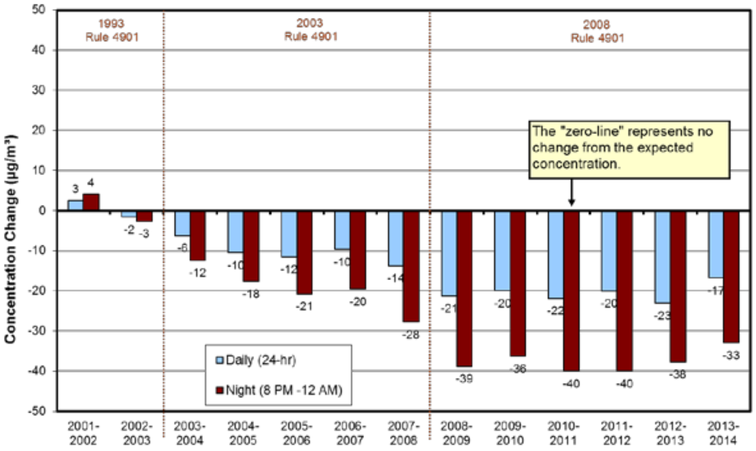
This statistical modeling indicates that significant improvement has been made after the 2003 and 2008 Rule 4901 amendments in Modesto, Fresno and Bakersfield (Figure 52). To date, there has been an average improvement of 16 µg/m^3 (40%) in the 24-hour average PM2.5 level since the 2003 and 2008 amendments. This improvement is exemplified in PM2.5 concentrations measured during the evening hours of 8:00 p.m. to 12:00 a.m., where the average concentrations have improved by 28 µg/m^3 (45%) over the same time period. The District's analysis is further described in the *End-of-Season Report on the 2013-2014 Wood-Burning Season* (http://www.valleyair.org/Board_meetings/GB/agenda_minutes/Agenda/2014/April/final/07.pdf)

Figure 52: Change in 24-hour and night-time (8 pm to 12 am) PM2.5 concentrations by Rule period in a) Modesto, b) Fresno, c) Bakersfield

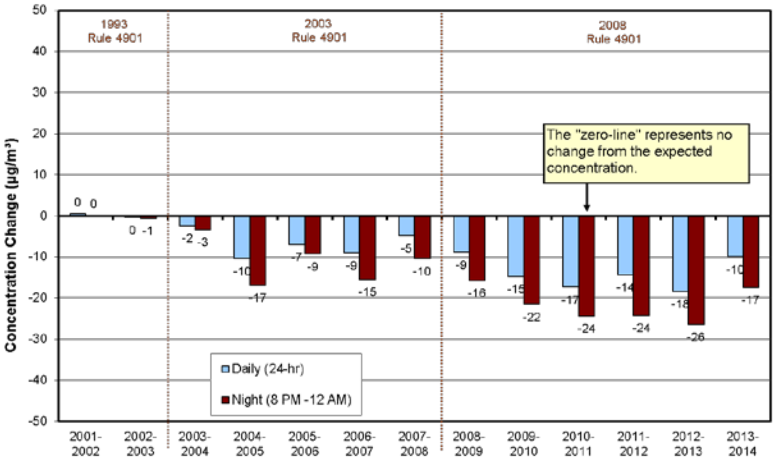
a) Modesto



b) Fresno



c) Bakersfield.



11. MODELED ATTAINMENT DEMONSTRATION

The U.S. EPA approved air quality modeling for the 2008 PM2.5 SIP provided the basis to predict future PM2.5 concentrations at each monitoring site in the San Joaquin Valley. The attainment demonstration uses the fundamental chemistry and associated response of different $PM_{2.5}$ constituents to emission controls reflected in the modeling in the 2008 PM2.5 SIP. This modeling science is coupled with air quality data reflecting 2013 design values and PM2.5 chemical composition, along with emission reductions expected in 2020 (for the annual standard demonstration) and in 2018 (for the 24-hour demonstration).

The implementation of new reductions from California's on-going emission control programs will provide the majority of the emission reductions needed to attain the annual PM2.5 standard throughout the San Joaquin Valley in 2020. Between 2012, the base year used in the photochemical modeling attainment demonstration and 2020, implementation of these control programs will reduce NOx emissions by 38 percent. The NO_x reductions result from ongoing implementation of both new vehicle standards for passenger and heavy-duty diesel vehicles and equipment, as well as rules accelerating the turnover of legacy diesel fleets. Implementation of stringent requirements for new off-road engines and in-use off road equipment lead to further NO_x reductions, along with District rules addressing stationary source NO_x emissions. The weight of evidence analysis has demonstrated that prior reductions in NOx have resulted in commensurate reductions in ambient concentrations of nitrate.

In addition, directly emitted PM2.5 emissions in aggregate are decreasing by eight percent. PM2.5 emission reductions result from ongoing implementation of diesel on- and off-road equipment measures as well as the District's recently strengthened rule for wood-burning fireplaces and heaters. These measures, along with additional reductions from enhancements to the District's commercial charbroiling rule slated for adoption in 2016 provide the necessary control strategy to bring the entire Valley into attainment of the 24-hour standard by 2018, and the annual standard by 2020.

Tables 5 and 6 list the Valley-wide emissions levels used in the annual and 24-hour PM2.5 attainment demonstrations, respectively. Baseline emission levels reflect the implementation of adopted ARB and District control measures. Three additional District rules that were adopted subsequent to the preparation of the baseline inventory plus one new commitment provide the remaining emissions reductions needed to reach the attainment targets.

Table 5. Annual average attainment level emissions in tons per day (tpd)

Emission Inventory	2020 Annual Average Emissions (tpd)		
	PM2.5	**NOx**	**SOx**
Baseline Emissions	62.8	206.9	7.9
Emission Reductions from District Control Measures			
• Rule 4901 Wood Burning Fireplaces and Wood Burning Heaters (Adopted)	1.6	0.0	0.0
• Rule 4905 Natural Gas-Fired, Fan-Type Residential Central Furnaces (Adopted)	0.0	0.4	0.0
• Rule 4308 Boilers, Steam Generators, and Process Heaters 0.075 to <2 MMBtu/hr (Adopted)	0.0	0.0	0.0
• Rule 4692 Commercial Charbroiling (Commitment)	0.4	0.0	0.0
Attainment Emission Levels	60.8	206.5	7.9

Table 6. Winter average attainment level emissions in tpd

Emission Inventory	2018 Winter Average Emissions (tpd)		
	PM2.5	**NOx**	**SOx**
Baseline Emissions	57.7	213.9	7.6
Emission Reductions from District Control Measures			
• Rule 4901 Wood Burning Fireplaces and Wood Burning Heaters (Adopted)	2.9	0.0	0.0
• Rule 4905 Natural Gas-Fired, Fan-Type Residential Central Furnaces (Adopted)	0.0	0.2	0.0
• Rule 4308 Boilers, Steam Generators, and Process Heaters 0.075 to <2 MMBtu/hr (Adopted)	0.0	0.0	0.0
• Rule 4692 Commercial Charbroiling (Commitment)	0.4	0.0	0.0
Attainment Emission Levels	54.4	213.7	7.6

Table 7 lists the 2013 annual design values along with projected 2020 annual design values ranging from 12.5 µg/m^3 to 15.0 µg/m^3, demonstrating the Valley will attain the annual standard in 2020.

Table 7. Modeled 2020 Annual PM2.5 Design Values

Monitoring Site	2013 Annual Design Value (µg/m^3)	2020 Annual Design Value (µg/m^3)
Bakersfield - California Street	16.4	13.7
Bakersfield - 410 E Planz	17.0	14.3
Clovis - N Villa Avenue	16.4	13.3
Fresno - 1st Street/Garland	15.4	12.5
Fresno - Hamilton and Winery	14.7	12.0
Hanford-S Irwin Street	17.0	13.9
Madera	18.1	15.0
Manteca-530 Fishback Rd	10.2	8.7
Merced - 2334 M Street	11.1	9.2
Merced – S Coffee Ave	13.3	11.0
Modesto - 14th Street	13.6	11.5
Stockton - Hazelton Street	13.8	12.0
Tranquility	7.9	6.6
Turlock-S Minaret Street	15.7	13.2
Visalia - N Church Street	16.6	13.5

Although 2013 24-hour design values show the entire Valley to be in attainment for the standard, the modeling analysis was also conducted for this standard. As previously described, the analysis includes new emission reductions in each year between now and 2018 from implementation of a combination of adopted ARB and District programs. As shown on Table 8, modeling results indicate these control programs will result in 2018 24-hour design values ranging between 24 µg/m^3 and 52 µg/m^3. For sites with 2013 design values over 60 µg/m^3, the modeled 2018 design values range between 46 µg/m^3 and 52 µg/m^3 (71-80 percent of the standard).

Table 8. Modeled 2018 24-hour PM2.5 Design Values

Monitoring Site	**2013 Annual Design Value (µg/m^3)**	**2020 Annual Design Value (µg/m^3)**
Bakersfield - California Street	16.4	13.7
Bakersfield - 410 E Planz	17.0	14.3
Clovis - N Villa Avenue	16.4	13.3
Fresno - 1st Street/Garland	15.4	12.5
Fresno - Hamilton and Winery	14.7	12.0
Hanford-S Irwin Street	17.0	13.9
Madera	18.1	15.0
Manteca-530 Fishback Rd	10.2	8.7
Merced - 2334 M Street	11.1	9.2
Merced – S Coffee Ave	13.3	11.0
Modesto - 14th Street	13.6	11.5
Stockton - Hazelton Street	13.8	12.0
Tranquility	7.9	6.6
Turlock-S Minaret Street	15.7	13.2
Visalia - N Church Street	16.6	13.5

a. Impact of preliminary 2014 PM2.5 data

The drought-related meteorological conditions that affected PM2.5 concentrations in the San Joaquin Valley during 2013 continued into 2014. Although complete data for 2014 is not yet available, this section provides a preliminary assessment of 2014 air quality data in relation to the attainment demonstration.

Despite the ongoing persistence of the drought, air quality conditions in 2014 generally improved at most locations, particularly in the northern and central portions of the Valley. This is an indication that although drought conditions are continuing, progress is resuming as a result of ongoing emission reductions. However, because 2014 design values will reflect the impact of multiple years of drought, a comparison to the 2013 design values used in the attainment demonstration is expected to be mixed, with some locations recording design values that are slightly lower, and other locations recording design values that are slightly higher. Based on an assessment of the PM2.5 levels predicted for 2020 as well as ongoing trends and analyses, consideration of 2014 design values is expected to remain consistent with the current attainment demonstration. However, ARB and the District will continue to monitor the impacts of the drought and its relationship to future PM2.5 attainment needs.

12. SUMMARY

Consideration of the entirety of information presented in the weight of evidence provides a consistent assessment that supports the modeled attainment date of 2018 for the 24-hour PM2.5 standard and 2020 for the annual PM2.5 standard. The substantial continuing reductions that will result from implementation of the ongoing control program, coupled with measures addressing residential wood burning and cooking, are consistent with the results predicted in the modeled attainment demonstration. This weight of evidence assessment is based upon the following factors:

- Over the last 12 years progress has occurred in reducing annual PM2.5 concentrations. The annual design value has decreased by over 30 to 35 percent.

- The 24-hour design value has decreased by 30 to 45 percent, while the number of exceedances has decreased by 60 to 80 percent.

- The attainment demonstration accounts for drought related meteorological conditions that caused the 2013 annual and 24-hour PM2.5 design values to be higher than in previous years.

- Both receptor and photochemical grid based modeling have identified residential wood burning as a significant contributor to wintertime PM2.5 concentrations. The reductions in the carbonaceous component of PM2.5 that have occurred can be linked to implementation of the District's residential wood burning curtailment program.

- Evaluation of emissions inventory data, monitoring studies, and photochemical modeling indicate that controlling NOx emissions is the most effective strategy to reduce ammonium nitrate concentrations.

- Evaluation of monitoring studies and photochemical modeling indicates that controlling VOCs is not an effective strategy to reduce nitrate concentrations.

- The decrease in ammonium nitrate concentrations observed at Valley monitoring sites tracks concurrent reductions in NOx emissions as well as trends in gaseous NOx concentrations.

- Substantial NOx and PM2.5 emission reductions will occur between 2012 and 2020 due to the implementation of on-going measures and additional new measures. As a result of these programs, NOx emissions will decrease by 38 percent, and PM2.5 emissions by nearly eight percent.

- The modeled attainment demonstration predicts that all sites in the Valley will attain the annual standard by 2020. This modeling assessment is consistent with the benefits seen from previous reductions in the sources and pollutants being addressed as part of the attainment strategy.

- The attainment demonstration shows that in 2018 the 24-hour PM2.5 standard will be attained.

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SAN JOAQUIN VALLEY PM2.5 WEIGHT OF EVIDENCE ANALYSIS

APPENDIX A1

CALIFORNIA REGIONAL PM10/PM2.5 AIR QUALITY STUDY PUBLICATIONS

CALIFORNIA REGIONAL PM10/PM2.5 AIR QUALITY STUDY PUBLICATIONS

1. Roth, P. M. et al., 1993, “A Proposed PM-10 Program for the San Joaquin Valley”, prepared by Envair for the San Joaquin Valleywide Air Pollution Study Agency.

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SAN JOAQUIN VALLEY PM2.5 WEIGHT OF EVIDENCE ANALYSIS

APPENDIX A2

ASSESSMENT OF THE REPRESENTATIVENESS OF 2011 PM2.5 BETA ATTENUATION MONITOR DATA FROM MADERA

Assessment of the Representativeness of 2011 PM2.5 Beta Attenuation Monitor Data from Madera

Overview

PM2.5 monitoring in Madera began in 2010 with deployment of the Federal Equivalence Method Beta Attenuation Monitor (FEM BAM) at the San Joaquin Valley Air Pollution Control District (SJVAPCD) Madera City monitoring site. Since there was no previous PM2.5 data record for Madera, there was no baseline for evaluating the PM2.5 levels measured with the BAM. Based on established concentration gradients within the San Joaquin Valley, concentrations measured in Madera are expected to be similar or slightly higher than measurements in Merced, but lower than those from Fresno. They should also depict a strong seasonal pattern, with low season average concentrations below 10 µg/m^3. However, the first complete data year, 2011, did not conform with these expectations.

Comparison of 2011 concentrations measured at Madera and Fresno revealed that on an annual basis, Madera was 30 percent higher compared with measurements in Fresno, or 4.8 µg/m^3. During what is typically regarded as the low PM season, measured concentrations at Madera were twice as high as those measured in Fresno.

As SJVAPCD monitoring staff continued to perform required operational checks on the BAM, the measurement differences between the two sites decreased. However, it was not until 2014 when additional technical adjustments consistent with BAM operational protocols were made, and parallel Federal Reference Method (FRM) monitoring was conducted for verification of measured levels, that measured concentrations from the BAM began to reflect the spatial and temporal variation characteristic of the Valley.

The analysis presented below indicates that 2011 data collected at Madera were not representative of air quality in the area. Nevertheless, use of these data in the attainment demonstration, coupled with data presented in the weight of evidence document, shows attainment of the 15 µg/m^3 annual PM2.5 standard by 2020.

PM2.5 FEM BAMs in the Monitoring Network

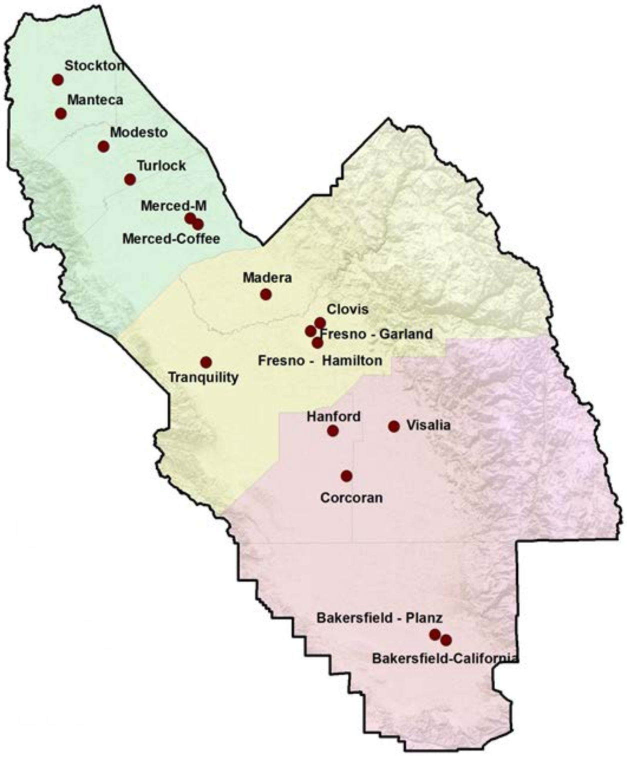
The BAM instruments play an important role in California's monitoring program because they collect continuous data and they are less resource intensive to operate. In many applications throughout the State, the BAM measurements have been found to be higher than FRM monitors run in parallel, especially when low concentrations are anticipated. Recognizing the potential issues with comparability of PM2.5 BAM data to filter-based FRM monitor data, U.S. EPA provided flexibility in how these data are used in determining compliance with National Ambient Air Quality Standards (NAAQS). The U.S. EPA enables each agency to specify if they intend to use data from PM2.5 FEM

BAMs for comparison to the NAAQS. U.S. EPA has previously approved requests to exclude FEM BAMs for use in establishing compliance with the NAAQS in both, the South Coast and San Diego.   However, this type of request requires parallel FRM/FEM monitoring, which was not available at Madera in 2011.

Comparison of PM2.5 FEM BAM at Madera and PM2.5 FRM at Fresno for 2011

Figure 1 shows the location of PM2.5 monitors in the San Joaquin Valley. Multiple years of PM2.5 data indicate that concentrations have a distinct spatial pattern, increasing from the northern portion to the southern portion of the Valley. Figure 2 illustrates trends in the design value for the three regions in the Valley. The two central Valley monitoring sites with FEM BAMs, Clovis and Madera, are not included in Figure 2, since readings from these two sites altered previously established FRM-based concentration gradients. Since 2005, the basin design value came from sites in the southern portion of the Valley. Based on this established spatial gradient, we expect concentrations at Madera to be higher than at Merced, but lower than at Fresno. In 2013 Madera had the highest annual design value in the basin.

Figure 1. San Joaquin Valley PM2.5 Monitoring Locations



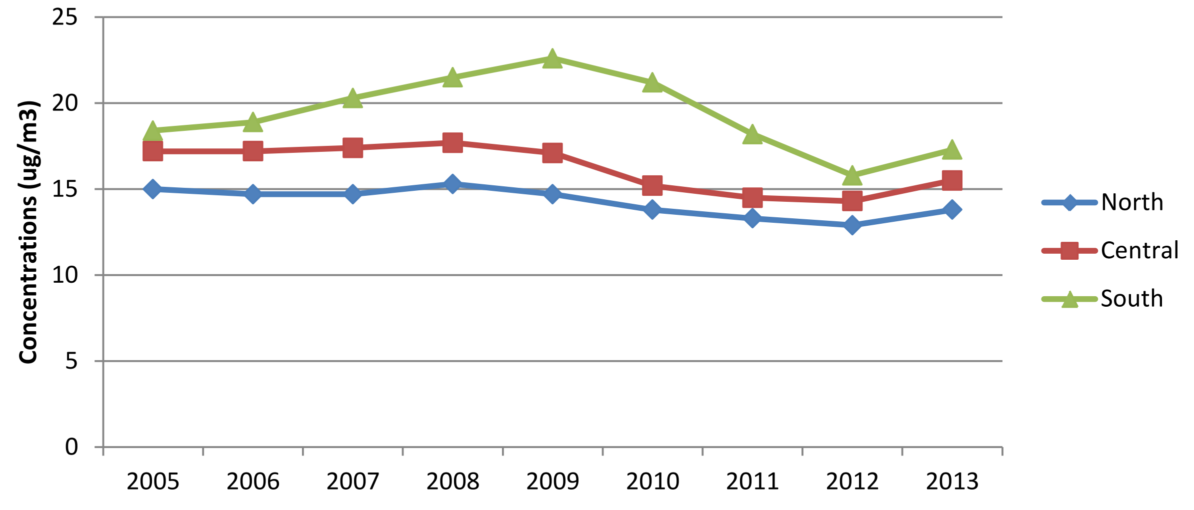


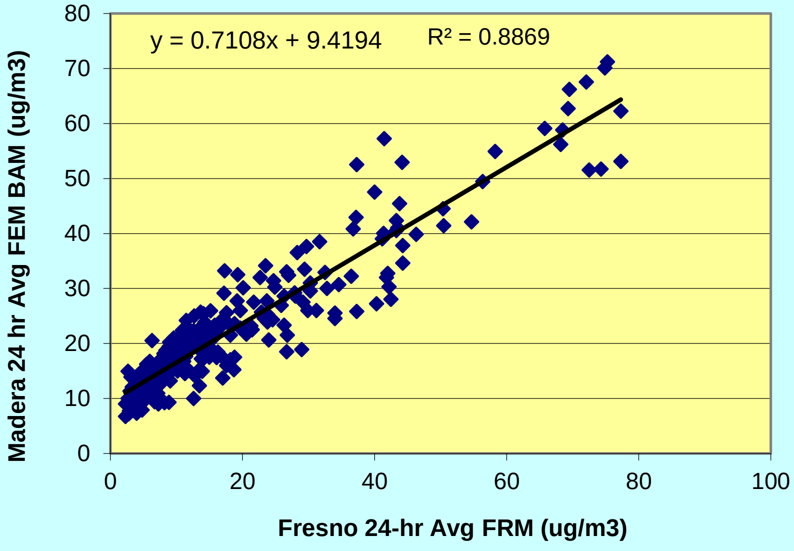
Figure 2. Gradient in PM2.5 Design Values Among Different Regions in the SJV
***Madera and Clovis BAM values excluded**

Comparison of 2011 Madera BAM data and Fresno FRM data revealed that PM2.5 concentrations at Madera were significantly higher compared to the FRM at Fresno. Table 1 and Figure 3 compare the data for two sites. Concentrations at the two sites correlated well, with a correlation coefficient of 0.94. This correlation suggests that the concentrations at both sites are driven by regional meteorological phenomena. However, the 2011 Madera and Fresno averages, based on matching data, were 20.9 µg/m^3 and 16.1 µg/m^3, respectively. During the low season the difference was further magnified, with Madera concentrations on average twice the level of Fresno. The very high intercept of more than 9.4 µg/m^3 suggests a bias in the FEM BAM reading at Madera.

Table 1. Comparison of PM2.5 FRM Concentrations at Fresno to PM2.5 FEM BAM Concentrations at Madera for 2011

FRM	*FEM*	*Count*	*Slope*	*Intercept*	*Correlation (r)*
Fresno-1st Average: 16.1 µg/m^3	Madera Average:20.9 µg/m^3	340	0.71	9.42	0.94

Figure 3. Comparability of Madera FEM BAM and Fresno FRM



Low Season BAM Data Significantly Impacted by Sampling Artifacts

PM2.5 concentrations in the Valley exhibit a pronounced seasonal pattern with high concentrations during winter and low concentrations the rest of the year. During the 2011 low season, PM2.5 concentrations at Madera were significantly higher than the rest of the sites in the Valley. As illustrated in Figure 4 and Table 2, the Madera BAM concentrations were twice the level of the closest FRM, located in Fresno.

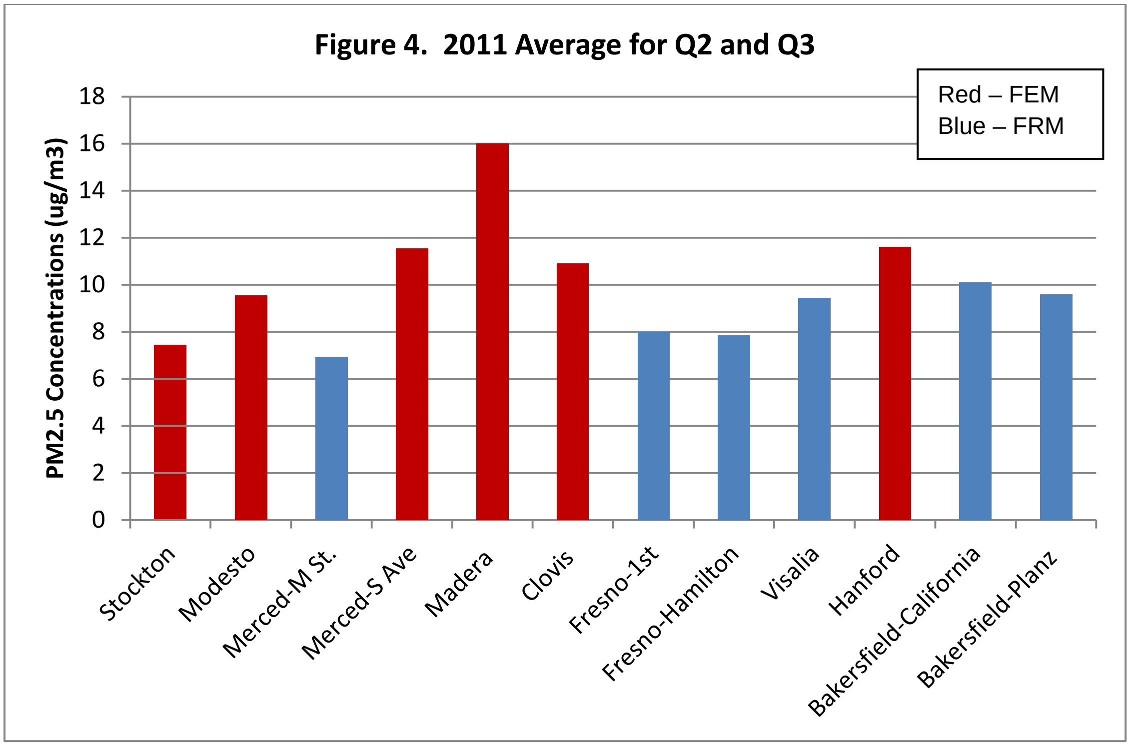


Table 2. Difference in Measured Concentrations between Madera and Fresno

Site Name (units)	***2011***	***2012***	***2013***
Madera (µg/m^3)	16.1	14.8	13.9
Fresno (µg/m^3)	8.1	9.0	8.4
[Madera] – [Fresno] (µg/m^3)	8	6	5
[Madera] – [Fresno] (as % of Fresno conc.)	100	63	65

The BAM sampling artifact at the Madera site is further illustrated by the number of days with low PM2.5 concentrations. Typically, half of the samples annually have concentrations less than 10 µg/m^3. In 2011, as shown in Table 3, over half of the samples collected at Fresno were below 10 µg/m^3, but only 7 percent of samples at Madera were below that level.

Table 3. Percent of Samples with PM2.5 concentrations below 10 µg/m^3

Year	***Madera***	***Fresno***
2011	7	52
2012	22	48
2013	16	46

Zero Adjustment Impact on BAM Readings at Madera

An annual background zero test is conducted on PM2.5 FEM BAMs to establish the value of any adjustment that may be needed due to a bias in measurement, including beta-source fluctuations, mechanically induced bias, and site-specific interferences such as radio frequencies or other electromagnetic perturbations. The zero adjustment test on the FEM monitor at Madera was initially conducted using internal air. In April of 2014, the instrument was, for the first time, adjusted using external air. Following this adjustment, low season concentrations shifted downward compared to the previous years (Figure 8) and are more consistent with other monitors in the Valley (Figure 9).

Figure 8. Comparison of Monthly Average PM2.5 Concentrations at Madera

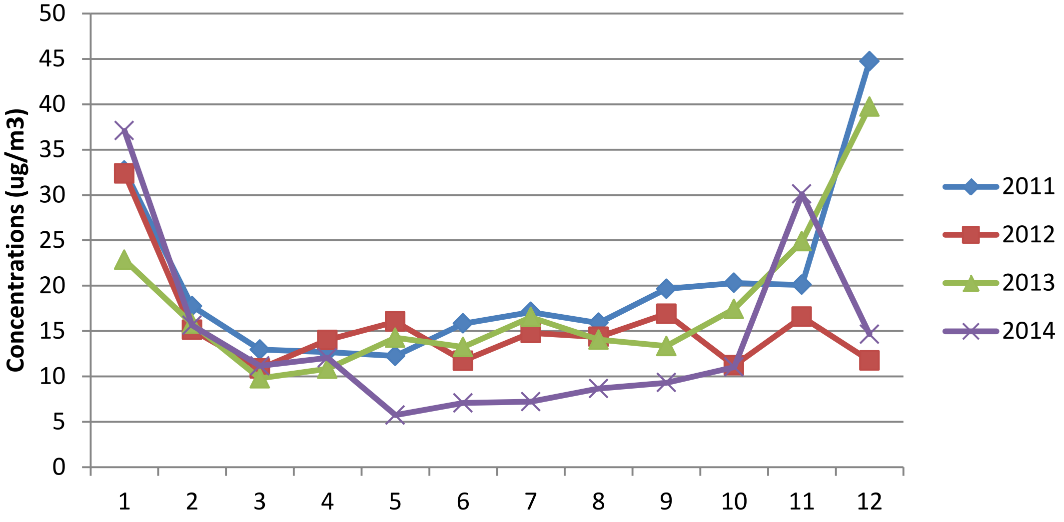


Figure 9. Comparison of 2014 Monthly Average PM2.5

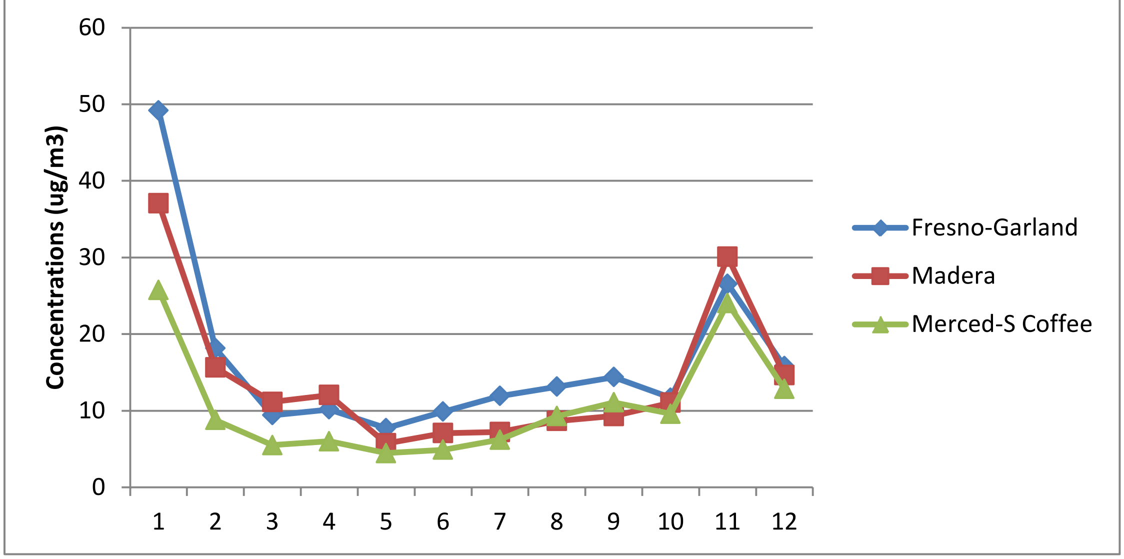
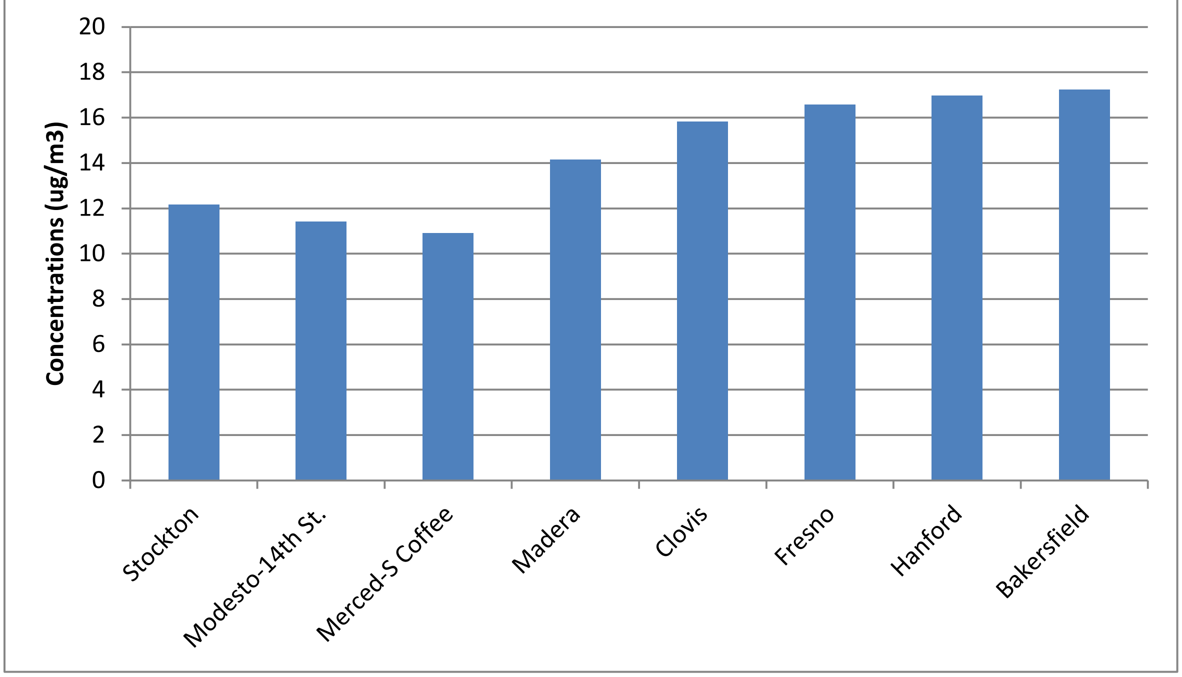


Figure 10 shows average concentrations based on 2014 data. The sites are organized based on their latitude, from north to south to illustrate that the concentration gradient is consistent with location. Figure 11 shows that in 2014 Madera is no longer the highest site in the basin or the highest site in the central portion of the Valley, and the spatial gradient is now consistent with past data patterns.

Figure 10. Average BAM Concentrations in 2014



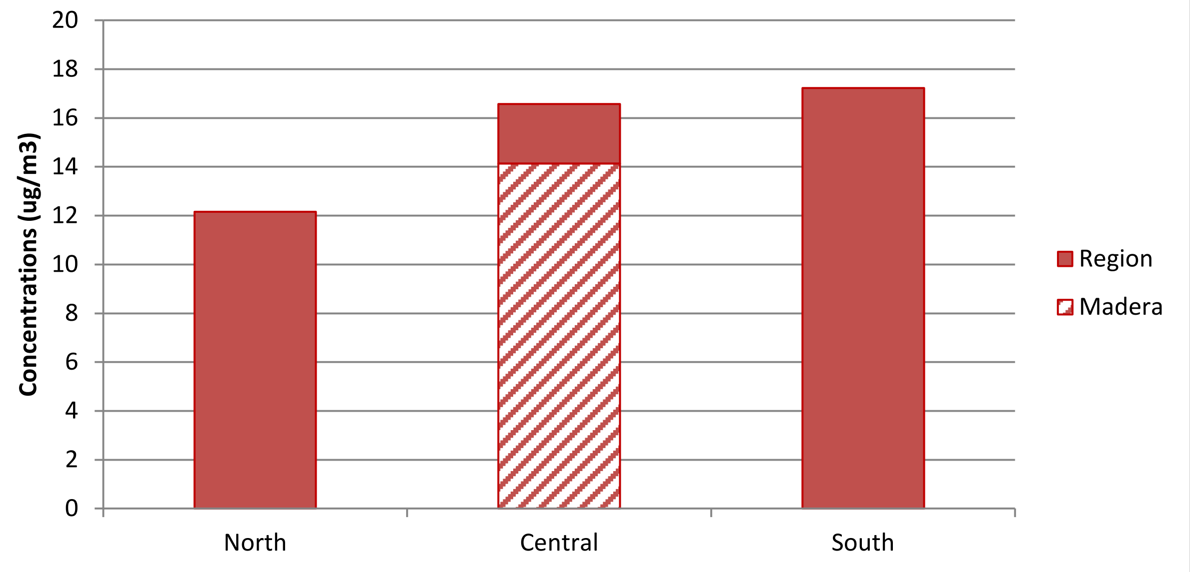


Figure 11. Gradient in Concentrations Based on 2014 BAM data

Parallel FRM Monitoring at Madera

To further understand the data collected at Madera, in July of 2014, an FRM sampler was deployed to run in parallel with the BAM at the Madera site. These parallel data show that after the shift in concentrations in late April/early May, the BAM monitor is now reporting concentrations consistent with the FRM. The parallel FRM/BAM data for July through September 2014 indicates the BAM is running about 7 percent or 0.6 µg/m^3 higher. The average BAM concentrations for July through September were 8.9 µg/m^3, which is about 50 percent lower compared to what Madera measured in previous years (Figure 12) and is more consistent with what other sites are measuring during these three months (Figure 13).

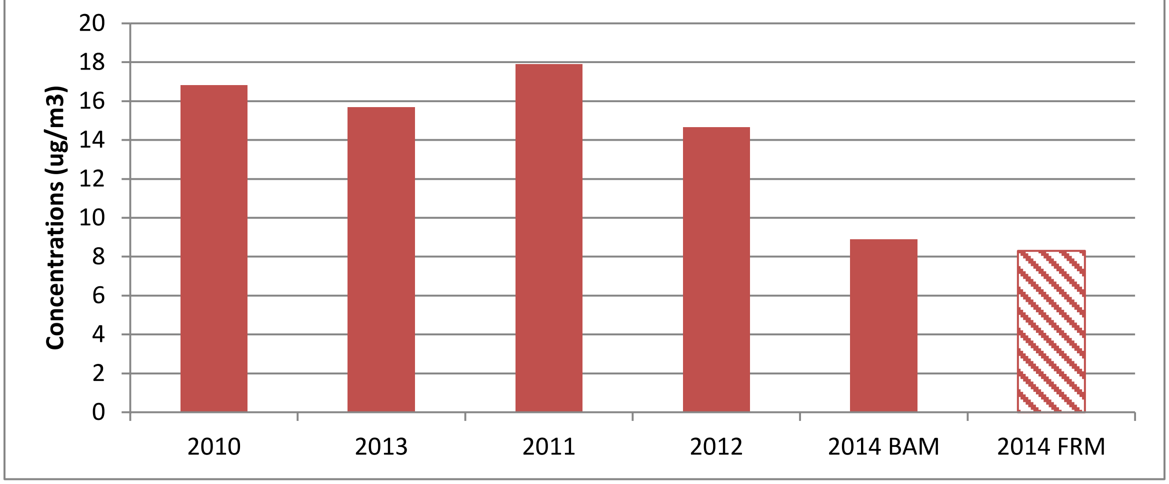


Figure 12. Average July through September Concentrations in Madera

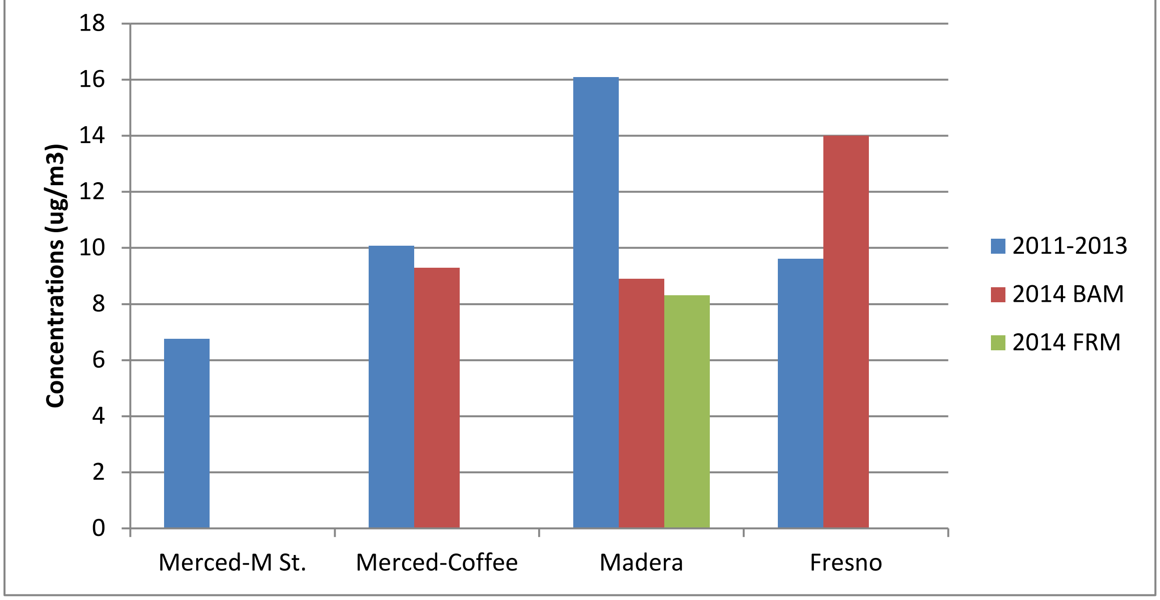


Figure 13. Comparison of July through September Average PM2.5

Conclusions

2011 PM2.5 FEM BAM data at Madera appear to be biased high due to sampling artifacts. While these data are not representative of air quality in the central portion of the Valley, staff has nevertheless included them in the attainment demonstration. In 2014 a PM2.5 FRM was deployed at Madera to run in parallel with the FEM BAM to help verify measured concentrations. It is expected that this parallel monitoring, along with the proper sampler maintenance and operation, will lead to future design values that are representative of air quality in the region. As listed in Table 4, the 2014 annual design value is already 2.1 µg/m^3 lower compared to 2013. Since the 2011 annual average will no longer be included in the calculation, we anticipate that the 2015 design value will be lower and the Madera site will continue to make progress towards attainment.

Table 4. Annual Average and Design Values for Madera

Annual Average (µg/m^3)				***Annual DV (µg/m^3)***	
2011	***2012***	***2013***	***2014***	***2013***	***2014***
20.4	16	17.8	14.1	18.1	16.0

SAN JOAQUIN VALLEY PM2.5 WEIGHT OF EVIDENCE ANALYSIS

APPENDIX A3

PM2.5 SOURCE APPORTIONMENT FOR THE SAN JOAQUIN VALLEY AIR BASIN USING THE CHEMICAL MASS BALANCE RECEPTOR MODEL

PM2.5 Source Apportionment for the San Joaquin Valley Air Basin Using the Chemical Mass Balance Receptor Model

1) Data Collection and Screening

PM2.5 chemical composition data collected at the Bakersfield-California and Fresno-1st Street sites were used for the Chemical Mass Balance (CMB) analysis. The two sites are part of the Chemical Speciation Network (CSN) and use the SASS (Spiral Aerosol Speciation Sampler, Met One, Grants Pass, OR.) for data collection. The Bakersfield-California and Fresno-1st samplers are configured with several channels, each channel containing one 47mmfilter with a 6.7 L/min flow rate. One channel contains a Whatman Teflon®-membrane filter for mass by gravimetry and elements by XRF. Another channel includes a magnesium oxide-coated aluminum (Al) honeycomb after the cyclone followed by a Nylasorb nylon-membrane filter for water-soluble anions i.e., NO_3^- and $SO_4^=$) and cations (i.e., ammonium [NH_4^+] and water-soluble sodium [Na^+] and potassium [K^+]) by IC. In the past, another channel containing a Whatman QMA quartz-fiber filter was used for OC and EC analysis by the STN thermal/optical transmittance (TOT) protocol. In recent years changes were made to the carbon sampling and analysis method. The collection method changed from the MetOne SASS to the URG3000N sampler, which is very similar to the IMPROVE module C sampler. The analytical method was changed from the NIOSH-like thermal optical transmittance (TOT) method to IMPROVE_A thermal optical reflectance (TOR). A new backup quartz filter is also collected using the URG3000N to help assess artifacts. The backup filter is placed behind the routine quartz sampler filter. This change took place on May 3, 2007 at Bakersfield and April 1, 2009 at Fresno.

Due to the change in carbon collection and analysis method, several data sets were generated for CMB modeling to allow separate analysis of old and new carbon data. Throughout this document we will refer to ‘old carbon’ data and ‘new carbon’ data. Old carbon data were collected using the SASS sampler and analyzed using the NIOSH-like thermal optical transmittance (TOT) method. New carbon data were collected using the modified IMPROVE version II Module C sampler, the URG3000N, and analyzed using the IMPROVE-A thermal optical reflectance (TOR) method. Both old and new carbon data were corrected for sampling artifacts prior to running CMB.

2) Data Preparation

Organic carbon (OC) data were corrected for sampling artifacts prior to running CMB. Old carbon data, collected using the SASS sampler and analyzed using the NIOSH-like thermal optical transmittance (TOT) method, were corrected by subtracting a California network-wide average organic carbon blank of 1 ug/m3 from the measured OC concentration. New carbon data were adjusted by subtracting network-wide monthly average concentrations measured on a backup filter from daily measurements of organic carbon [88370]. The monthly average backup concentrations are shown in Table 1.

Table 1. Organic Carbon Monthly Average Concentrations on Backup Filter

Month	1	2	3	4	5	6	7	8	9	10	11	12
Avg Blank Value (ug/m3)	0.66	0.54	0.48	0.43	0.43	0.48	0.54	0.49	0.53	0.50	0.60	0.57

3) Source Profiles

The major source types which have been found to contribute to primary PM2.5 in the San Joaquin Valley are motor vehicle exhaust, vegetative burning, geological material, marine-derived aerosols, residual or crude oil combustion, and tire and brake wear. Most of the source profiles applicable to the San Joaquin Valley were determined during the California Regional PM10/PM2.5 Air Quality Study (CRPAQS) or earlier. Therefore, the profiles used in this analysis, listed in Table 4, are the same profiles that were used in the previous analysis for the 2008 San Joaquin Valley PM2.5 Plan.

Motor vehicle profiles for diesel (DIES) and gasoline (GAS) (Fujita et al., 2005) were used in modeling PM2.5 concentrations. Since more specific organic markers for gasoline and diesel were not available at the receptor site, the two profiles were collinear and had to be combined into a single profile representing motor vehicle emissions. Diesel and gasoline vehicle emissions source profiles were combined in proportions equivalent to their county-level contributions to the PM2.5 emissions to produce a single emission-weighted overall source profile. Table 2 lists PM2.5 emissions (EMFAC 2011, July 2011) that were used as a basis for creating county-based composite profiles for Bakersfield and Fresno.

Table 2. Average 2004-2010 PM2.5 Exhaust Emissions (tons per day)

County		Gasoline Vehicles	Diesel Vehicles
Kern County	2004-2006 (K6GASDIE)	0.12	2.54
	2008-2010 (K9GASDIE)	0.09	1.88
Fresno County	2004-2006 (F6GASDIE)	0.12	1.33
	2008-2010 (F9GASDIE)	0.08	0.97

Table 4. Source Profiles (as Percent of the PM2.5 Mass) Used in the CMB Modeling

PNO	38			35			13			18			41			54			32		
SOURCE	AMNIT			AMSUL			WBOakEuc			AgBWheat			OC			MARINE75			TireBrke		
N3IC	77.50	±	7.75	0.00	±	0.00	0.57	±	0.07	0.16	±	0.02	0.00	±	0.00	22.88	±	2.60	0.19	±	1.14
S4IC	0.00	±	0.00	72.70	±	7.27	1.30	±	0.83	0.44	±	0.04	0.00	±	0.00	7.20	±	0.82	0.78	±	2.10
N4CC	22.55	±	2.26	27.30	±	2.73	0.58	±	0.47	0.59	±	0.04	0.00	±	0.00	0.00	±	0.10	0.16	±	0.73
NAAC	0.00	±	0.00	0.00	±	0.00	0.38	±	0.15	0.54	±	0.04	0.00	±	0.00	28.80	±	3.27	0.10	±	0.42
KPAC	0.00	±	0.00	0.00	±	0.00	2.89	±	0.45	6.79	±	0.50	0.00	±	0.00	1.07	±	0.12	0.05	±	0.17
OCTC	0.00	±	0.00	0.00	±	0.00	59.58	±	4.75	57.03	±	4.54	100.00	±	10.00	0.00	±	0.10	18.81	±	24.53
ECTC	0.00	±	0.00	0.00	±	0.00	5.20	±	1.12	10.31	±	0.85	0.00	±	0.00	0.00	±	0.10	4.55	±	5.99
ALXC	0.00	±	0.00	0.00	±	0.00	0.07	±	0.05	0.07	±	0.01	0.00	±	0.00	0.00	±	0.00	0.32	±	1.89
SIXC	0.00	±	0.00	0.00	±	0.00	0.22	±	0.10	0.13	±	0.01	0.00	±	0.00	0.01	±	0.00	0.69	±	1.81
PHXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.01	0.00	±	0.01	0.00	±	0.00	0.00	±	0.00	0.00	±	0.05
CLXC	0.00	±	0.00	0.00	±	0.00	1.72	±	2.02	6.16	±	0.44	0.00	±	0.00	38.74	±	4.40	0.04	±	0.08
KPXC	0.00	±	0.00	0.00	±	0.00	2.86	±	0.93	5.50	±	0.39	0.00	±	0.00	1.07	±	0.12	0.10	±	0.36
CAXC	0.00	±	0.00	0.00	±	0.00	0.15	±	0.10	0.10	±	0.03	0.00	±	0.00	1.10	±	0.12	0.28	±	1.04
TIXC	0.00	±	0.00	0.00	±	0.00	0.01	±	0.02	0.01	±	0.01	0.00	±	0.00	0.00	±	0.00	0.03	±	0.38
MNXC	0.00	±	0.00	0.00	±	0.00	0.01	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.48	±	0.29
FEXC	0.00	±	0.00	0.00	±	0.00	0.09	±	0.06	0.07	±	0.00	0.00	±	0.00	0.00	±	0.00	58.11	±	31.26
CUXC	0.00	±	0.00	0.00	±	0.00	0.01	±	0.00	1.02	±	0.07	0.00	±	0.00	0.00	±	0.00	0.16	±	0.69
ZNXC	0.00	±	0.00	0.00	±	0.00	0.04	±	0.02	0.01	±	0.00	0.00	±	0.00	0.00	±	0.00	0.35	±	2.37
BRXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.03	±	0.00	0.00	±	0.00	0.18	±	0.02	0.00	±	0.01
RBXC	0.00	±	0.00	0.00	±	0.00	0.01	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.01	±	0.01
SRXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.02	±	0.00	0.23	±	0.66
PBXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.06	±	0.03
VAXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00
NIXC	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00	0.00	±	0.00

Table 4, continued.

PNO	79	80	83	84	66	67	85	86
SOURCE	F6GASDIE	K6GASDIE	F9GASDIE	K9GASDIE	FDFREANN	FDKERANN	CHCRUC	SFCRUC
N3IC	0.22 ± 1.24	0.16 ± 1.24	0.21 ± 1.24	0.16 ± 1.24	0.02 ± 0.28	0.05 ± 0.16	0.00 ± 0.05	0.00 ± 0.01
S4IC	2.77 ± 7.25	2.60 ± 7.25	2.74 ± 7.25	2.61 ± 7.25	0.56 ± 0.72	0.47 ± 0.29	14.72 ± 6.24	20.32 ± 4.24
N4CC	0.98 ± 3.24	0.89 ± 3.24	0.96 ± 3.24	0.89 ± 3.24	0.04 ± 0.18	0.13 ± 0.20	0.76 ± 0.08	0.01 ± 0.01
NAAC	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.17 ± 0.07	0.26 ± 0.24	0.25 ± 0.06	0.76 ± 0.40
KPAC	0.10 ± 0.08	0.10 ± 0.08	0.10 ± 0.08	0.10 ± 0.08	0.27 ± 0.12	0.80 ± 1.25	0.01 ± 0.01	0.06 ± 0.01
OCTC	43.05 ± 27.33	42.40 ± 27.33	42.93 ± 27.33	42.41 ± 27.33	14.34 ± 8.66	10.29 ± 5.32	1.99 ± 1.33	0.09 ± 0.12
ECTC	50.59 ± 17.73	51.50 ± 17.73	50.75 ± 17.73	51.49 ± 17.73	1.92 ± 1.29	0.69 ± 0.72	3.01 ± 1.12	0.00 ± 0.07
ALXC	0.11 ± 0.14	0.11 ± 0.14	0.11 ± 0.14	0.11 ± 0.14	9.97 ± 2.95	7.67 ± 2.53	0.00 ± 0.05	0.00 ± 0.01
SIXC	1.14 ± 4.12	0.99 ± 4.12	1.11 ± 4.12	0.99 ± 4.12	26.77 ± 9.63	22.05 ± 5.29	0.00 ± 0.08	0.01 ± 0.02
PHXC	0.14 ± 0.51	0.13 ± 0.51	0.14 ± 0.51	0.13 ± 0.51	0.33 ± 0.91	0.33 ± 0.91	0.00 ± 0.57	0.00 ± 0.17
CLXC	0.07 ± 0.30	0.06 ± 0.30	0.07 ± 0.30	0.06 ± 0.30	0.11 ± 0.08	0.46 ± 0.48	0.05 ± 0.01	0.02 ± 0.00
KPXC	0.07 ± 0.08	0.07 ± 0.08	0.07 ± 0.08	0.07 ± 0.08	2.30 ± 0.92	3.26 ± 1.59	0.00 ± 0.00	0.04 ± 0.01
CAXC	0.50 ± 1.42	0.49 ± 1.42	0.50 ± 1.42	0.49 ± 1.42	3.01 ± 0.67	5.54 ± 3.03	0.00 ± 0.03	0.06 ± 0.00
TIXC	0.01 ± 0.08	0.01 ± 0.08	0.01 ± 0.08	0.01 ± 0.08	0.48 ± 0.05	0.44 ± 0.24	0.01 ± 0.00	0.01 ± 0.00
MNXC	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.00 ± 0.01	0.11 ± 0.02	0.11 ± 0.08	0.00 ± 0.00	0.01 ± 0.00
FEXC	0.44 ± 0.44	0.44 ± 0.44	0.44 ± 0.44	0.44 ± 0.44	5.30 ± 0.58	5.09 ± 2.84	0.71 ± 0.09	0.21 ± 0.02
CUXC	0.01 ± 0.05	0.01 ± 0.05	0.01 ± 0.05	0.01 ± 0.05	0.02 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	0.00 ± 0.00
ZNXC	0.27 ± 0.41	0.26 ± 0.41	0.27 ± 0.41	0.26 ± 0.41	0.14 ± 0.08	0.07 ± 0.05	0.01 ± 0.00	0.26 ± 0.03
BRXC	0.03 ± 0.06	0.03 ± 0.06	0.03 ± 0.06	0.03 ± 0.06	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
RBXC	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
SRXC	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.00 ± 0.00	0.00 ± 0.00
PBXC	0.01 ± 0.03	0.01 ± 0.03	0.01 ± 0.03	0.01 ± 0.03	0.18 ± 0.13	0.09 ± 0.32	0.00 ± 0.00	0.00 ± 0.00
VAXC	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.42 ± 0.04	0.82 ± 0.06
NIXC	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	2.48 ± 0.25	0.79 ± 0.09

Biomass burning was represented using an agricultural burning profile (AgBWheat) from June through October and a composite residential wood burning profile (WBOakEuc) the rest of the year. The agricultural burning profile (AgBWheat) was based on burning of wheat stubble (Fitz et al., 2000). The residential wood burning profile (WBOakEuc) was used to represent residential wood combustion during colder months and was calculated as an average of oak and eucalyptus.

Geological material in the San Joaquin Valley comes from a variety of sources, including roads (paved and unpaved), agricultural operations such as land preparation and harvesting, construction, and soil erosion. The Central California Fugitive Dust Characterization Study acquired 47 samples from 37 areas (Chow et al., 2003). These included: 1) paved road dust from urban and rural areas, 2) unpaved road dust, 3) agricultural soil from five crop fields (almond, cotton, grape, safflower, and tomato), 4) dairy and feedlot soil, 5) salt buildup deposits from irrigation canal drainages, and 6) building construction/earthmoving soil.

In addition to these latest profiles, some older soil profiles collected in the Valley in the late 80's were also used to create composite profiles that best represent fugitive dust sources at each site in the San Joaquin Valley. Information on the relative fractions of paved and unpaved road dust, as well as agricultural dust, along with information on the seasonality of agricultural operations and predominant crop types were used to determine which source profiles to include in each composite. Site specific composite profiles were then used in the CMB analysis. Table 3 lists geological profiles included in the composites created for modeling PM2.5 concentrations. Appendix A includes additional information about geological profiles.

Table 3. Geological Composite Source Profiles

Composite Profile ID	Sample	% Weight	Applicable Area
FDKERANN	SOIL31	25	Bakersfield
	FDPVR1	25	
	FDCTF	25	
	SOIL13	25	
FDFREANN	SOIL03	70	Fresno
	FDALM	10	
	FDGRA1	10	
	FDTOM1	10	

Sea salt was represented using a reacted sea salt profile, MARINE75, in which 25 percent of the Cl was replaced by nitrate on a molar basis (Chow et al., 1996a).

Tire and brake samples were collected as part of the 'Development of a Gas and Particulate Matter Organic Speciation Profile Database' conducted by CE-CERT (Fitz et al., 2000). Tire and brake samples were composited into a single weighted average profile. The two profiles were weighted based on EMFAC 2011 emissions, which estimate a 9 to 1 ratio of brake emissions to tire emissions.

Secondary nitrate and sulfate were represented by pure ammonium nitrate (NH_4NO_3) and ammonium sulfate $(NH_4)_2SO_4$. A "pure" OC profile was used to represent other unidentified primary sources, contributions from secondary OC, and the possible positive OC sampling artifacts.

Crude-oil combustion profiles were included to help explain ambient concentrations of vanadium (V) and nickel (Ni). The profile representing the Santa Fe crude-oil broiler at the Westside Kern County oil field helped to explain vanadium and nickel concentrations at Bakersfield, while the crude-oil profile representing the Chevron Racetrack boiler at the Kern River oil field provided a better fit at Fresno.

4) Fitting Species

Table 5 lists fitting species used in CMB runs.

Table 5. CMB Fitting Species

Nitrate	Silicon	Zinc
Sulfate	Chlorine	Bromine
Ammonium	Potassium	Rubidium
Soluble Sodium	Calcium	Strontium
Soluble Potassium	Titanium	Lead
Organic Carbon	Manganese	Vanadium
Elemental Carbon	Iron	Nickel
Aluminum	Copper	

5) Runs

PM2.5 chemical composition data were collected on a one in three days schedule at each site. Table 6 shows the number of samples included under each scenario.

Table 6. Number of Samples included in the CMB Runs

Site	Old Carbon	New Carbon
BAC	157	267
FSF	390	200

Data for each sampling day were run individually under several scenarios. Each run included the following profiles: ammonium nitrate, ammonium sulfate, motor vehicle, fugitive dust, tire and brake wear, marine, and in the case of Bakersfield, crude oil combustion. In the case of Fresno, the crude oil combustion profile was included only when it was necessary to explain the vanadium and nickel contributions. Biomass burning and 'other OC' profiles were included as needed. First, all data were run with a biomass burning profile (AgBWheat from June through October, WBoakEuc the rest of the year) and the 'other OC'. The results were examined to determine if all source contributions were positive and performance parameters were within acceptable ranges. If using the biomass burning profile along with the 'other OC' gave unsatisfactory results, the data were run again using just one of the two profiles, as described below.

1. Run 1 included a biomass burning profile and 'other OC'.
2. Run 2 included a biomass burning profile but not the 'other OC' profile. It was geared towards days when primary sources of organic carbon (biomass burning, motor vehicle exhaust, and geological material) sufficiently accounted for the ambient organic carbon.
3. Run 3 included 'other OC' but no biomass burning profile. It was geared towards days with no biomass burning and applied only when soluble potassium concentration was reported as zero.

Data from several runs were combined into a single data file to best represent source contributions. Data were combined as follows:

1. Days with estimated positive contributions from wood burning and 'other OC' were included in the composite file.
2. Days with estimated negative contributions from 'Other OC' were treated as follows:
    a. If there should have been no burning on that day because the soluble potassium concentration was zero, run 3 which includes the 'other OC' and no wood burning was utilized.
    b. If there could have been wood burning because the soluble potassium concentration was greater than zero, run 2 which includes biomass burning was used.
3. Occasionally, the results were still unsatisfactory and profiles were adjusted individually for a particular day.

Composite files were used for subsequent analysis. Table 7 shows the number of data points from each run included in the composite file.

Table 7. Data included in the composite file*.

Site	Carbon Type	Run 1		Run2	Run 3	Special Run
		WBOakEuc	AgBWheat			
BAC	Old	68	41	4	16	5
BAC	New	80	113	28	12	0
FSF	Old	176	105	7	40	9
FSF	New	52	66	21	56	6

* Data with performance measures far exceeding the acceptable criteria were not included in the composite

6) Comparison of CMB Estimates using Old and New Carbon

The Bakersfield-California site has 14 days with parallel old and new carbon data. Since these data were collected during the low season, the average PM2.5 concentration was only 13.6 ug/m3. The CMB model was applied to the old and new carbon data to evaluate the impact of changing carbon collection and analysis on source contribution. Using the old carbon, 10 percent more of the mass was apportioned to sources. Regardless of what carbon data were used, the model apportioned almost the same concentration to each source, except ‘other OC’. Using the old carbon data, on average, 2.5 ug/m3 was assigned to the ‘other OC’. Switching to the new carbon data reduced the ‘other OC’ estimate to 1 ug/m3. There were also several days when the motor vehicle contribution estimate differed slightly depending on which carbon data were used. Even though, on average there is no difference in measured EC between the old and new carbon method, on these particular days the measurements differed and that difference was reflected in the motor vehicle contribution. The new OC measurement is, on average, about 50 percent lower compared to the old one. This impacts how much mass gets apportioned to the ‘other OC’ but has no impact on motor vehicle or biomass burning contributions. Figures 3 through 6 compare percent of mass and contribution from major carbon sources using old and new carbon data.

Figure 3. Compare Percent Mass

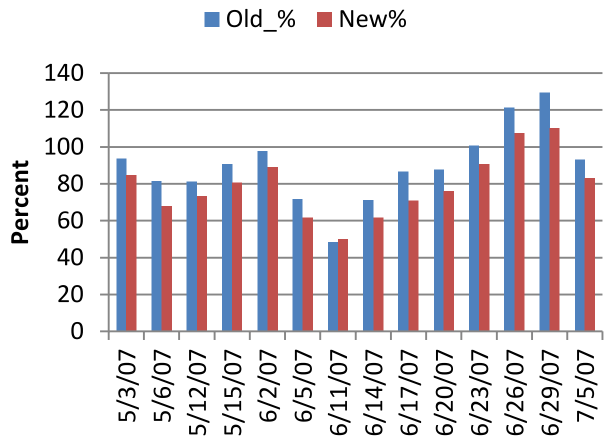


Figure 4. Compare Woodburning Estimate

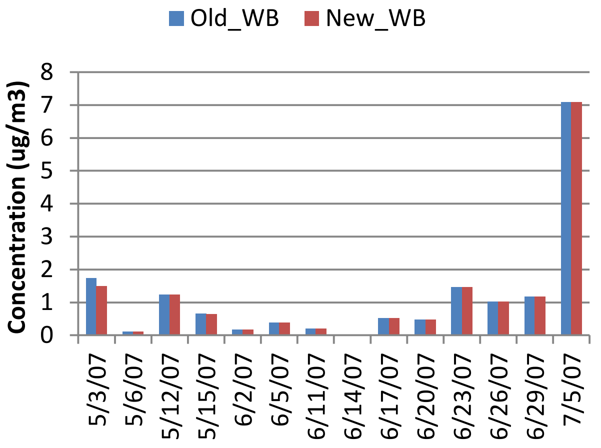


Figure 5. Compare Motor Vehicle Estimate

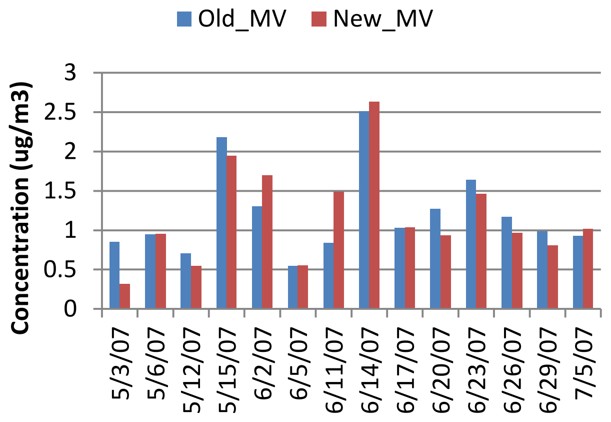
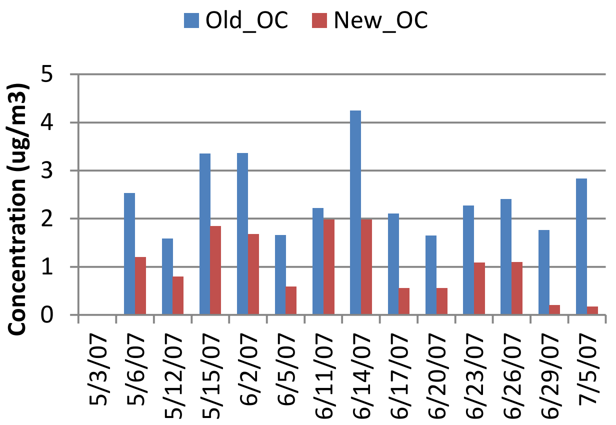


Figure 6. Compare 'Other OC' Estimate



7) Results

The CMB model was applied to 424 samples at BAC (157 with old carbon and 267 with new carbon) and 590 samples at FSF (390 with old carbon and 200 with new). Source contribution estimates were averaged to determine a typical contribution. Separately, days with concentrations greater than 30 ug/m3 were averaged to determine the typical contribution on a high PM2.5 day.

Performance measures and statistics used to evaluate the validity of CMB source apportionments include chi-square, r-square, and percent of mass accounted for by the estimated source contributions. The target values for these performance measures are chi-square less than 4, r-square greater than 0.8, and percent of mass accounted for by the estimated source contributions between 80% and 120%. The average performance measures for both sites were within the acceptable limits as shown in Tables 8 and 10.

The results are discussed separately for each site for two reasons. First of all, each site switched to the new method at a different time. Second of all, 2009 had to be excluded from the annual average calculation at Bakersfield due to missing data.

a) Bakersfield (BAC)

The average PM2.5 concentration based on old carbon data for 2006 was 20.5 ug/m3. Based on the new carbon data, the 2008 and 2010 average PM2.5 concentration was 18.6 ug/m3. Between 2006 and 2007 (old carbon data) there were 29 high days with chemical composition data. The average PM2.5 concentration on these days was 47 ug/m3,. Between 2007 and 2010 (new carbon data), there were 36 high days with chemical composition data, with the average PM2.5 concentration of 46.7 ug/m3. Sources identified by the CMB accounted for 79 to 94 percent on annual basis and 94 to 95 percent on high days.

i) Annual

Ammonium nitrate dominated the PM2.5 mass contributing 42 to 47 percent of mass. Ammonium sulfate and biomass burning were the next most important sources contributing 10 to 12 percent of mass. Biomass burning contributed 9 to 10 to percent of the mass. The ‘Other OC’ contribution depended on the carbon data method; using old carbon apportioned 16 percent of mass to the ‘other OC’ while using new carbon reduced that contribution to 8 percent. Geological material comprised 7 to 10 percent of the mass. Each of the remaining sources (tire and brake wear, sea salt, and oil combustion) contributed no more than 1 percent of the mass.

ii) High Days

The ammonium nitrate contribution was even more significant on high days, ranging from 59 to 67 percent. Biomass burning and motor vehicles each contributed 9 to 13 percent. The ‘Other OC’ contribution ranged from 3 percent using new carbon to 10 percent using old carbon. Geological material contributed about 2 percent. Each of the remaining sources, tire and brake wear, sea salt, and oil combustion contributed less than 1 percent of the mass.

b) Fresno (FSF)

The average PM2.5 concentration based on old carbon data for 2006 to 2008 was 20.3 ug/m3. Based on the new carbon data, the 2010 average PM2.5 concentration was 14.2 ug/m3. Between 2006 and 2009 (old carbon data) there were 67 high days with chemical composition data. The average PM2.5 concentration on these days was 46.3 ug/m3. Between 2009 and 2010 (new carbon data), there were 22 high days with chemical composition data, with the average concentration of 40.6 ug/m3. Sources identified by the CMB accounted for 74 to 97 percent of the mass on an annual basis and 82 to 93 percent on high days.

i) Annual

Ammonium nitrate dominated the PM2.5 mass contributing 40 to 43 percent of the mass. Biomass burning contributed about 16 percent of the mass. Motor vehicles contributed slightly less, 11 to 13 percent. The ammonium sulfate contribution was 9 to 11 percent. The ‘Other OC’ contribution, once again, depended on carbon data; using old carbon apportioned 18 percent of mass to the ‘other OC’ while using new carbon reduced that contribution to 9 percent. Geological material comprised 4 to 6 percent of the mass. Each of the remaining sources contributed no more than 1 percent of the mass.

ii) High Days

The ammonium nitrate contribution was even more significant on high days when 52 to 54 percent of the mass was ammonium nitrate. Biomass burning was the second most significant source, contributing 19 to 23 percent. The motor vehicle contribution ranged from 9 to 12 percent. The ‘Other OC’ ranged from 4 percent using new carbon data to 13 percent using old carbon data. The remaining sources contributed less than 1 percent of the mass.

Table 8. BAC Source Contribution (ug/m3)

Source	Profile Name	Annual Average		High Days (>=30 ug/m3)	
		2006	2008 and 2010	2006-2007	2007-2010
# of samples	Obs Count	90	138	29	36
Mconc	Mconc	20.5 ± 1.1	18.6 ± 1.0	47.0 ± 2.4	46.7 ± 2.4
Cconc	Cconc	19.4 ± 1.5	15.6 ± 1.2	45.0 ± 3.1	43.9 ± 3.1
Rsquare	Rsquare	0.9	0.9	0.9	0.9
CHIsquare	CHIsquare	3.1	2.7	1.8	1.4
%MASS	%MASS	94.3	79.3	95.5	93.8
AMNIT	AMNIT	8.2 ± 0.8	7.4 ± 0.7	26.7 ± 2.5	29.6 ± 2.5
AMSUL	AMSUL	2.0 ± 0.6	1.9 ± 0.5	2.5 ± 1.2	3.4 ± 1.3
Biomass burning	Seasonal*	1.9 ± 0.4	1.5 ± 0.3	5.7 ± 1.0	4.0 ± 0.7
Motor Vehicle	K9GASDI**	2.4 ± 1.0	1.9 ± 0.6	4.2 ± 1.6	4.2 ± 1.4
OC	OC	3.2 ± 1.1	1.2 ± 0.7	4.3 ± 1.7	1.3 ± 1.2
Tire and Brake	TireBrk	0.2 ± 0.1	0.2 ± 0.1	0.3 ± 0.2	0.3 ± 0.2
Sea Salt	MARINE75	0.1 ± 0.1	0.1 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
Geological	FDKERANN	1.3 ± 0.3	1.6 ± 0.3	0.7 ± 0.3	0.8 ± 0.3
Oil Refinery	SFCRUC	0.3 ± 0.1	0.1 ± 0.1	0.3 ± 0.3	0.2 ± 0.3

Table 9. BAC Source Contribution (%)

Source	Profile Name	Annual Average		High Days (>=30 ug/m3)	
		2006	2008 and 2010	2006-2007	2007-2010
# of samples	Obs Count	90	138	29	36
AMNIT	AMNIT	42.2	46.8	59.3	67.4
AMSUL	AMSUL	10.2	11.9	5.6	7.8
Biomass burning	Seasonal*	9.6	9.3	12.8	9.1
Motor Vehicle	KGASDI**	12.3	11.8	9.3	9.6
OC	OC	16.2	7.7	9.5	2.9
Tire and Brake	TireBrk	1.0	1.3	0.7	0.7
Sea Salt	MARINE75	0.4	0.5	0.6	0.5
Geological	FDKERANN	6.7	10.3	1.6	1.7
Oil Refinery	SFCRUC	1.3	0.5	0.6	0.3

* AgBWheat from June through October, WBoakEuc the rest of the year

** K6GASDIE for old carbon and K9GASDIE for new carbon

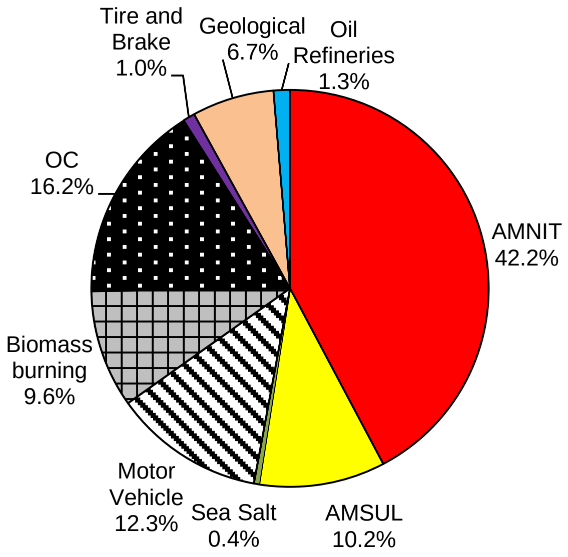


Figure 7. BAC 2006 Average Old Carbon

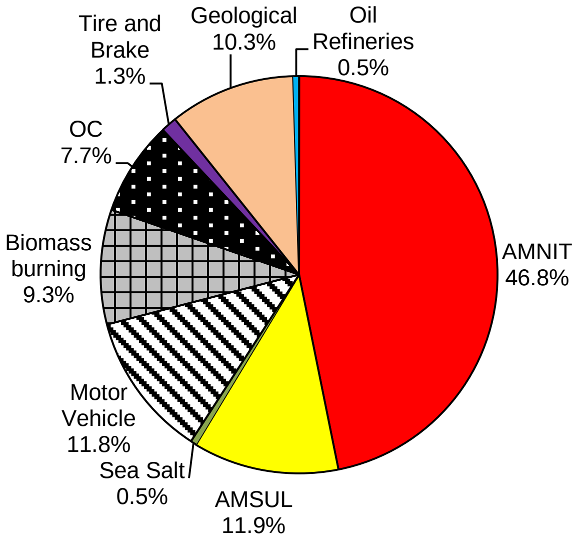


Figure 8. BAC 2008 and 2010 Average New Carbon

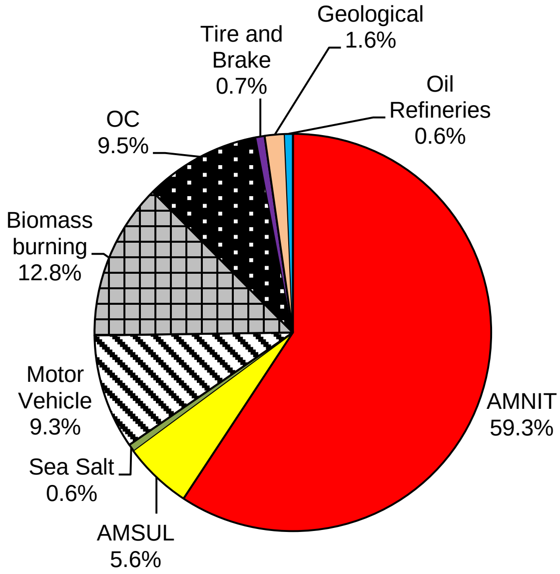


Figure 9. BAC Average High Day Old Carbon (2006-2007)

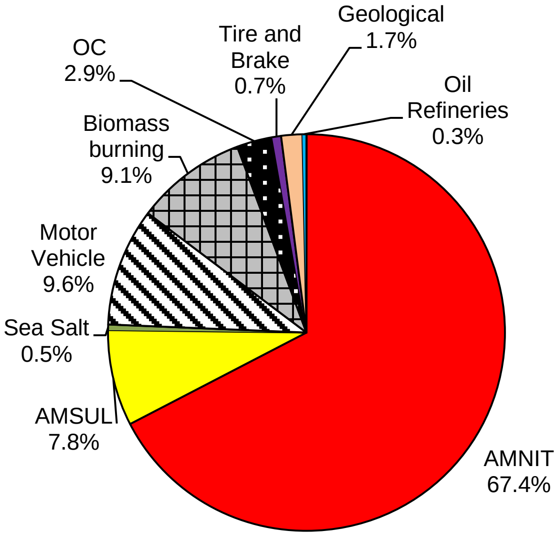


Figure 10. BAC Average High Day New Carbon (2007-2010)

Table 10. FSF Source Contribution (ug/m3)

Source	Profile Name	Annual Average 2006-2008	Annual Average 2010	High Days (>=30 ug/m3) 2006-2009	High Days (>=30 ug/m3) 2009-2010
# of samples	Obs Count	275	105	67	22
Mconc	Mconc	20.3 ± 1.1	14.2 ± 0.8	46.3 ± 2.3	40.6 ± 2.1
Cconc	Cconc	19.0 ± 1.5	10.8 ± 0.8	43.0 ± 2.9	33.1 ± 2.3
Rsquare	Rsquare	0.8	0.9	0.9	0.9
CHIsquare	CHIsquare	4.3	3.5	1.7	1.4
%MASS	%MASS	96.7	74.3	92.9	81.5
AMNIT	AMNIT	7.5 ± 0.7	4.7 ± 0.5	22.4 ± 2.1	17.8 ± 1.7
AMSUL	AMSUL	1.7 ± 0.5	1.2 ± 0.4	2.1 ± 1.1	2.0 ± 1.0
Biomass burning	Seasonal*	3.1 ± 0.5	1.7 ± 0.3	8.0 ± 1.2	7.6 ± 1.1
Motor Vehicle	FGASDI**	2.1 ± 0.9	1.4 ± 0.5	4.0 ± 1.5	3.8 ± 1.3
OC	OC	3.3 ± 1.1	1.0 ± 0.5	5.7 ± 2.0	1.5 ± 1.3
Tire and Brake	TireBrk	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
Sea Salt	MARINE75	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.2	0.2 ± 0.2
Geological	FDFREANN	0.8 ± 0.2	0.6 ± 0.1	0.2 ± 0.2	0.1 ± 0.1
Oil Combustion	CHCRUC	0.01 ± 0.0		0.1 ± 0.0	0.0 ± 0.0

Table 11. FSF Source Contribution (%)

Source	Profile Name	Annual Average 2006-2008	Annual Average 2010	High Days (>=30 ug/m3) 2006-2009	High Days (>=30 ug/m3) 2009-2010
# of samples	Obs Count	275	105	67	22
AMNIT	AMNIT	40.0	43.2	52.0	53.6
AMSUL	AMSUL	9.1	11.4	4.9	6.0
Biomass burning	WBOakEuc	16.5	15.7	18.7	22.9
Motor Vehicle	F9GASDI	11.1	13.3	9.3	11.5
OC	OC	17.5	9.2	13.4	4.4
Tire and Brake	TireBrk	0.8	0.8	0.5	0.5
Sea Salt	MARINE75	0.6	0.9	0.5	0.7
Geological	FDFREANN	4.2	5.6	0.5	0.3
Oil Combustion	CHCRUC	0.1	0.0	0.1	0.0

* AgBWheat from June through October, WBoakEuc the rest of the year

** F6GASDIE for old carbon and F9GASDIE for new carbon

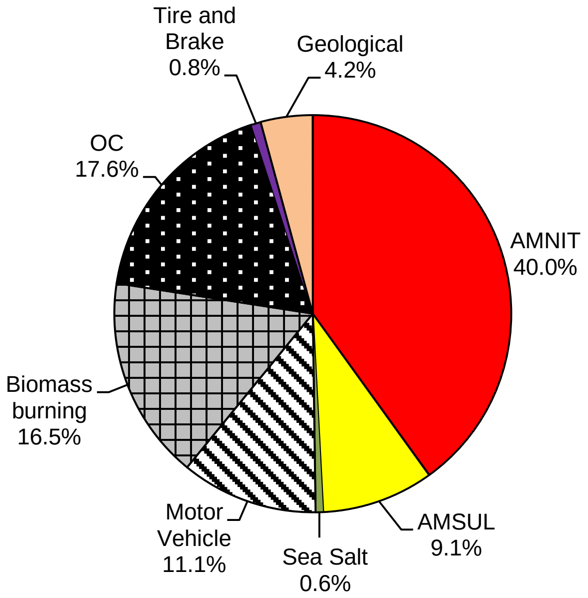


Figure 11. FSF 2006-2008 Average Old Carbon

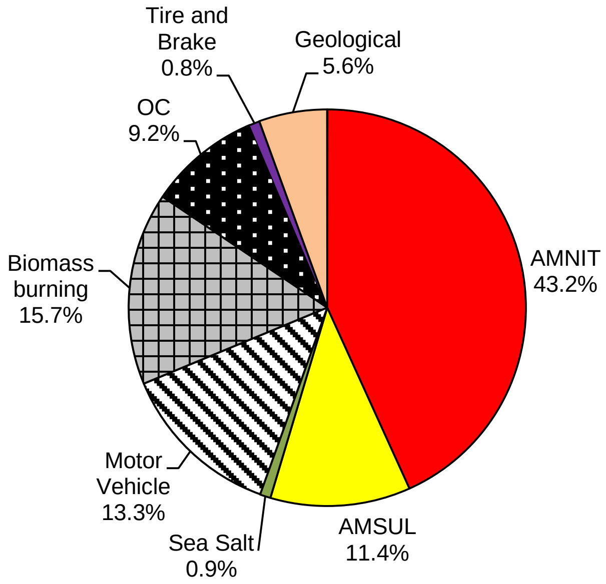


Figure 12. FSF 2010 Average New Carbon

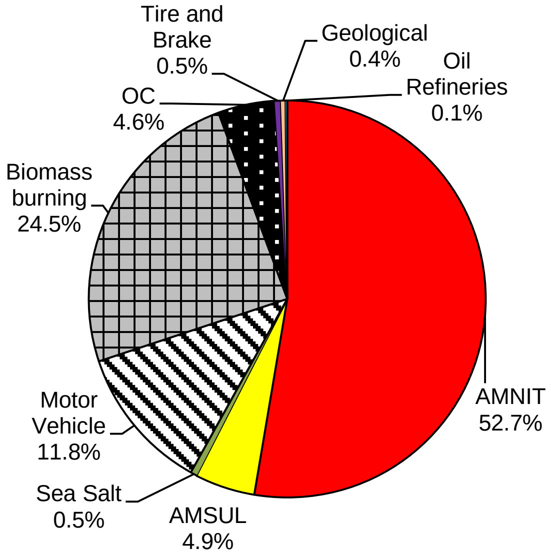


Figure 13. FSF Average High Day Old Carbon (2006-2009)

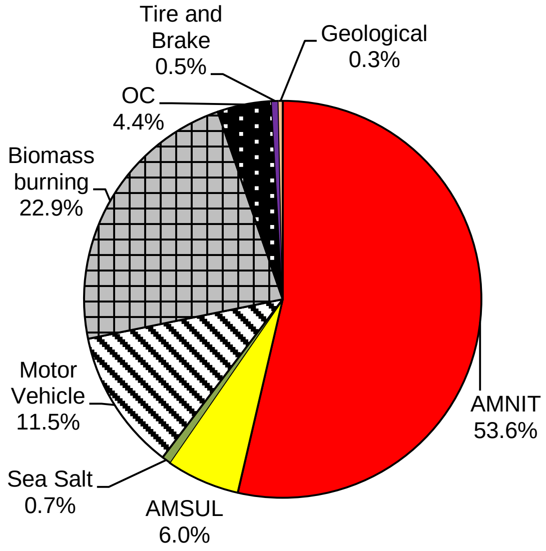


Figure 14. FSF Average High Day New Carbon (2009-2010)

Contributions on individual exceedance days are illustrated in Figures 15 through 18. The highest contribution from each source is also summarized in Tables 12 and 13.

Figure 15. PM2.5 Source Contribution on High Days 2006-2007
Bakersfield, Old Carbon

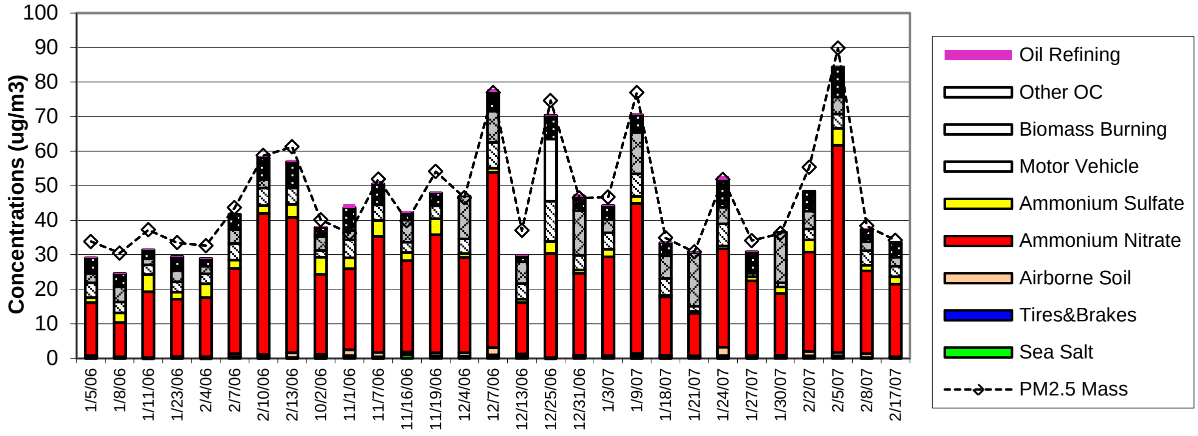


Figure 16. PM2.5 Source Contribution on High Days 2007-2010
Bakersfield, New Carbon

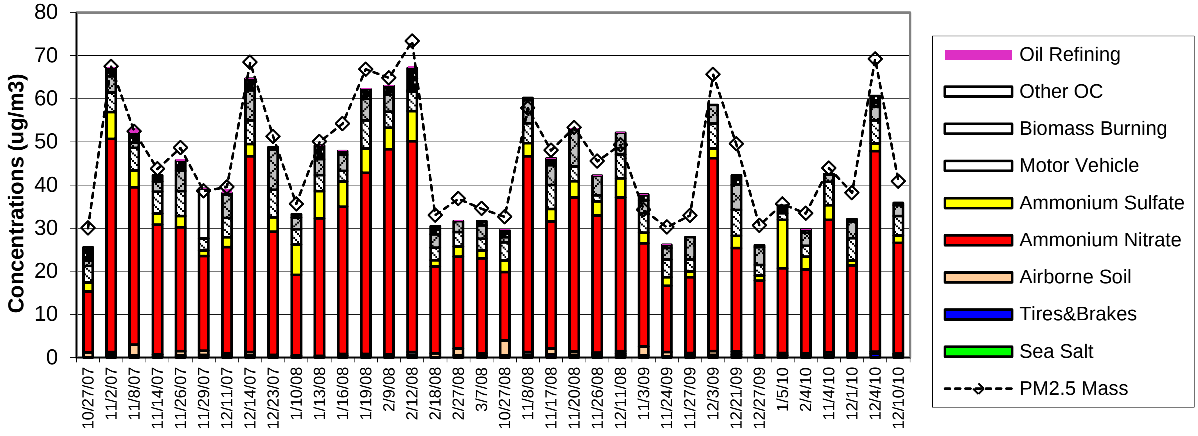


Figure 17. PM2.5 Source Contribution on High Days 2006-2009
Fresno, Old Carbon

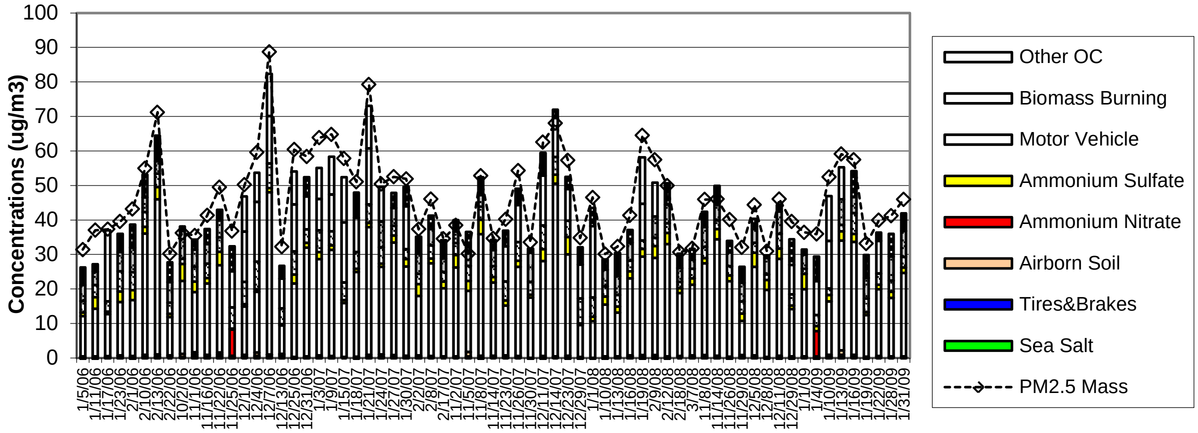


Figure 18. PM2.5 Source Contribution on High Days 2009-2010
Fresno, New Carbon

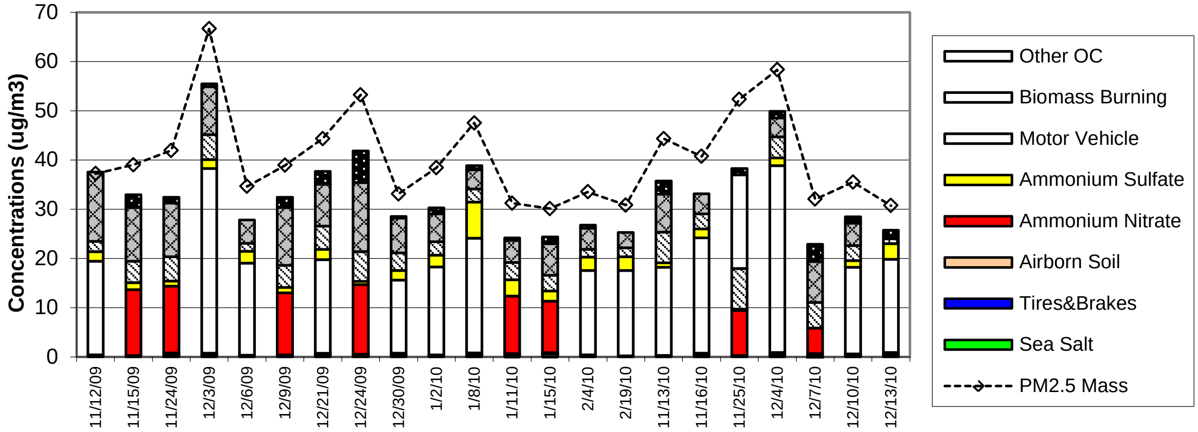


Table 12. BAC Highest Contribution by Source

Source	Old Carbon		New Carbon	
	Contribution (ug/m3)	Date	Contribution (ug/m3)	Date
Ammonium Nitrate	60	2/5/07	50	2/12/08
Ammonium Sulfate	5	10/2/06	11	1/5/10
Biomass Burning	18	12/25/06	12	11/29/07
Motor Vehicle	12	12/25/06	7	1/19/08
Other OC	9	2/5/07	5	2/12/08
Tire & Brake	0.6	1/24/07	0.8	12/4/10
Sea Salt	1	11/16/06	0.7	11/26/08
Geological	2.5	11/24/07	2.5	11/8/07
Oil Combustion	1	11/24/07	1	11/8/07

Table 13. FSF Highest Contribution by Source

Source	Old Carbon		New Carbon	
	Contribution (ug/m3)	Date	Contribution (ug/m3)	Date
Ammonium Nitrate	50	12/14/07	38	12/4/10
Ammonium Sulfate	5	12/23/07	7	1/8/10
Biomass Burning	21	1/1/08	19	11/25/10
Motor Vehicle	8	12/4/06	8	11/25/10
Other OC	13	1/19/08	6	12/24/09
Tire & Brake	0.6	12/7/06	0.4	11/24/09
Sea Salt	0.6	2/9/08	0.4	12/10/10
Geological	1.4	11/8/07	0.6	12/4/10
Oil Combustion	2	2/8/07		

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Appendix A

Summary of Geological Profiles Used in CMB Modeling

Source Type	Subtype	County	Sample ID	Source
FDKERANN				
Agricultural Soil		Kern	Soil 31	Houck, et al, 1989
Paved Road	Urban	Kern	FDPVR1	Central California Fugitive Dust Study
Animal Husbandry	Feedlot (Composite)	Kern&Fresno	FDCTF	
Unpaved Road Dust	Unpaved Parking lot	Kern	Soil 13	Houck, et al, 1989
FDFREANN				
Paved Road		Fresno	Soil 03	Houck, et al, 1989
Agricultural Soil	Almonds (Composite)	Kern, Fresno, King, and Madera	FDALM	Central California Fugitive Dust Study
Agricultural Soil	Grapes	Fresno	FDGRA1	
Agricultural Soil	Tomato (Composite)	Fresno	FDTOM1	

SAN JOAQUIN VALLEY PM2.5 WEIGHT OF EVIDENCE ANALYSIS

APPENDIX A4

SOURCE APPORTIONMENT OF PM2.5 MEASURED AT THE FRESNO AND BAKERSFIELD CHEMICAL SPECIATION NETWORK SITES IN SAN JOAQUIN VALLEY USING THE POSITIVE MATRIX FACTORIZATION MODEL

Source Apportionment of $PM_{2.5}$ Measured at the Fresno and Bakersfield Chemical Speciation Network Sites in San Joaquin Valley Using the Positive Matrix Factorization Model

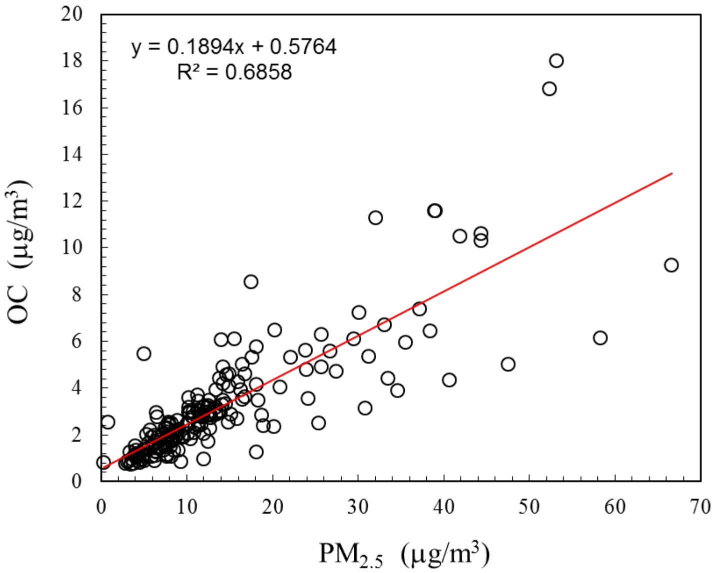
Sample Collection and Data Screening

$PM_{2.5}$ chemical speciation samples were collected on a one-in-three day schedule at the Fresno-First St. and Bakersfield-California Ave. Chemical Speciation Network (CSN) monitoring sites located in the San Joaquin Valley (SJV). There were good agreements between $PM_{2.5}$ data collected by the speciation samplers and the collocated Federal Reference Method (FRM) samplers in matched Fresno data (*340 samples, slope* = 1.00, *Intercept* = 1.08, r^2 = 0.97) and Bakersfield (*175 samples, slope* = 0.94, *Intercept* = 0.92, r^2 = 0.94) between 2008 and 2010.

The Thermal Optical Transmittance (TOT) protocol had been used to analyze carbon mass collected on the quartz filters. This method was changed to the Thermal Optical Reflectance (TOR) protocol and TOR organic carbon (OC) and elemental carbon (EC) concentrations were available starting from January 2008 and April 2009 at the Bakersfield and Fresno monitoring sites, respectively. Only the speciation data for which TOR OC and EC concentrations were available were considered in this source apportionment study.

Since a carbon denuder that minimizes the positive sampling artifact caused by adsorption of gaseous organic materials was not included upstream of quartz filter in the CSN samplers, and none of the reported CSN data were blank corrected, an integrated OC artifact concentration that includes OC adsorption and desorption was estimated utilizing the intercept of the regression of OC concentrations against $PM_{2.5}$ mass concentrations (Tolocka et al. 2001, Kim et al. 2005). Samples for which $PM_{2.5}$ or OC concentrations had an error flag and samples for which the $PM_{2.5}$ or OC data were not available were excluded from the regression analysis between $PM_{2.5}$ and OC concentrations. Comparing co-located $PM_{2.5}$ data measured by CSN and FRM samplers, and comparing $PM_{2.5}$ and Sulfur (S) concentrations, outliers were censored for the two data sets. Using 189 data points out of 353 data points between 2009 and 2010 at Fresno and 187 data points out of 192 data points at Bakersfield between 2008 and 2010, the intercept s of 0.576 $\mu g/m^3$ and 1.480 $\mu g/m^3$ in $PM_{2.5}$ regression against OC concentrations are considered to be the integrated OC artifact concentrations at Fresno and Bakersfield, respectively (Figure 1). The OC concentrations analyzed in this study were corrected by subtracting the integrated OC artifact concentrations.

Fresno-First St.



Bakersfield-California Ave.

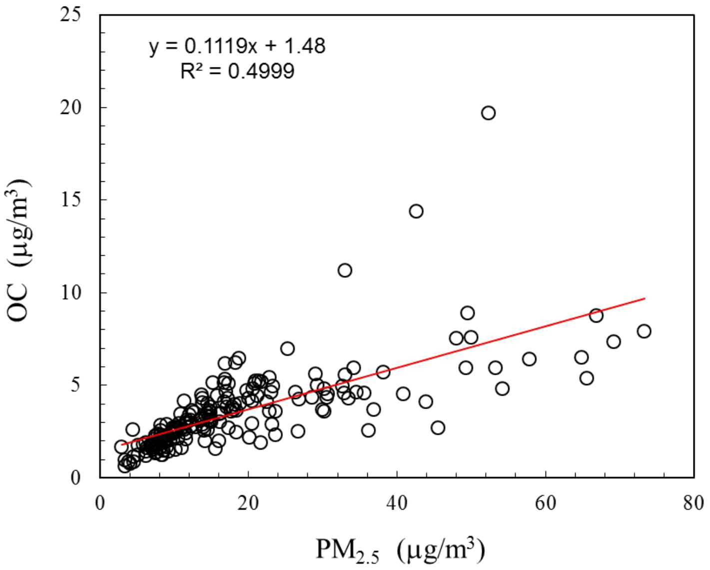


Figure 1. OC artifact estimations: $PM_{2.5}$ concentrations versus OC concentrations.

The Positive matrix factorization model version 2 (PMF2) model was used for the source apportionment of $PM_{2.5}$ at the Fresno and Bakersfield monitoring sites. Samples were excluded from the data set for which the $PM_{2.5}$, artifact corrected OC, or EC data were not available or below zero, or for which $PM_{2.5}$ artifact corrected OC, or EC had an error flag. Samples for which the sum of all measured species were larger than twice the $PM_{2.5}$ concentrations or the sum of all measured species were less than 50% of $PM_{2.5}$ concentrations were also excluded. Finally, samples that contain fireworks particles collected on Independence Day and New Year's Day were excluded since they had unusually high concentrations of OC, EC, K^+, Na^+ and metals. Overall, 10.3% of the Fresno data and 16.5% of the Bakersfield data were excluded in this study.

For the chemical species screening, X-Ray Fluorescence (XRF) S was excluded from the analyses to prevent double counting of mass concentrations. Due to the higher analytical precision compared to XRF Na and XRF K, IC Na^+ and IC K^+ were included in the analyses. Chemical species below MDL values more than 90% were excluded. As recommended by Paatero and Hopke (2003), the species that had a Signal-to-Noise (*S/N*) ratio below 0.2 were excluded. Thus, a total of 174 samples and 21 species including $PM_{2.5}$ mass concentrations collected between April 2009 and December 2010 were used for the Fresno site. For the Bakersfield site, a total of 147 samples and 24 species including $PM_{2.5}$ mass concentrations collected between January 2008 and December 2010 were used. Since new TOR OC and EC concentrations were not accompanied by detection limit and uncertainty values, a comprehensive set of uncertainty structure (i.e., 7% of measured concentration) estimated by Kim et al. (2005) and 0.1 $\mu g/m^3$ of detection limit value estimated from the State and Local Air Monitoring Stations (SLAM) speciation data were used in this study. Summaries of $PM_{2.5}$ speciation data are provided in Tables A1 and A2 in the Appendix.

The procedure of Polissar et al. (1998) was used to assign input data for PMF2. The measurement values are used for the input concentration data, and the sum of the analytical uncertainty and one-third of the detection limit value is used as the input uncertainty data assigned to each measured value. Concentration values below the detection limit are replaced by half of the detection limit values, and their input uncertainties are set at five-sixth of the detection limit values. Missing values are replaced by the geometric mean of the measured values for each species. To down-weight these replaced data and then to reduce their influence on the solution, their accompanying uncertainties are set at four times the geometric mean value. The conditional probability function (CPF) analysis was used to estimate the possible directions of the local source impacts (Kim and Hopke, 2004). The CPF was calculated for each source using the PMF2 source contributions coupled with wind data. As recommended by Paatero and Hopke (2003), which is to down-weight the variable in the analysis so that the noise does not compromise the solution, it was found necessary to increase the input uncertainties of OC, EC, and Cl by a factor of 3 for the Fresno data and OC and Na^+ by a factor of 3 for the Bakersfield data to obtain physically interpretable PMF2 results.

PMF Results

Seven major sources were resolved from PMF2 analyses for both sites (matrix rotational parameter: Fresno FPEAK = 0.1; Bakersfield FPEAK = 0). The comparison of the reconstructed $PM_{2.5}$ contributions (sum of contributions from all sources) with measured $PM_{2.5}$ concentrations shown in Figure 2 indicates that the resolved sources effectively reproduce the measured values and account for most of the variation in the $PM_{2.5}$ concentrations (*slope* = 0.88, $r^2 = 0.95$ for Fresno data; *slope* = 0.93, $r^2 = 0.91$ for Bakersfield data).

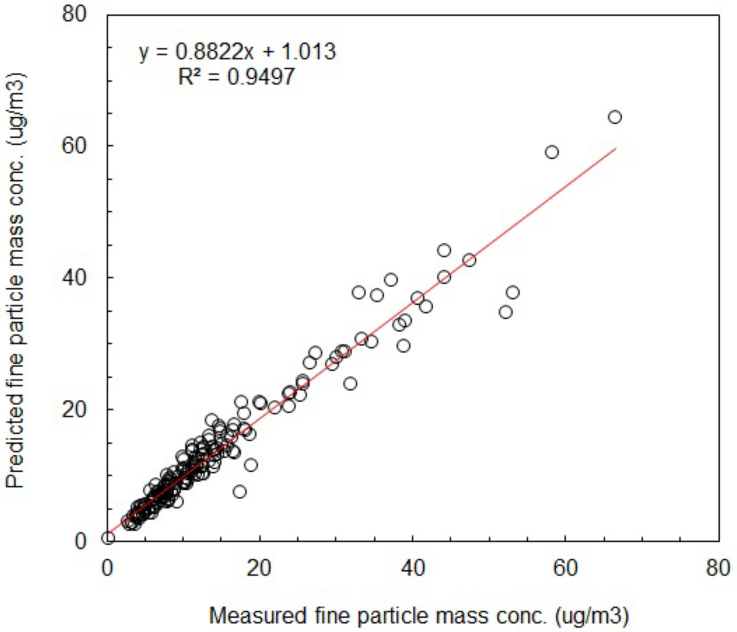
Average Source Contributions

As shown in Figure 3 and Table A3 which present average source contributions, secondary nitrate contributed the most at both sites (35% at the Fresno site, 41% at the Bakersfield site). The pie charts indicate that three major sources (i.e., secondary nitrate, secondary sulfate, and motor vehicle) contributed 74% of $PM_{2.5}$ concentrations at both sites. Figure 4 shows monthly average source contributions. Secondary nitrate, motor vehicle, and biomass smoke contributed the most in winter. The source profiles, corresponding source contributions, weekday/weekend variations, monthly averaged source contributions, and potential source directions are presented in Figures A1 through A10 in the Appendix.

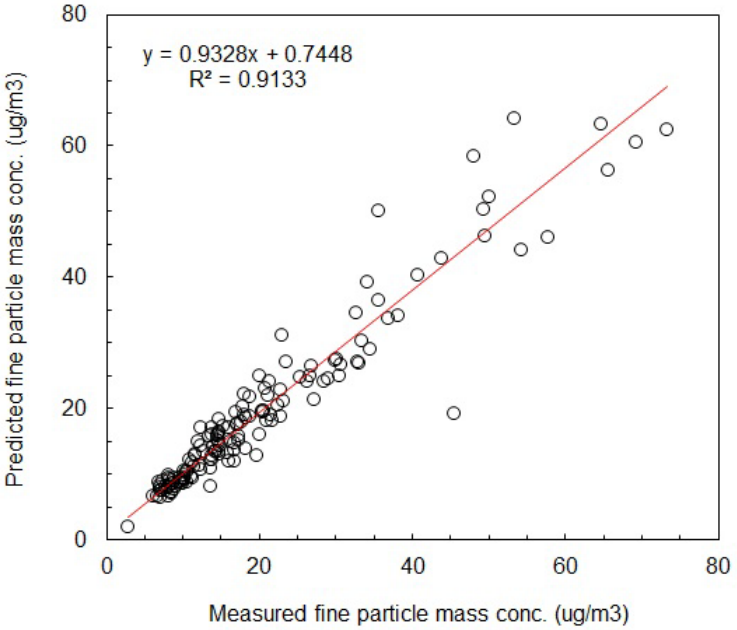
The secondary nitrate factor was identified by its high concentration of NO_3^- and NH_4^+. It consisted of NH_4NO_3 and several minor species such as secondary OC and EC that transport together. It contributed the most at both sites, accounting for 35% and 41% of the $PM_{2.5}$ mass concentrations at Fresno and Bakersfield, respectively. Bakersfield showed higher secondary nitrate concentrations than Fresno. Secondary nitrate particles had winter- high trends at both sites. Secondary sulfate was identified by its high concentration of SO_4^{2-} and NH_4^+ and accounted for 27% and 20% of the $PM_{2.5}$ mass concentration at Fresno and Bakersfield, respectively. Secondary nitrate and secondary sulfate did not show clear weekday/weekend variations. Secondary sulfate showed seasonal variations with higher concentrations in summer when the photochemical activity was highest at both sites. The CPF plots for secondary nitrate pointed S and NE at both sites. The CPF plots for secondary sulfate pointed SE at the Fresno site and SW at the Bakersfield site.

The motor vehicle factor was identified by its high concentration of OC, EC, NO_3^-, and minor species such as Fe (Watson et al., 1994). Motor vehicle emissions contributed 12% and 13% of the $PM_{2.5}$ mass concentrations at Fresno and Bakersfield, respectively. Motor vehicle emissions did not show clear weekday/weekend variations at either site, however there was a winter-high seasonal trend.

The biomass smoke factor was characterized by OC, EC, and K^+ (Watson et al., 2001) and contributed 11% and 10% to the $PM_{2.5}$ mass concentrations at Fresno and Bakersfield, respectively. The biomass smoke category reflects contributions from residential wood burning and smoke from commercial cooking. The biomass smoke did not show weekday/weekend variations. The biomass smoke did show winter-high trends suggesting that it was mostly contributed by residential wood burning. The CPF plots for the biomass smoke pointed to high contributions from NE and S at both sites.



Fresno-First St.



Bakersfield-California Ave.

Figure 2. Measured versus PMF predicted $PM_{2.5}$ mass concentrations.

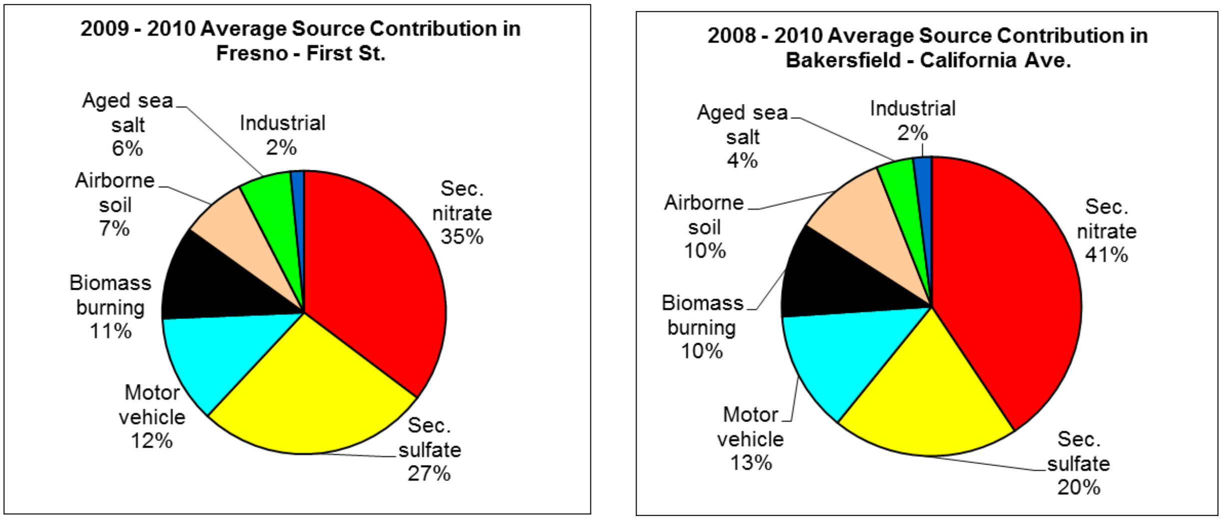


Figure 3. Average source contributions.

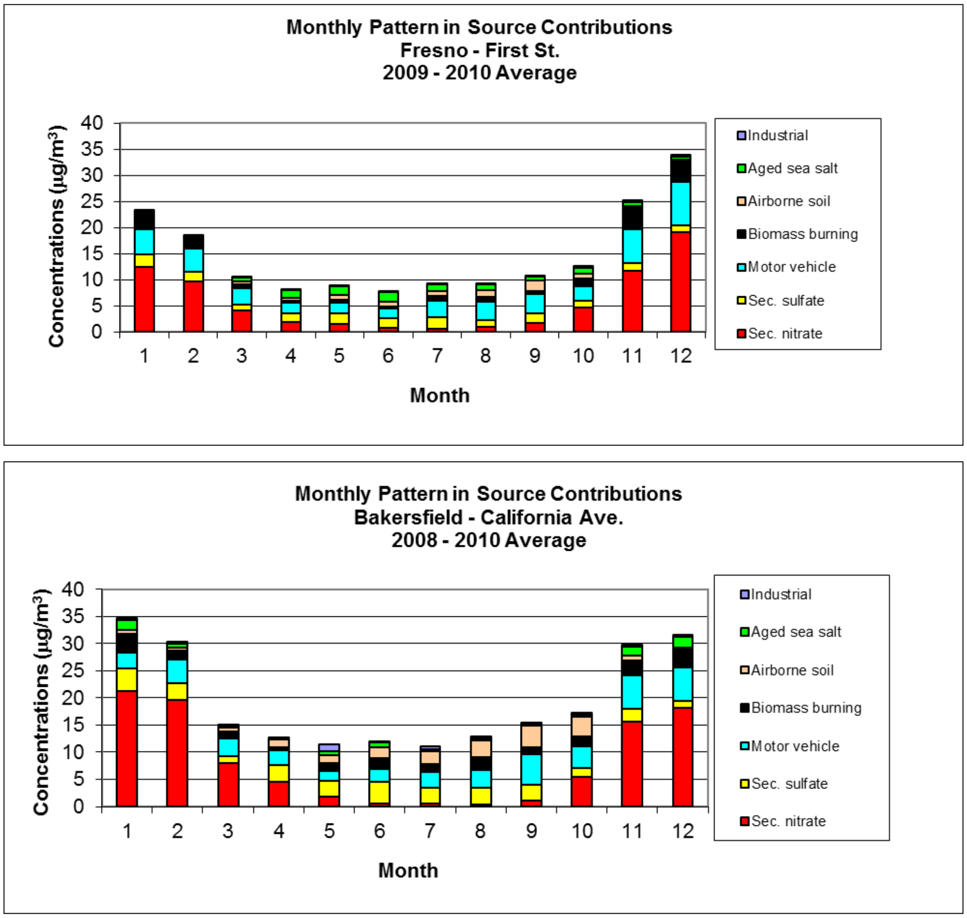


Figure 4. Monthly average source contributions.

The airborne soil factor was identified by its high concentrations of Si, Al, Ca and Fe. It contributed 7% and 10% to the $PM_{2.5}$ mass concentration at Fresno and Bakersfield, respectively. Airborne soil reflects wind-blown dust as well as re-suspended crustal materials by road traffic as indicated by the presence of OC or EC in the source profiles. Airborne soil did not show clear weekday/weekend variation. Both sites exhibited autumn-high seasonal trends. The CPF plots for airborne soil suggested high contributions from SW and S at both sites.

The aged sea salt factor was represented by its high concentrations of NO_3^-, SO_4^{2-}, and Na^+, accounting for 6% the $PM_{2.5}$ mass concentration at Fresno and 4% at Bakersfield. Aged sea salt reflects particles in which Cl^- in the fresh sea salt is partially displaced by acidic gases during the transport and collected along with NO_3^- and SO_4^{2-} (Song and Carmichael, 1999). Aged sea salt did not show weekday/weekend variation at either site. Aged sea salt had high contributions in summer at the Fresno site. Interestingly, it had a high contribution in winter at the Bakersfield site. The CPF plot for aged sea salt at Fresno site pointed towards NE. The CPF plot for aged sea salt at Bakersfield site suggested high contributions from NE and S.

A possible industrial source such as metal processing that was characterized by OC, EC, Fe, and Zn was identified at both sites. This source accounted for 2% of the $PM_{2.5}$ mass concentrations at both sites. It showed weak weekday-high variations at the Bakersfield site. The industrial source showed winter-high variations at the Fresno site. The CPF plot suggested high contributions from NE and SW at both sites.

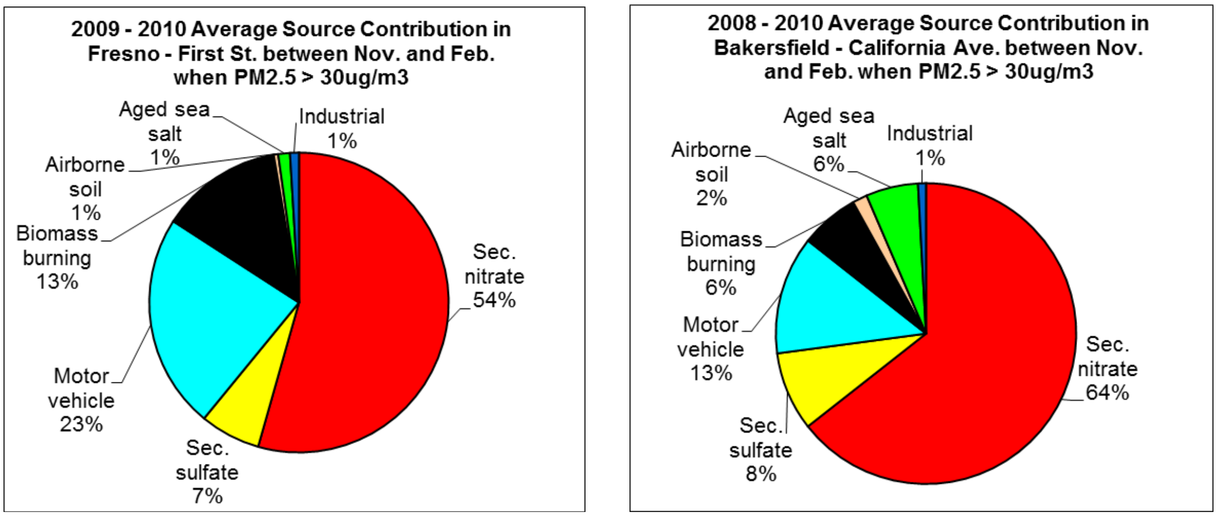


Figure 5. Average source contributions in Fresno – First St. and Bakersfield – California Ave. when $PM_{2.5}$ concentrations were higher than 30 µg/m^3 in the high $PM_{2.5}$ season (Nov. - Feb.).

Higher $PM_{2.5}$ Day Contributions

The average source contributions when $PM_{2.5}$ concentrations were higher than 30 µg/m^3 in the high $PM_{2.5}$ season (Nov. - Feb.) are shown in Figure 5 for percentiles and in Table A4 for mass concentrations. The contributions from secondary nitrate and motor vehicle were increased from 35% up to 54% and from 12% up to 23%, respectively, at the Fresno site. The biomass burning contributions also increased slightly from 11% up to 13% at Fresno site. At the Bakersfield site, the contributions from secondary nitrate increased from 41% up to 64% and aged sea salt from 4% up to 6%.

Conclusions

$PM_{2.5}$ speciation and related meteorological data collected at the Fresno-First St. and Bakersfield-California Ave. CSN monitoring sites between 2008 and 2010 were analyzed by PMF2. Seven major $PM_{2.5}$ sources were identified at both monitoring sites: secondary nitrate, secondary sulfate, motor vehicle, biomass smoke, airborne soil, aged sea salt, and industrial. Annual average and high day source contributions showed that secondary nitrate, secondary sulfate, motor vehicles, and biomass burning were the largest contributors to $PM_{2.5}$ concentrations.

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APPENDIX

Table A1. Summary of $PM_{2.5}$ species mass concentrations at Fresno.

Species	Arithmetic mean ($\mu g/m^3$)	Geometric mean ($\mu g/m^3$)	Minimum ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Number of below MDL values (%)
$PM_{2.5}$	14.5649	11.2762	0.3000	66.6000	0.6
OC	2.7861	1.9428	0.1600	17.4240	0.0
EC	0.7934	0.5764	0.0769	5.0400	0.6
SO4	1.2507	1.1155	0.2440	5.3900	0.6
NO^{3-}	3.6499	1.9445	0.0445	29.1000	0
NH_4^+	1.3964	0.8936	0.1380	9.3500	0.6
Al	0.0646	0.0418	0.0013	0.6330	25.3
Br	0.0042	0.0032	0.0001	0.0338	15.5
Ca	0.0420	0.0310	0.0027	0.2860	4.0
Cl	0.0563	0.0156	0.0001	0.5130	40.2
Cr	0.0026	0.0018	0.0000	0.0387	75.3
Cu	0.0044	0.0032	0.0001	0.0163	28.7
Fe	0.1007	0.0843	0.0129	0.6890	0
K^+	0.1072	0.0770	0.0169	0.6460	32.8
Mg	0.0200	0.0138	0.0002	0.1140	68.4
Mn	0.0019	0.0015	0.0000	0.0126	62.1
Na^+	0.1373	0.0972	0.0176	0.8720	3.4
Ni	0.0074	0.0017	0.0000	0.1850	65.5
Si	0.1682	0.1100	0.0006	1.6400	1.7
Ti	0.0057	0.0043	0.0001	0.0448	61.5
Zn	0.0067	0.0045	0.0004	0.0296	25.3

Table A2. Summary of $PM_{2.5}$ species mass concentrations at Bakersfield.

Species	Arithmetic mean (µg/m^3)	Geometric mean (µg/m^3)	Minimum (µg/m^3)	Maximum (µg/m^3)	Number of below MDL values (%)
$PM_{2.5}$	20.9253	17.1631	2.9000	73.3000	0
OC	2.4981	1.7591	0.0400	18.2200	1.3
EC	1.1390	0.9764	0.2160	3.0900	0
SO4	1.6927	1.4718	0.1200	8.0600	0
NO^{3-}	6.4908	3.2626	0.3520	35.7000	0
NH_4^+	2.5874	1.5187	0.3160	14.8000	0.7
Al	0.1276	0.0818	0.0013	1.0800	12.7
As	0.0015	0.0013	0.0001	0.0056	73.3
Br	0.0058	0.0048	0.0001	0.0299	4.7
Ca	0.1096	0.0791	0.0065	0.6770	1.3
Cl	0.0436	0.0192	0.0002	0.3270	26.0
Co	0.0013	0.0010	0.0000	0.0047	76.0
Cr	0.0021	0.0016	0.0001	0.0156	80.0
Cu	0.0089	0.0064	0.0002	0.0570	10.0
Fe	0.1923	0.1555	0.0020	1.0900	0
K^+	0.1091	0.0931	0.0183	0.5280	16.0
Mg	0.0238	0.0160	0.0002	0.2310	60.7
Mn	0.0034	0.0025	0.0003	0.0276	32.7
Na^+	0.1556	0.1229	0.0168	0.6980	1.3
Ni	0.0010	0.0009	0.0000	0.0042	84.7
Si	0.3586	0.2322	0.0217	3.4300	0.7
Sr	0.0019	0.0017	0.0001	0.0120	84.0
Ti	0.0103	0.0068	0.0001	0.0818	46.7
Zn	0.0127	0.0084	0.0006	0.1300	8.7

Table A3. Average source contributions (µg/m^3) to $PM_{2.5}$ mass concentration.

Sources	Average source contribution (± 95 % distribution)	
	Fresno	Bakersfield
Secondary nitrate	4.89 (1.09)	8.07 (1.85)
Secondary sulfate	1.72 (0.16)	2.60 (0.39)
Motor vehicle	3.70 (0.44)	4.01 (0.39)
Biomass smoke	1.47 (0.28)	2.02 (0.28)
Airborne soil	0.83 (0.14)	1.97 (0.37)
Aged sea salt	1.04 (0.16)	0.79 (0.22)
Industrial	0.22 (0.03)	0.40 (0.11)
Estimated $PM_{2.5}$ (µg/m^3)	13.86 (1.57)	19.85 (2.27)
Measured $PM_{2.5}$ (µg/m^3)	14.56 (1.74)	20.48 (2.33)

Table A4. Average source contributions (μg/m^3) to $PM_{2.5}$ mass concentration at Fresno-First St. and Bakersfield-California Ave. when $PM_{2.5}$ mass concentrations were higher than 30 μg/m^3 between Nov. and Feb.

Sources	Average source contribution (Nov. – Feb.)	
	Fresno	Bakersfield
Secondary nitrate	20.14	28.83
Secondary sulfate	2.42	3.80
Motor vehicle	8.58	5.69
Biomass smoke	4.87	2.83
Airborne soil	0.18	0.71
Aged sea salt	0.47	2.52
Industrial	0.35	0.38
No. of days	21	25

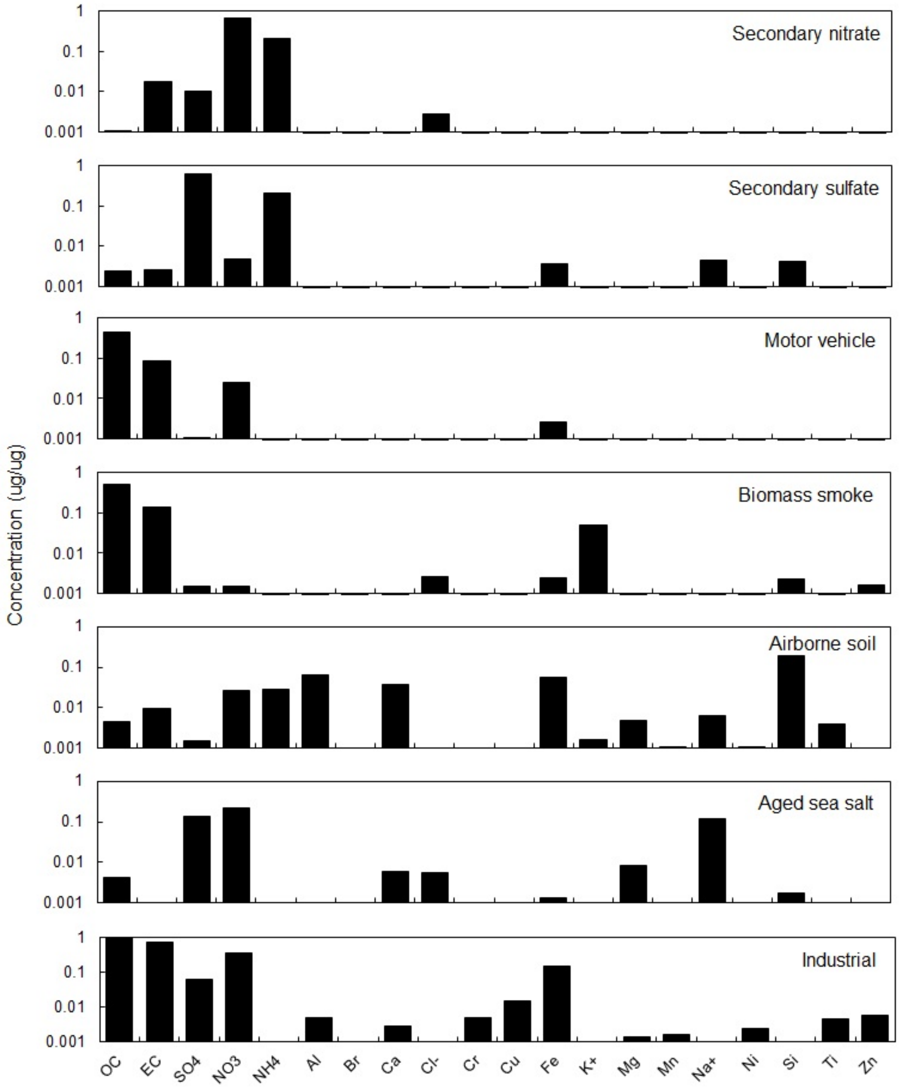


Figure A1. Source profiles deduced from $PM_{2.5}$ samples measured at Fresno-First St. (prediction ± standard deviation).

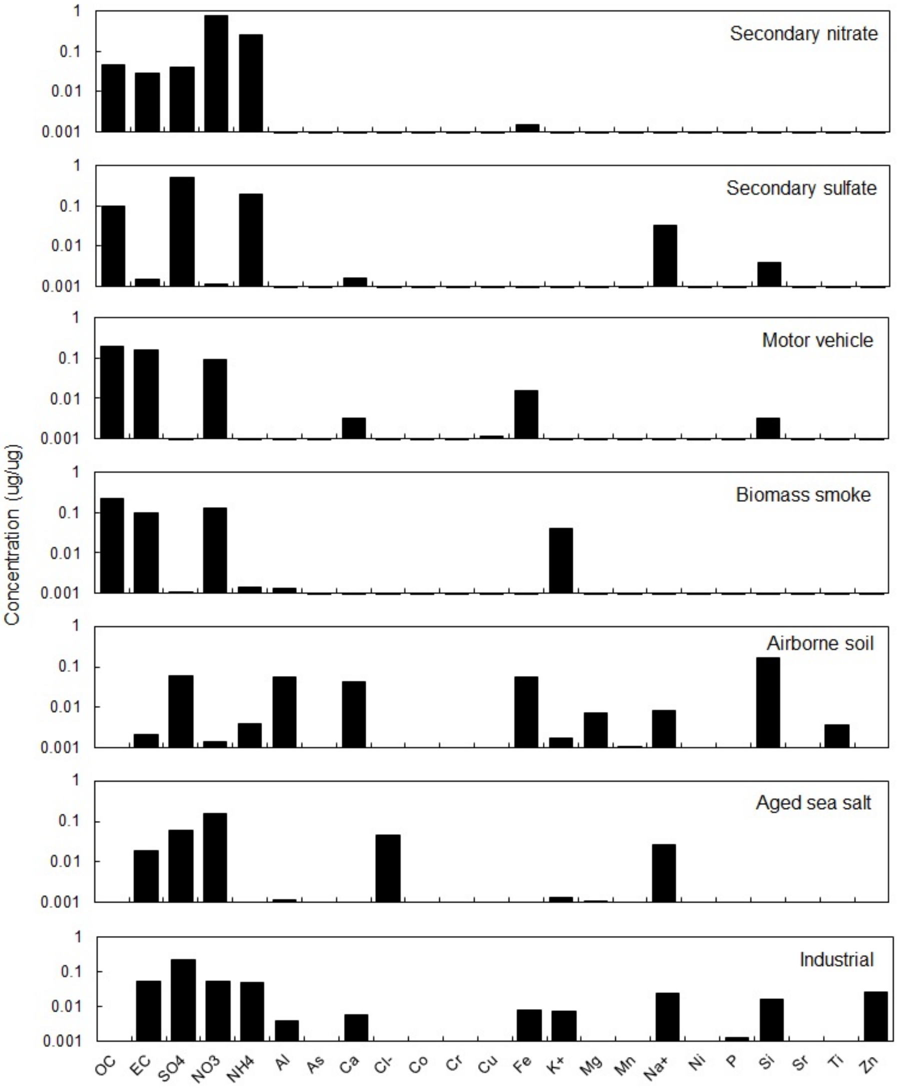


Figure A2. Source profiles deduced from $PM_{2.5}$ samples measured at Bakersfield-California Ave. (prediction ± standard deviation).

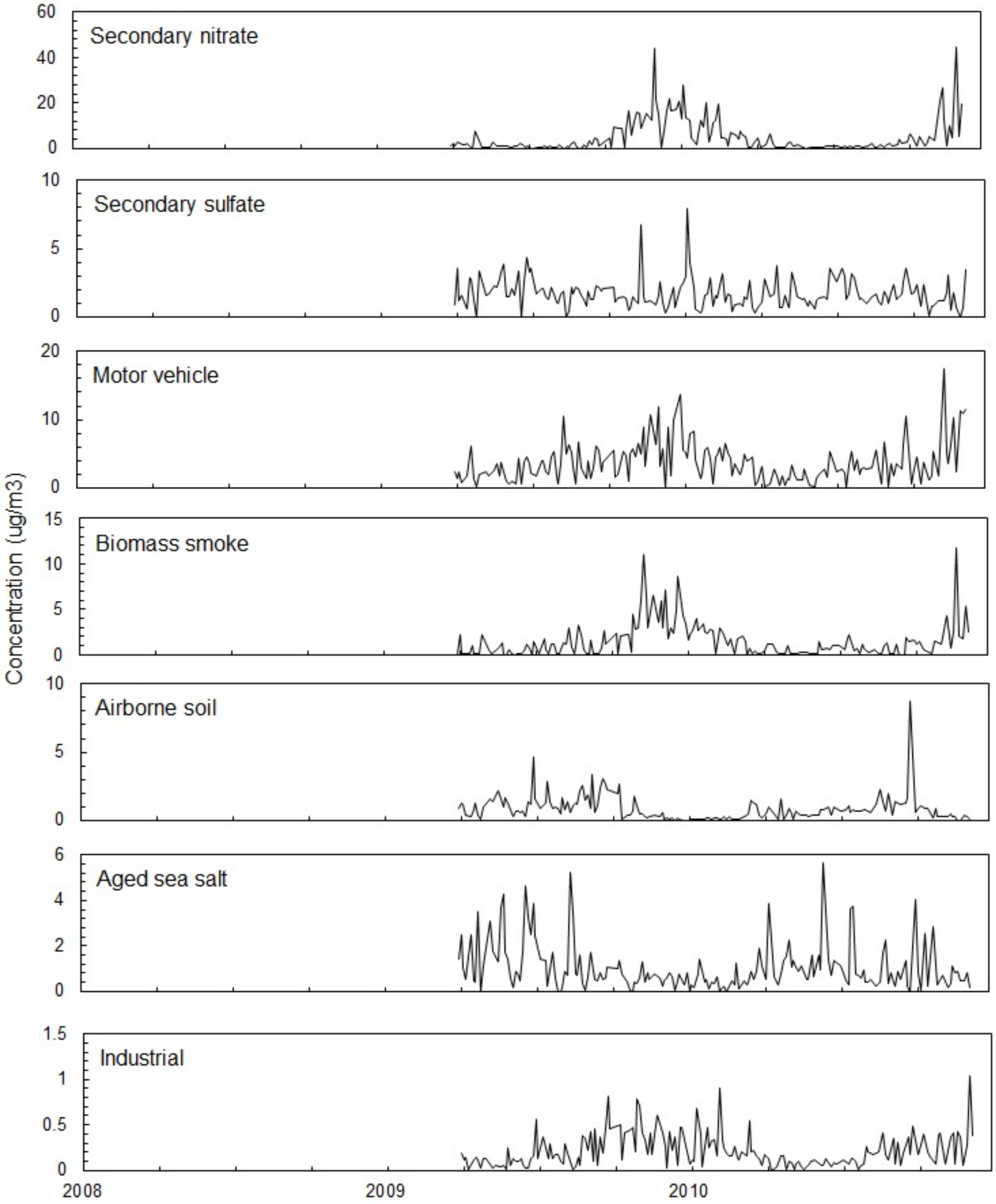


Figure A3. Source contributions deduced from $PM_{2.5}$ samples measured at Fresno-First St.

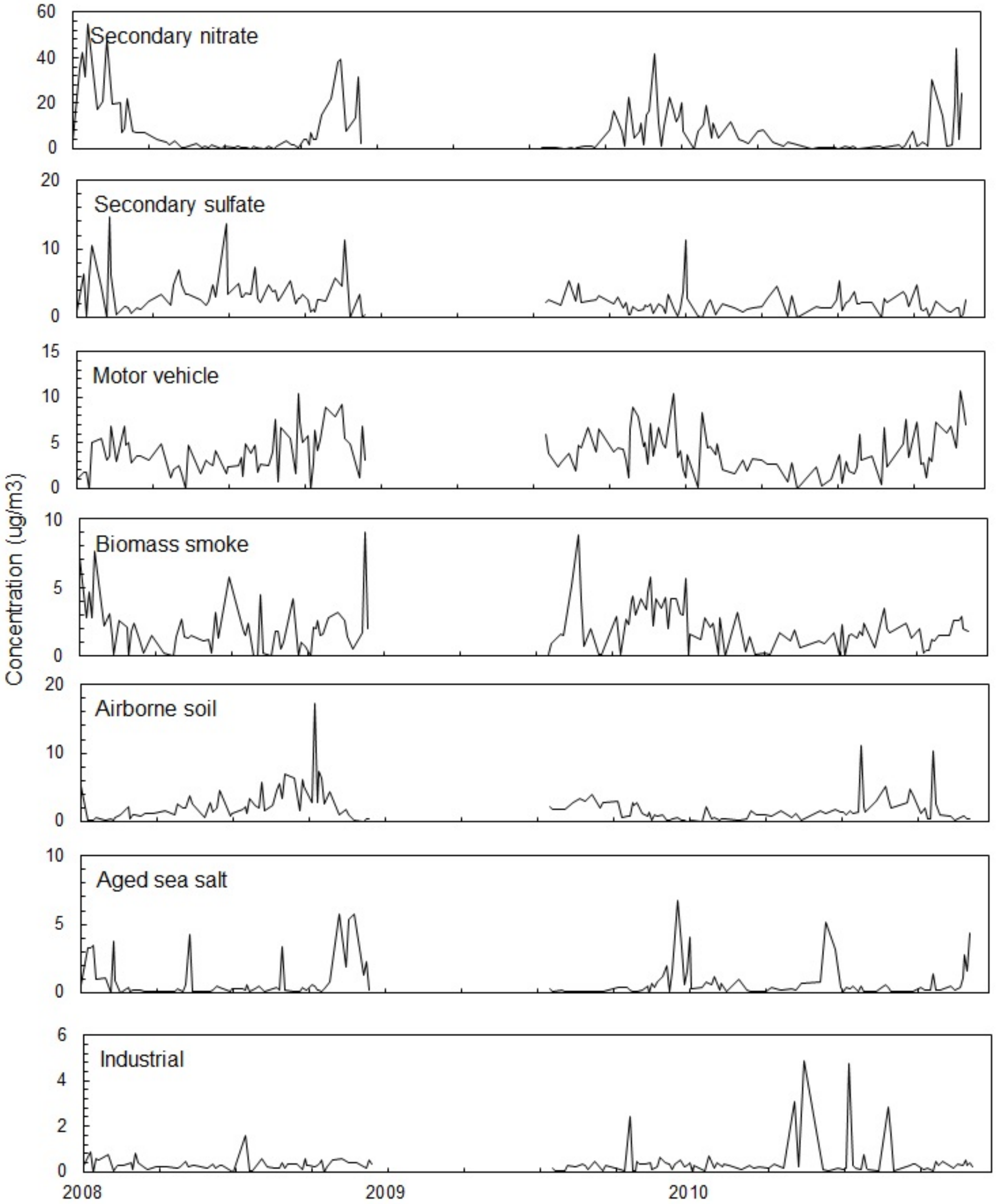


Figure A4. Source contributions deduced from $PM_{2.5}$ samples measured at Bakersfield-California Ave. (missing data: Jan. - Jun. 2009)

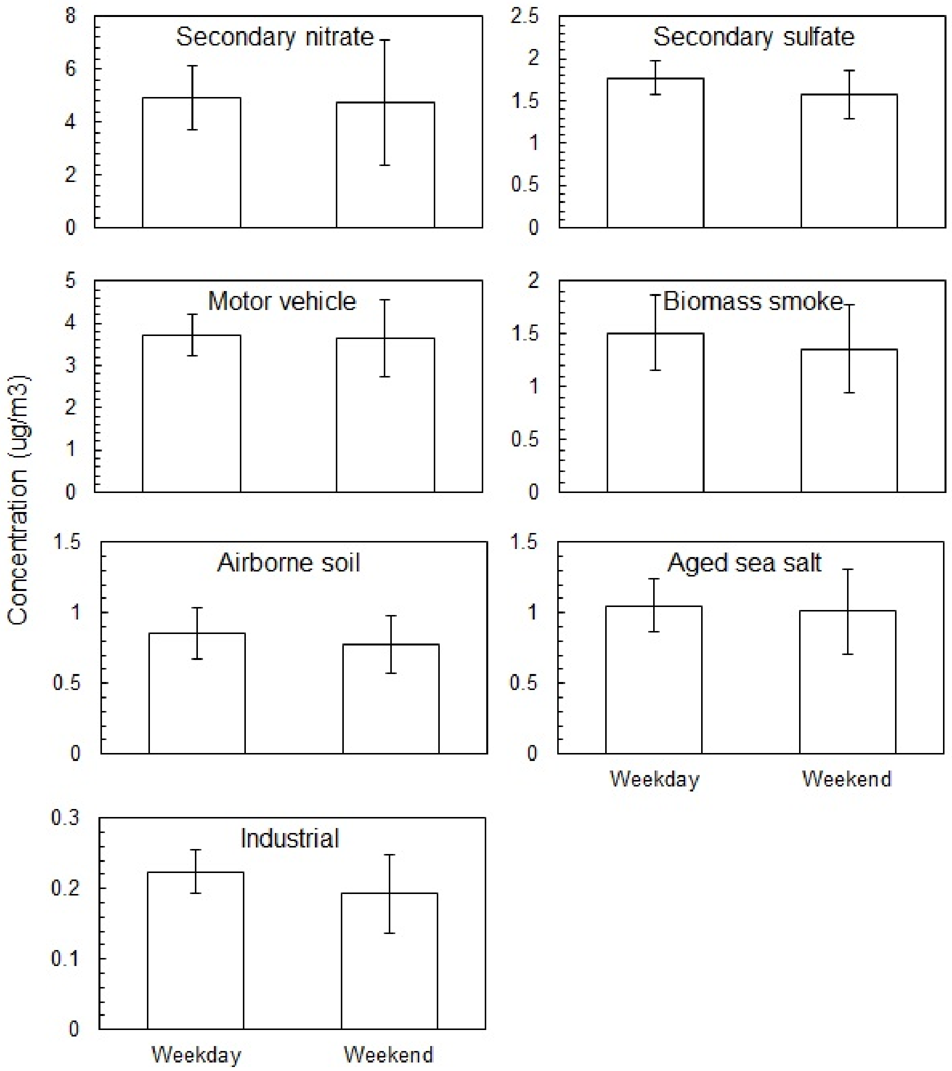


Figure A5. Weekday/weekend variations at Fresno-First St. (mean ± 95 % distribution).

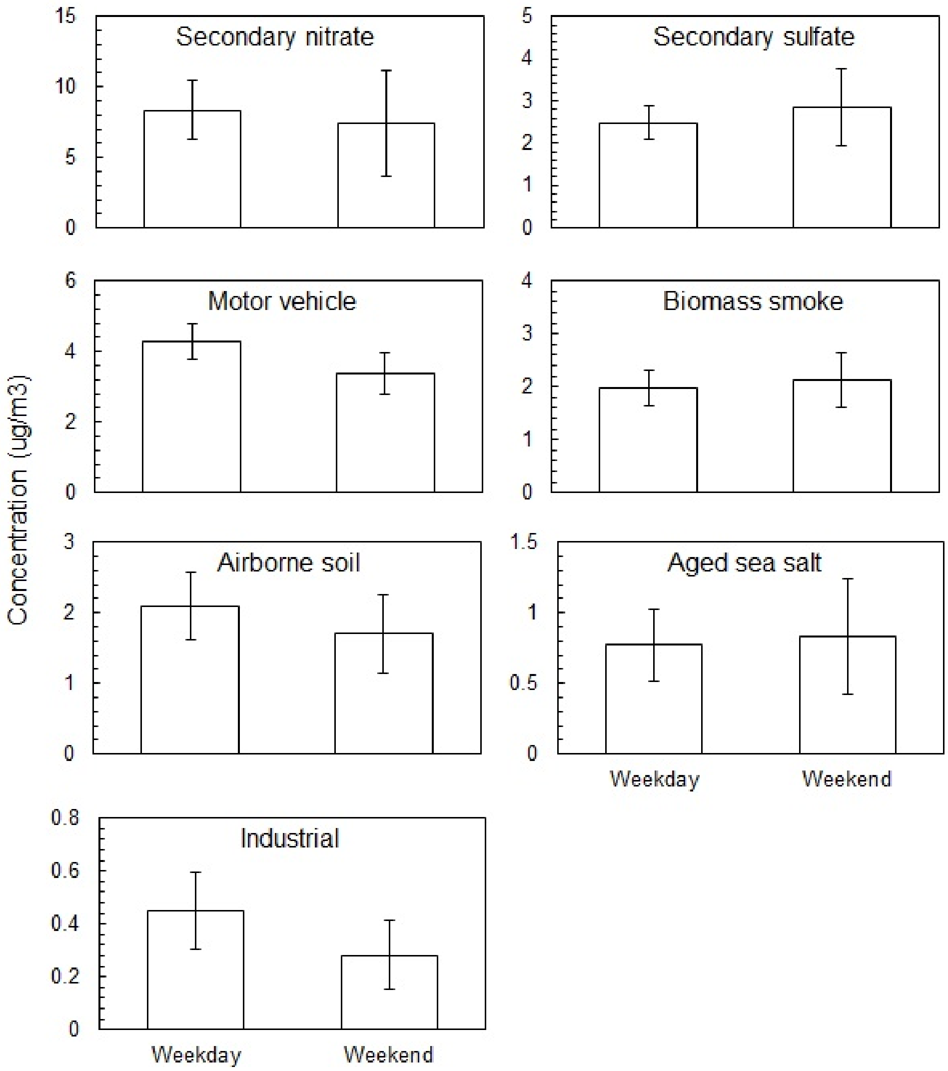


Figure A6. Weekday/weekend variations at Bakersfield-California Ave. (mean ± 95 % distribution).

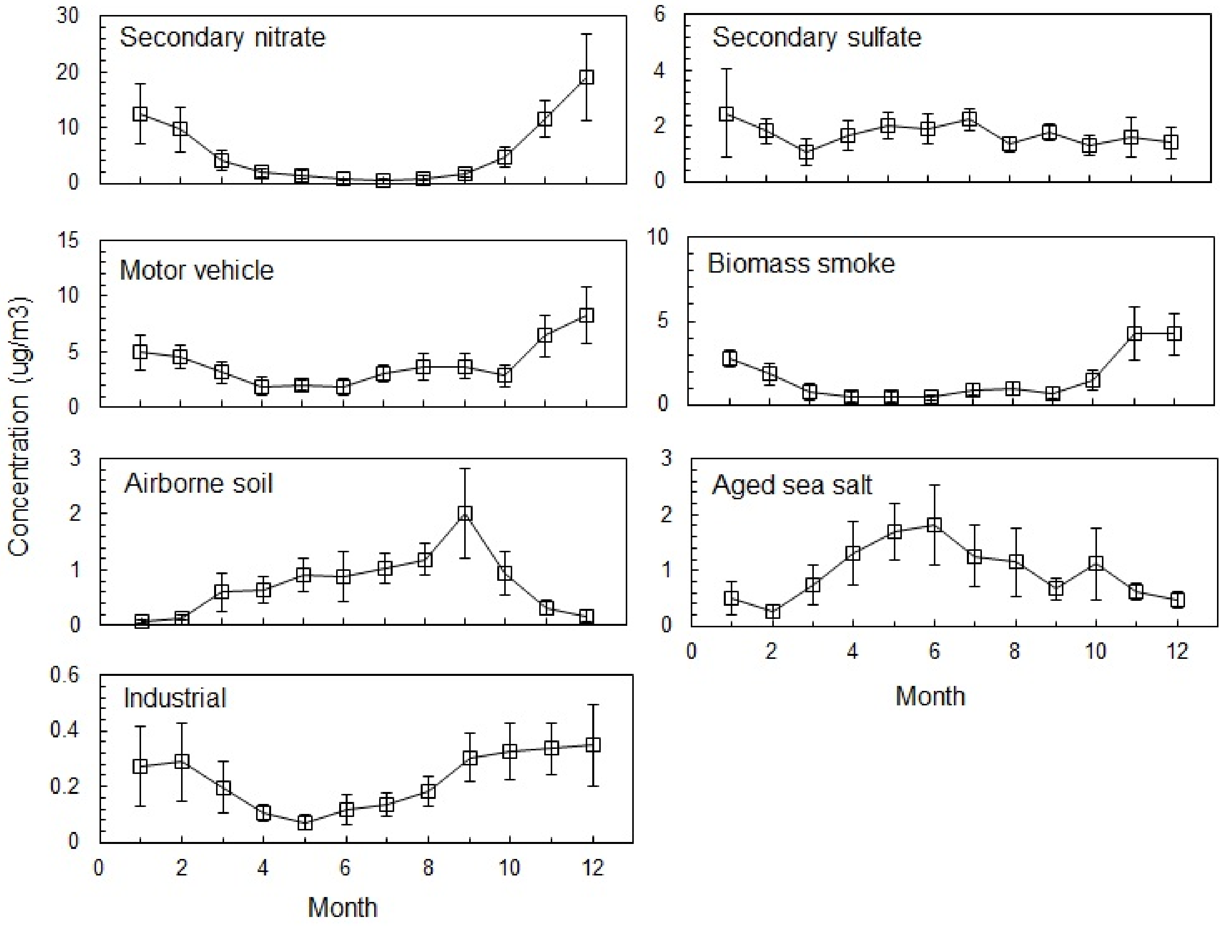


Figure A7. The monthly variations of source contributions to $PM_{2.5}$ mass concentration at Fresno-First St. (mean ± 95 % distribution).

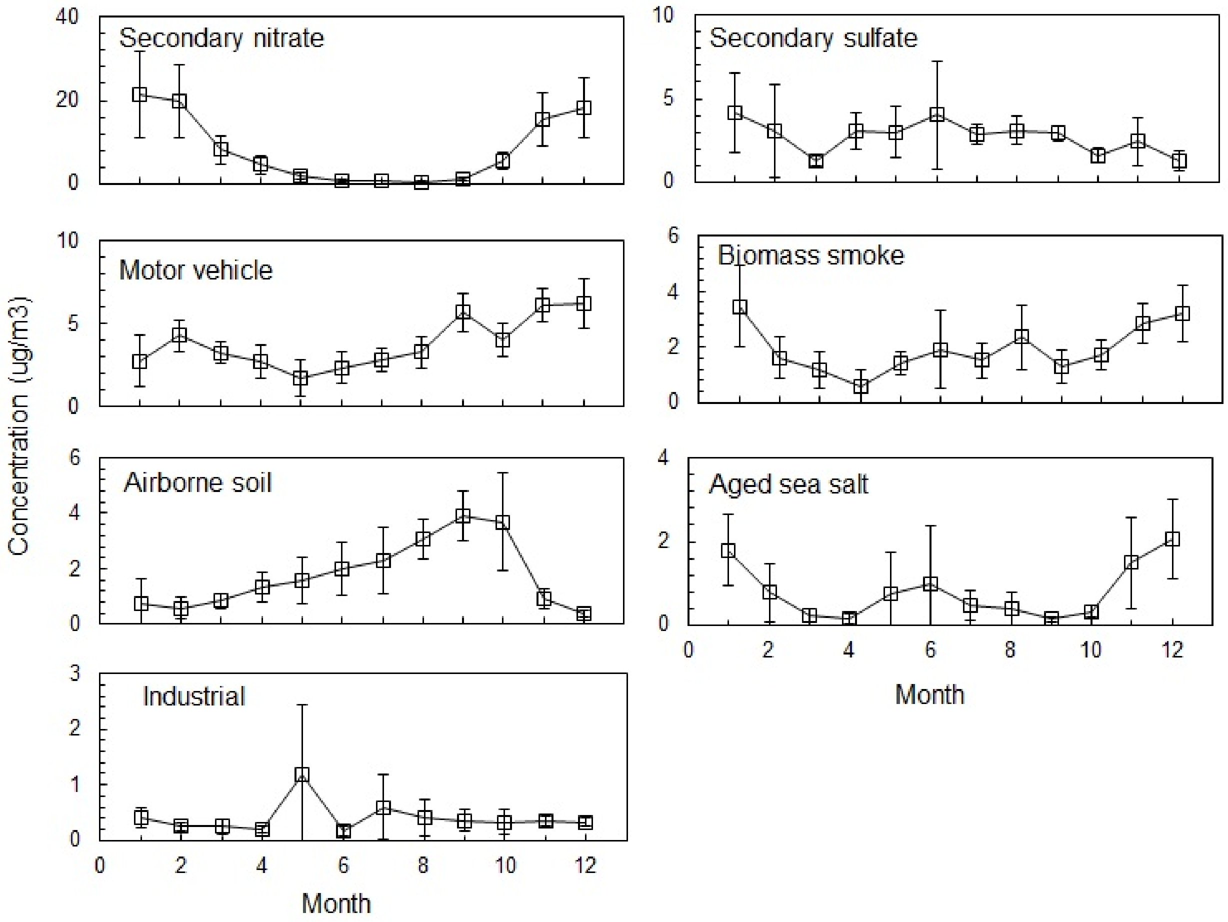
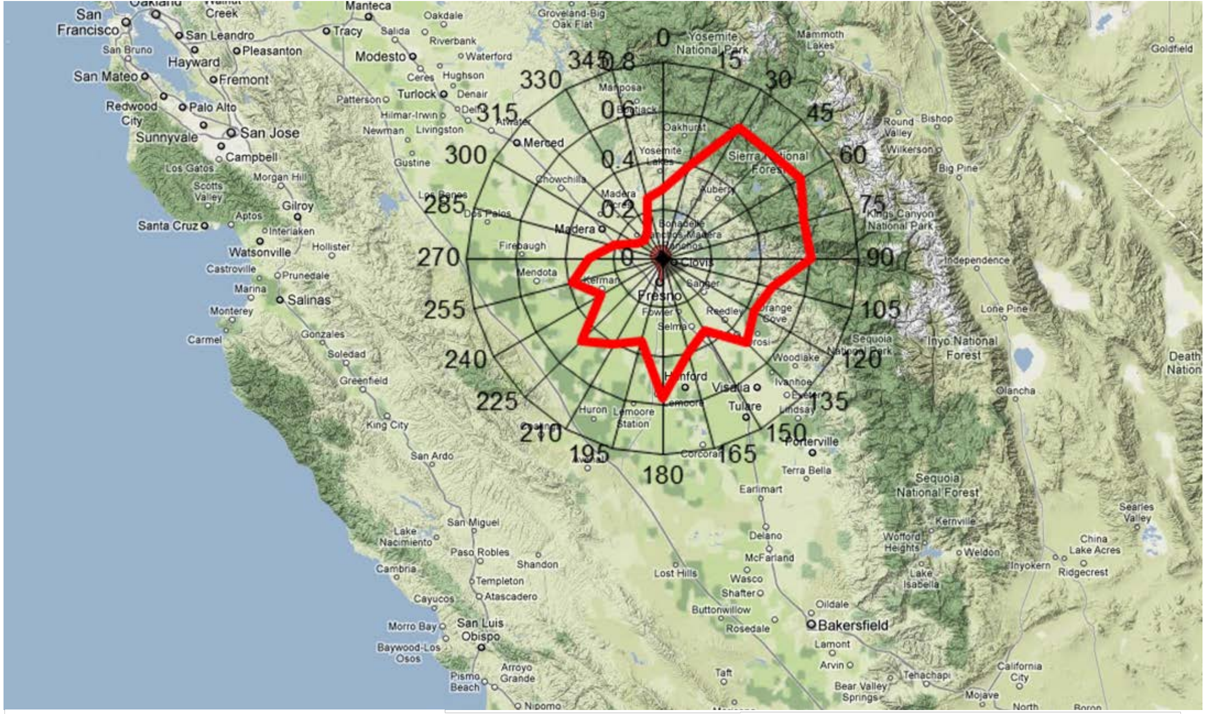


Figure A8. The monthly variations of source contributions to $PM_{2.5}$ mass concentration at Bakersfield-California Ave. (mean ± 95 % distribution).

Secondary nitrate



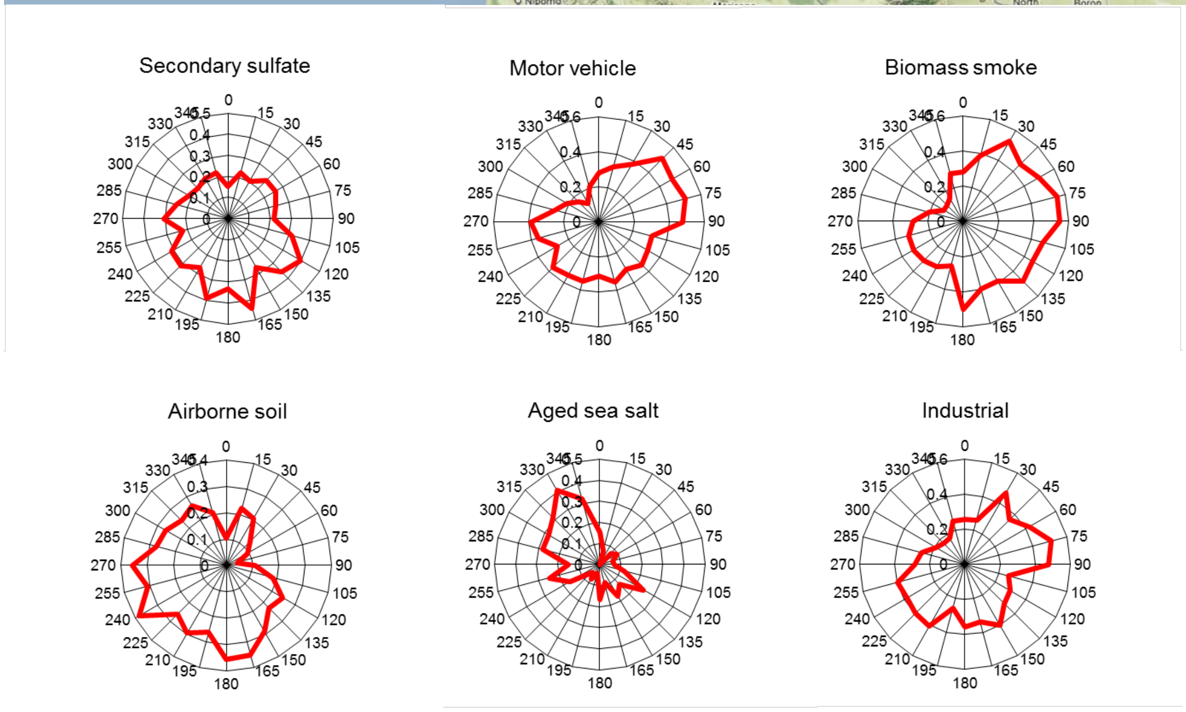


Figure A9. Conditional probability function plots for the highest 25% of the mass contributions at Fresno-First St.

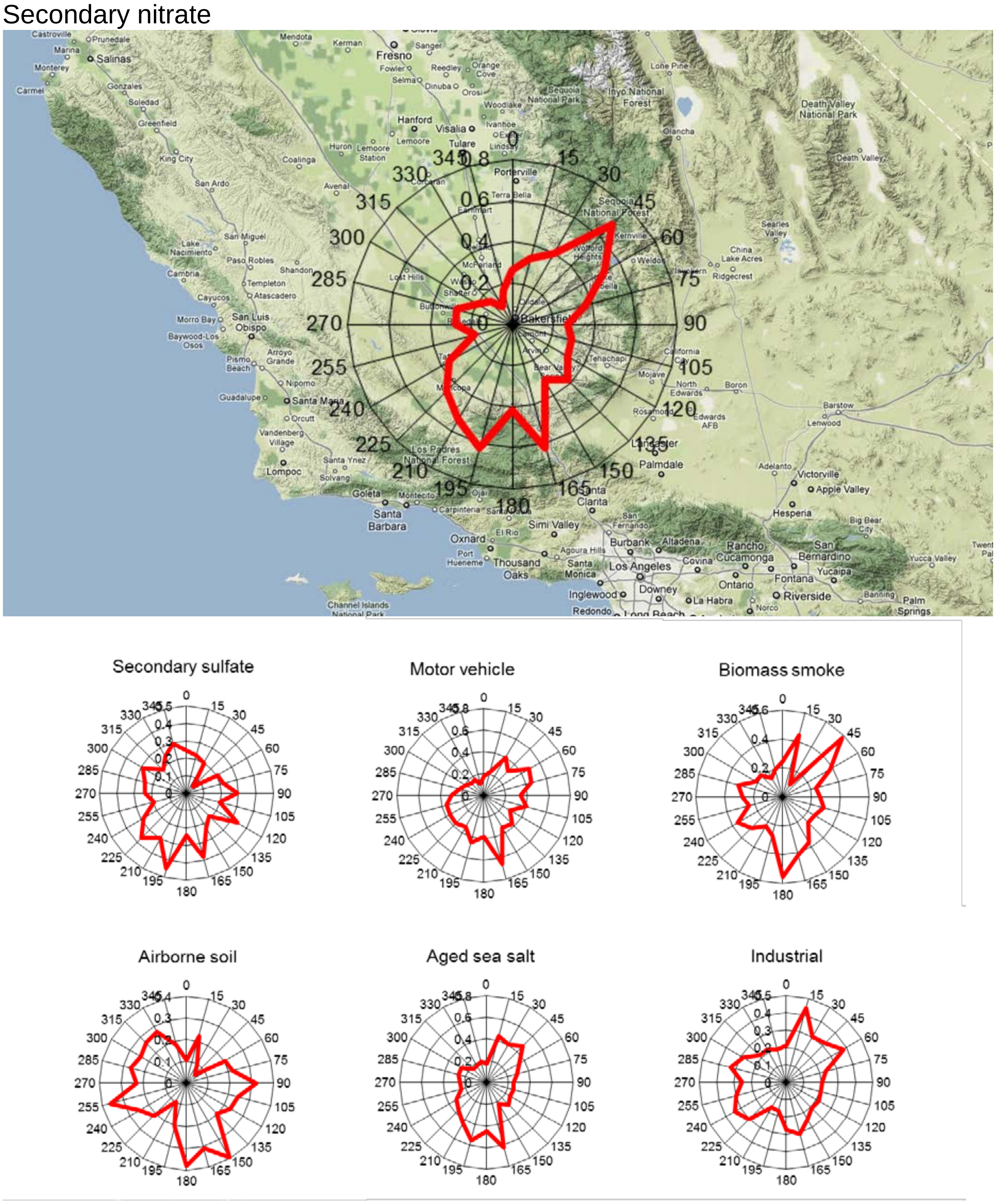


Figure A10. Conditional probability function plots for the highest 25% of the mass contributions at Bakersfield-California Ave.