

Chapter 2

PM2.5 Challenges and Trends in the San Joaquin Valley

2015 Plan for the 1997 PM2.5 Standard
SJVUAPCD

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Chapter 2: PM_{2.5} Challenges and Trends in the San Joaquin Valley

While presented with unique geographical and meteorological challenges, the San Joaquin Valley (Valley) has made significant progress in reducing total emissions of directly emitted emissions of particulate matter that is 2.5 microns or less in diameter (PM_{2.5}) and PM_{2.5} precursor emissions and in improving air quality for Valley residents. Through progressively more stringent regulations, improved control technologies, and innovative non-regulatory measures such as incentive programs, the annual average amount of directly emitted PM_{2.5} emissions has been steadily decreasing. Similarly, the overall amount of oxides of nitrogen (NO_x) and oxides of sulfur (SO_x) emissions continue to decrease.

Achieving PM_{2.5} reductions has been challenging given frequent meteorological conditions conducive to PM_{2.5} formation that are characteristic of the Valley, and which are outside human (and regulatory) control. Annual fluctuations in weather patterns affect the Valley's carrying capacity (the ability to disperse pollutants), which is reflected in long and short-term ambient air quality trends. Until the exceptional weather conditions experienced due to the recent drought, the District was on track to attain the 1997 annual PM_{2.5} standard before the federally mandated deadline of December 2014.

2.1 CHALLENGES OF THE NATURAL ENVIRONMENT

The Valley's natural environment supports one of the most productive agricultural regions in the country: the Sierra Nevada provides the necessary water for growing the abundance of crops, and a temperate climate provides a long growing season. However, these same natural factors present significant challenges for air quality: the surrounding mountains trap pollution and block air flow, and the mild climate keeps pollutant-scouring winds at bay most of the year. Despite the challenges, the San Joaquin Valley Air Pollution Control District (District) and the Valley are making progress in attaining the national ambient air quality standards (NAAQS) and improving public health for Valley citizens.

2.1.1 Unique Climate and Geography

The challenge of PM_{2.5} NAAQS attainment in the Valley is grounded in the unique topographical and meteorological conditions found in the region. The Valley, as seen in Figure 2-1, is an inter-mountain valley encompassing nearly 25,000 square miles. Surrounded by mountain ranges to the west, east, and south, the air flow through the Valley can be blocked, leading to severely constrained dispersion. During the winter, high-pressure systems can cause the atmosphere to become stagnant for longer periods of time, where wind flow is calm and air movement is minimal. These stagnant weather systems can also cause severe nighttime temperature inversions, which exacerbate the build-up of PM_{2.5} and related precursors both beneath and above the evening inversion layer.

Figure 2-1 San Joaquin Valley Air Basin

Normally, temperature decreases with increasing altitude, but during temperature inversions the normal temperature gradient is reversed, with temperatures *increasing* with altitude, causing warmer air to be above cooler air. Figure 2-2 shows that this reversal of the “normal” pattern impedes the upward flow of air, causes poor dispersion, and traps pollutants near the earth’s surface. Temperature inversions are common in the Valley throughout the year. Since the inversion is often lower than the height of the surrounding mountain ranges, the Valley effectively becomes a bowl capped with a lid that traps emissions near the surface. When horizontal dispersion (transport flow) and vertical dispersion (rising air) are minimized, PM_{2.5} concentrations can build quickly, especially in the winter. These naturally occurring meteorological conditions have the net effect of spatially concentrating direct PM_{2.5} concentrations near their sources; promoting the formation and regional buildup of secondary species, particularly ammonium nitrate; and chemically aged organic carbon species, resulting in an increase in their relative toxicity. Given these challenges, the Valley needs even more effective emissions reductions to attain the PM_{2.5} NAAQS; and the District continues to pursue these reductions through its numerous air quality attainment plans, prohibitory regulatory control strategy and innovative non-regulatory emission reduction strategy which includes a robust incentive program, a comprehensive legislative platform, and rigorous outreach and education efforts.

Figure 2-2 Atmosphere with and without a Temperature Inversion

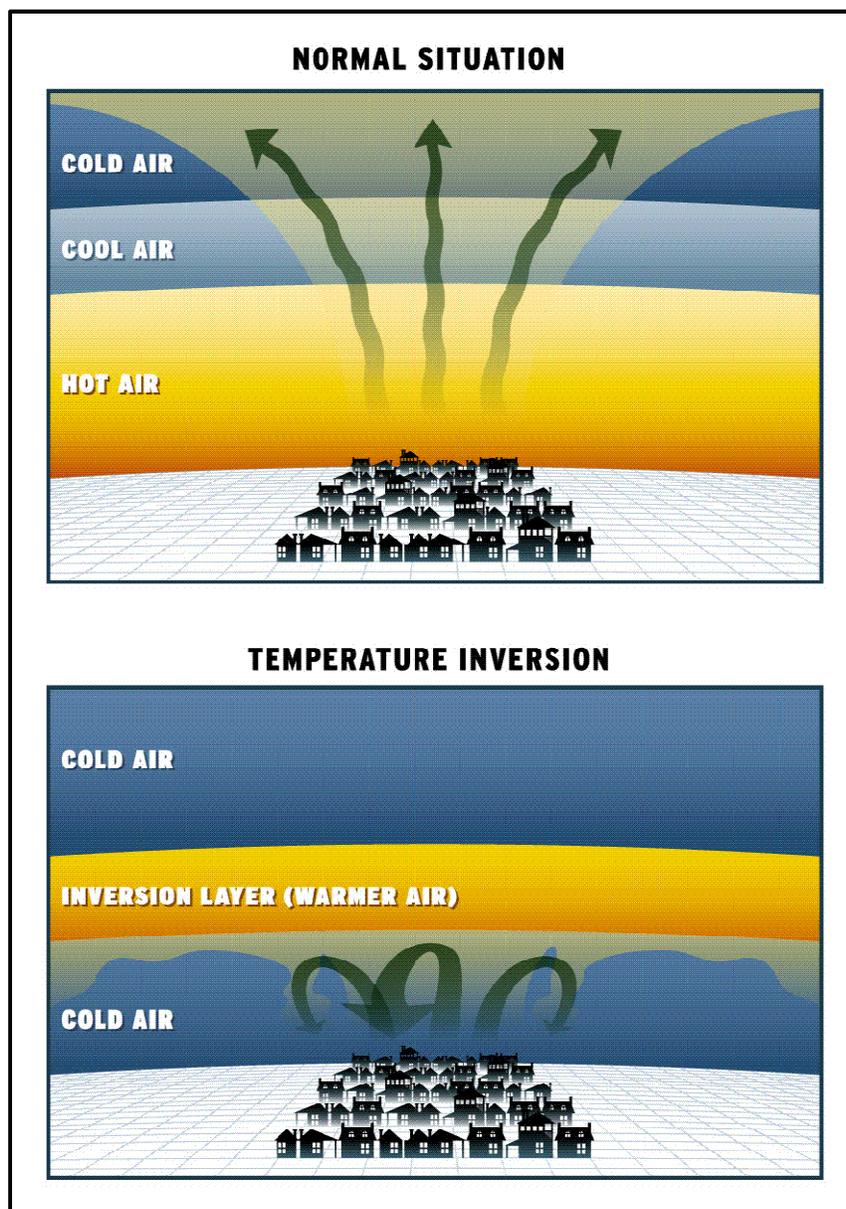


Image source: http://fden-2.phys.uaf.edu/212_spring2007_web.dir/Amber_Smith/Effects_of_Inversions.htm

2.1.2 The Valley's Carrying Capacity

In the context of air quality, carrying capacity refers to the density of emissions that an air basin can “absorb” or “carry” and still meet ambient air quality standards for a given pollutant. The key factors that shape variations in a regional carrying capacity include meteorology, climate, and the topography. Some air basins may have a high total pollutant emission rate (emissions per person or area), but if those emissions are easily dispersed or removed from the basin, that basin is much more likely to meet air quality standards despite high emission rate. On the other hand, an air basin may have a

lower emission rate, but because of unfavorable environmental factors (low air flow, stagnant air, inversions) those pollutant concentrations typically accumulate (possibly above the standard) and remain in the air basin until weather patterns change. The latter scenario describes the Valley, and the first scenario is analogous to the Los Angeles (L.A.) air basin, especially for NO_x emissions and the formation of ozone.

As an example, total NO_x emissions for the L.A. basin were 754 tons per day (tpd) in 2008. During that year, the L.A. basin recorded 80 days above the 1997 national 8-hour ozone standard. For the same year, the total NO_x emissions for the Valley air basin were 409 tpd (over a much larger area), yet the Valley recorded 82 days above the standard. NO_x dispersal is primarily dependent on summertime weather patterns. The L.A. basin experiences regular coastal winds through much of the summer that not only disburse pollutants from the air basin, but also moderates temperatures. Conversely, the Valley, surrounded by mountain ranges, routinely experiences stagnant weather patterns (less wind) and extended periods of high temperatures, both of which build and concentrate ozone to levels above the standard. In this real example, it is obvious that the Valley has a much lower carrying capacity than the L.A. basin for NO_x, a precursor to ozone formation.

While not as drastic as the NO_x-ozone example above (in terms of emission rate), the Valley's carrying capacity for PM_{2.5}, when compared to the L.A. basin, is greatly affected by prevailing weather during the winter months and the region's topography (surrounding mountains). For 2008, the annual average direct PM_{2.5} emission rate for the L.A. basin was 80 tpd; during that year, that basin recorded 19 days above the national PM_{2.5} 24-hour standard. For the same year, the Valley's annual average direct PM_{2.5} emission rate was 82 tpd; however, the Valley recorded 66 days above the 24-hour standard. During this same time period, the NO_x and SO_x emissions, which are also precursors to PM_{2.5}, were significantly lower in the Valley compared to the L.A. Basin (NO_x—409 tpd and 754 tpd, respectively, as stated above; and SO_x—13 tpd and 54 tpd, respectively). As noted in Section 2.2.1, temperature inversions are common during the winter months in the Valley. During these sometimes lengthy stagnant air episodes, PM_{2.5} emissions from daily activities rapidly build up to levels above the standard. It is during these events (or anticipation of these events) that the District's Check-Before-You-Burn program and Real-time Air Advisory Network (RAAN) system intervene to inform (or require) the public to limit activity that generates PM_{2.5} emissions.

The District uses quantitative carrying capacity analysis in its modeling of attainment demonstrations. Such analyses can determine which combinations of PM_{2.5} and PM_{2.5} precursor emissions reductions can contribute to future attainment given anticipated population and activity growth, potential regulations or control measures, and the unchanging natural physical constraints.

2.2 THE VALLEY'S UNIQUE CHALLENGES

In addition to the climate and geography challenges discussed above, the Valley also has multiple other unique challenges that continue to impact the Valley's progress toward attainment of air quality standards. The Valley has significant naturally occurring biogenic emissions. The California landscape also allows for air pollutant transport within the Valley, as well as between the Valley and other air basins. The Valley is also one of the fastest growing regions in the state. From 2010 to 2020, the Valley's population is expected to increase by 18% (Table 1-1). In contrast, the total population for the State of California is projected to increase by only 9% over the same time period. Increasing population generally means increases in air pollutant emissions as a result of increased consumer product use and more automobile and truck travel. Between 2010 and 2020, the Valley's total vehicle miles traveled (VMT) will increase about 21%,¹ consistent with the Valley's population growth. The Valley is also home to the state's major arteries for goods and people movement, which adds to the increase in vehicular traffic.

Table 1-1 Estimated Valley Population by County (2010-2020)²

County	Estimated 2010	Projected 2020
Fresno	932,926	1,083,889
Kern*	841,609	1,041,469
Kings	152,996	179,722
Madera	151,136	183,176
Merced	256,345	301,449
San Joaquin	686,651	795,631
Stanislaus	515,229	582,746
Tulare	443,567	536,429
Total	3,980,459	4,704,511

*Kern County is separated into two air districts: San Joaquin Valley and Eastern Kern. This data is the Valley-portion of Kern only.

Although reducing mobile source emissions is critical to the Valley's attainment of air quality standards, the District does not have direct regulatory authority to reduce motor vehicle tailpipe emissions, which are regulated by the EPA and ARB. The District must collaborate with interagency partners and use innovative approaches to reduce mobile source emissions.

As Chapter 3 of this plan details, the formation and composition of PM_{2.5} can be complex, with some species impacting health more than others. Long-term trends show that PM_{2.5} concentrations throughout the Valley have declined since monitoring of this pollutant first began and are projected to continue on that trend. In addition to declining

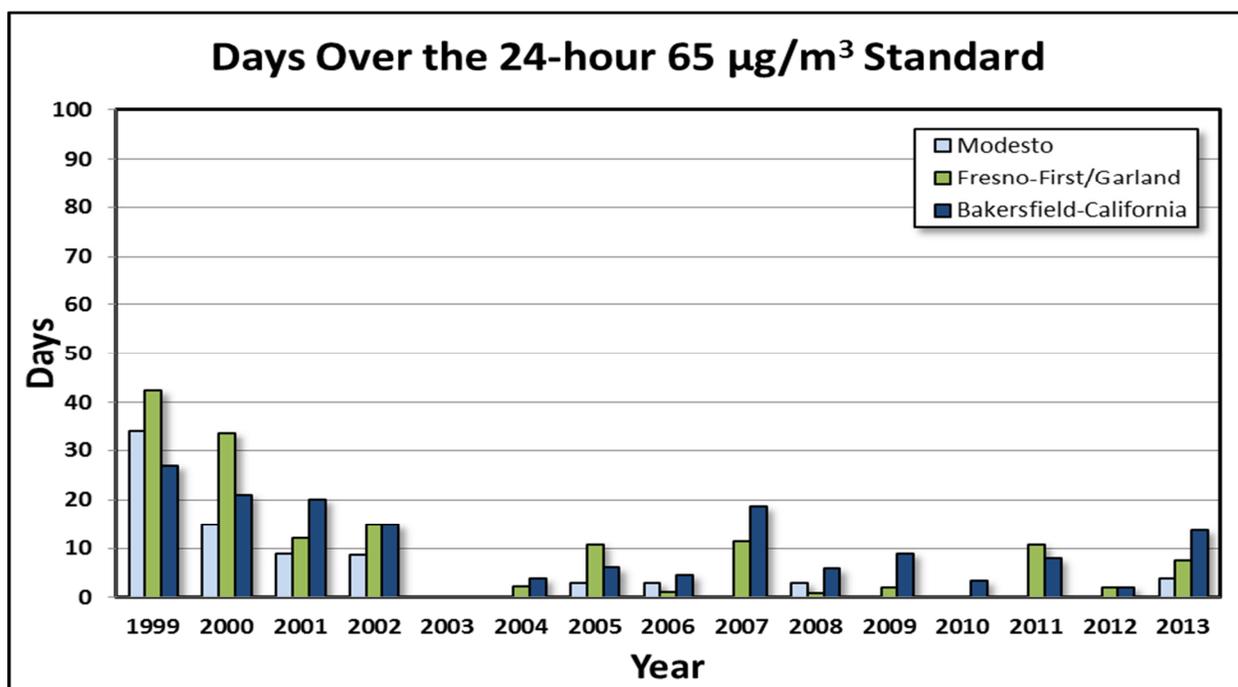
¹ California Air Resources Board: 2009 Almanac – Population and Vehicle Trends Tool. Retrieved July 2012 from http://www.arb.ca.gov/app/emsinv/trends/ems_trends.php

² California Department of Finance [DOF]: Interim Population Projects for California and its Counties 2010-2050. (May 2012). Retrieved from <http://www.dof.ca.gov/research/demographic/reports/projections/interim/view.php>

PM2.5 concentrations, most emissions inventories of PM2.5 precursors are also projected to decrease despite future population growth.

The District also assesses long-term trends of PM2.5 concentration by looking at the number of days per year that a monitoring site measures concentrations over the PM2.5 1997 24-hour NAAQS limit of 65 µg/m³. Figure 2-3 shows the trend in numbers of days that air monitoring sites recorded 24-hour PM2.5 averages over 65 µg/m³ at the Modesto (Stanislaus County), Fresno-First/Garland (Fresno County), and Bakersfield-California (Kern County) air monitoring sites. An overall downward trend is apparent when comparing the early years of 1999 and 2000 to recent years. The current pattern shows generally that the northern Valley has the fewest days over the standard, that the southern Valley has the most days over the standard, and that the central Valley registers somewhere between the two.

Figure 2-3 Trend in Days over the 24-hour PM2.5 Standard



2.3 PM2.5 EMISSIONS INVENTORY TRENDS

The emissions inventory is the foundation for the attainment planning process. The District and the California Air Resources Board (ARB) maintain an accounting of PM2.5 and precursor emissions for the Valley based on known sources within the Valley and those sources outside the Valley that influence Valley air quality (inter-region transport). The District requires detailed accounting of emissions from regulated sources throughout the Valley. ARB makes detailed estimations of emissions from mobile, area, and geologic sources using known emissions factors for each source or activity and accounting for relevant economic and population data. Together, these feed into the emissions inventory that represents an estimate of how much direct pollution is going into the Valley air basin as a result of the cumulative pollutant-generating activities and sources.

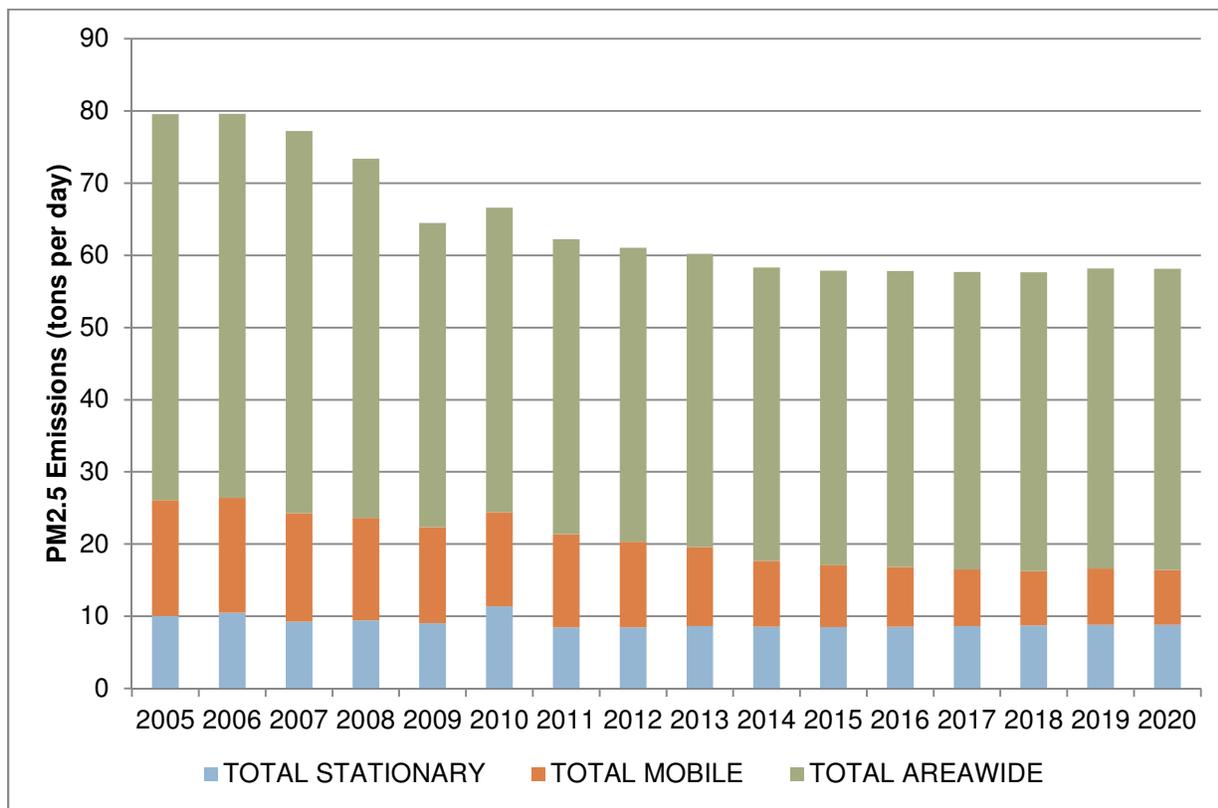
The District uses the emissions inventory to develop control strategies, to determine the effectiveness of permitting and control programs, to provide input into air quality modeling, to fulfill reasonable further progress requirements, and to screen regulated sources for compliance investigations.

The following general list represents the major inventory categories for which emissions are recorded and tracked. Appendix B to this plan contains the detailed accounting of the emissions inventory with projected emissions based on anticipated growth of each source and the anticipated control (regulatory or non-regulatory) of each source, if applicable.

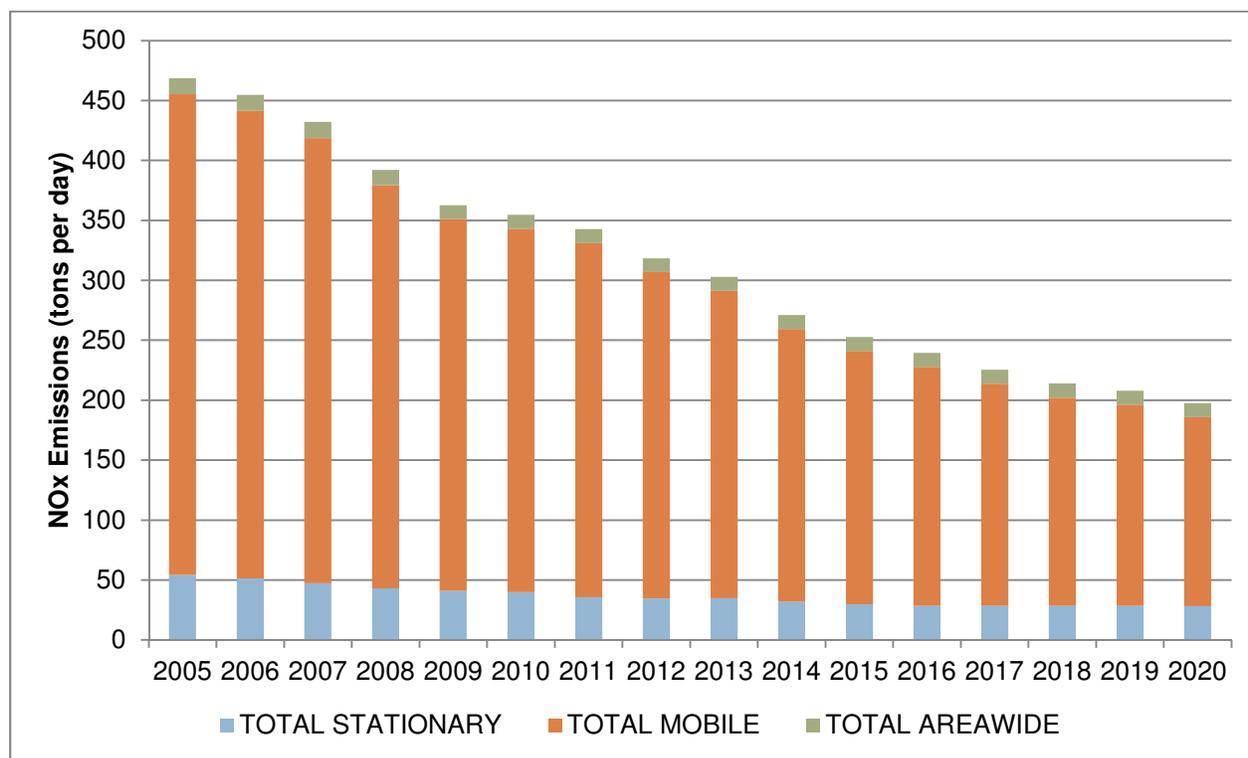
- **Mobile sources** – motorized vehicles
 - On-road sources include automobiles, motorcycles, buses, and trucks
 - Other or off-road sources include farm and construction equipment, lawn and garden equipment, forklifts, locomotives, boats, aircraft, and recreational vehicles
- **Stationary sources** – fixed sources of air pollution
 - Power plants, refineries, and manufacturing facilities
 - Aggregated point sources, i.e. facilities (such as gas stations and dry cleaners) that are not typically inventoried individually, but are estimated as a group and reported as a single source category
- **Area sources** – human activity that takes place over a wide geographic area
 - Includes consumer products, residential wood burning, controlled burning, tilling, and unpaved road dust
- **Natural sources** – naturally occurring emissions
 - Geologic sources, such as petroleum seeps
 - Biogenic sources, such as emissions from plants
 - Wildfire sources

Figure 2-4 shows the PM2.5 emissions inventory trend for the mobile, stationary, and area source categories.

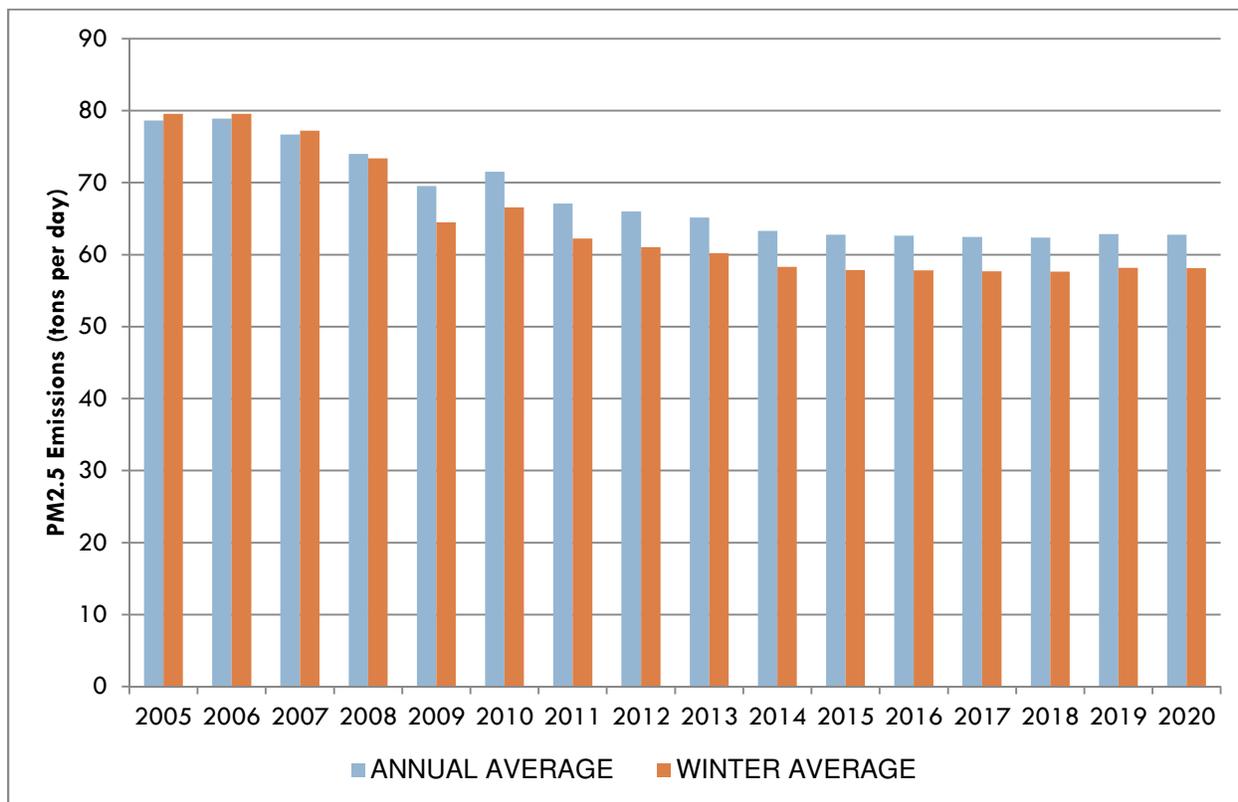
Figure 2-4 Valley PM2.5 Winter Emissions Inventory Trend



Because NOx is a significant PM2.5 precursor, the District relies heavily on NOx emissions to also reduce PM2.5 emissions. Figure 2-5 summarizes the NOx emissions inventory trends for the mobile, stationary, and area source categories. District and ARB control strategies for NOx play a significant role in reducing both ozone and PM2.5 emissions.

Figure 2-5 Valley Winter NOx Emissions Inventory Trend

Emissions inventory trends show the progress made through progressive regulatory and non-regulatory activities, e.g. as rules are amended with tighter emission limits, or as reduction technologies improve, overall emissions decrease. Figure 2-6 shows how the overall tons of PM_{2.5} emissions per day have decreased in the past and are anticipated to continue decreasing in the future based on anticipated growth and controls. Figure 2-6 also shows the comparative emission inventory reduction of winter PM_{2.5}. Winter PM_{2.5} emissions have decreased significantly, in large part due to the effectiveness of Rule 4901 (Wood Burning Fireplaces and Wood Burning Heaters). Continued emissions reductions are based on current control strategies that will continue to take effect into the future. In light of the Valley's projected increase in population, the projected emissions reductions highlight the success of the control measures adopted and enforced by the District, ARB, and other regulatory agencies.

Figure 2-6 Valley PM_{2.5} Annual and Winter Inventory Trends

2.4 PM_{2.5} AIR QUALITY TRENDS

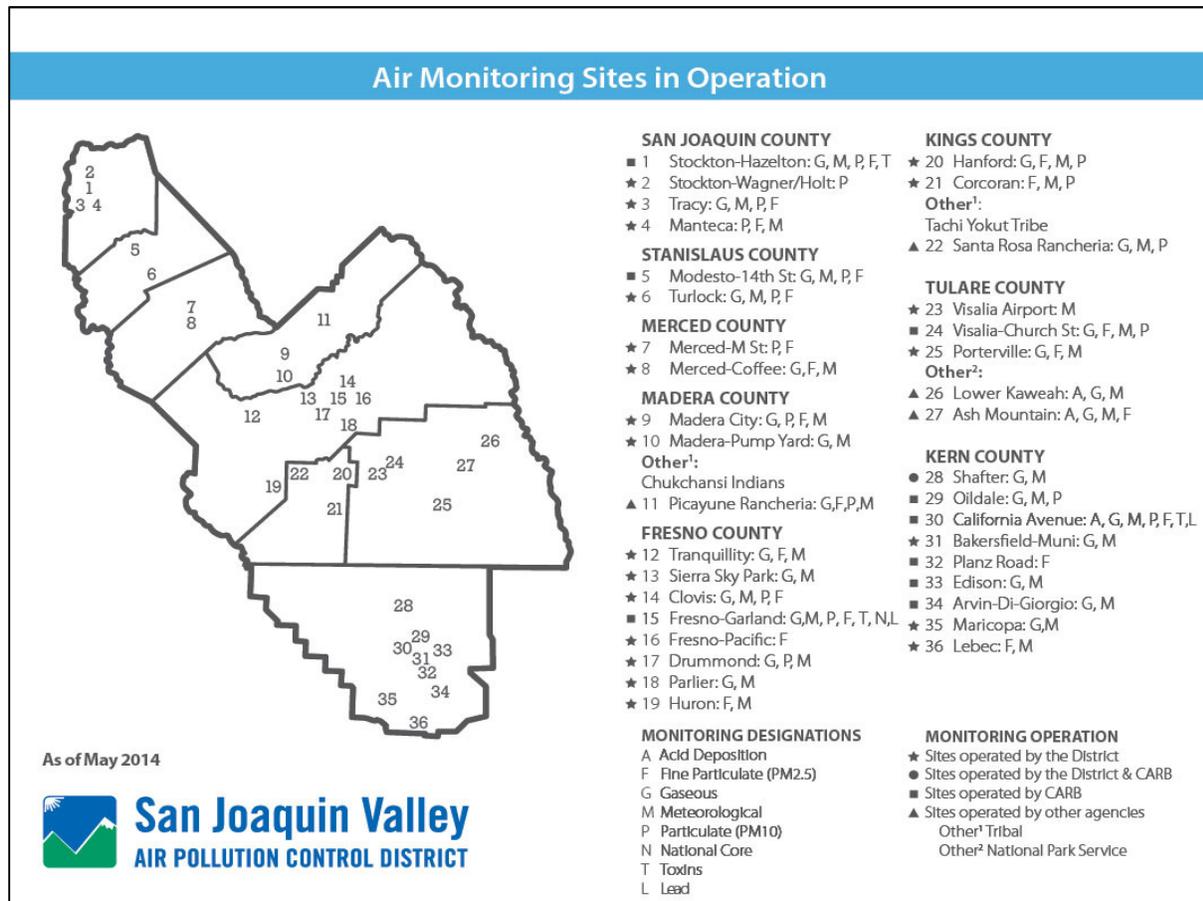
As a public health agency charged with monitoring Valley air quality and ensuring progress toward meeting national air quality standards, the District has established an extensive air monitoring network that provides ongoing data for evaluating such progress. Information from this extensive monitoring network, which began measuring PM_{2.5} concentrations in 1999, allows the District to track air quality trends that show progress toward attainment and inform the planning process for reaching attainment.

2.4.1 Air Monitoring Network

Numerous pollutants and meteorological parameters are measured throughout the Valley on a daily basis using an extensive air monitoring network managed by the District, ARB, and other agencies. This network measures pollutant concentrations necessary to show progress toward compliance with the NAAQS. The network also provides real-time air quality measurements used for daily air quality forecasts, residential wood-burning declarations, Air Alerts, and RAAN. Air quality monitoring networks are designed to monitor areas with high population densities, areas with high pollutant concentrations, areas impacted by major pollutant sources, and areas representative of background concentrations. Together, the District and the ARB operate 33 air monitoring stations throughout the Valley; 20 of these sites measure PM_{2.5}, either through the use of filter-based monitors that measure each 24-hour period

or hourly monitors that use light energy to provide near-continuous concentration levels. Figure 2-7 shows the Valley's network of air monitoring sites.

Figure 2-7 Air Monitoring Sites in the Valley



PM_{2.5} is measured and expressed as the mass of particles contained in a cubic meter of air (micrograms per cubic meter, or $\mu\text{g}/\text{m}^3$). The data collected from the District's network of PM_{2.5} monitors is used to calculate design values for the 24-hour and annual PM_{2.5} standards, as outlined in U.S. Environmental Protection Agency (EPA) guidance and regulations.^{3,4}

2.4.2 Air Quality Progress

Air quality progress can be assessed in several ways. The calculation of *design values* is the official method used to determine whether an area is in attainment of a standard; however, other indicators can reveal more about the progress being made toward attaining that standard. Comparing the days per year when each monitor exceeded the

³ Environmental Protection Agency [EPA]: Office of Air Quality Planning and Standards. (1999, April). *Guideline on Data Handling Conventions for the PM NAAQS* (EPA-454/R-99-008). Retrieved from <http://www.epa.gov/ttn/oarpg/t1/memoranda/pmfinal.pdf>

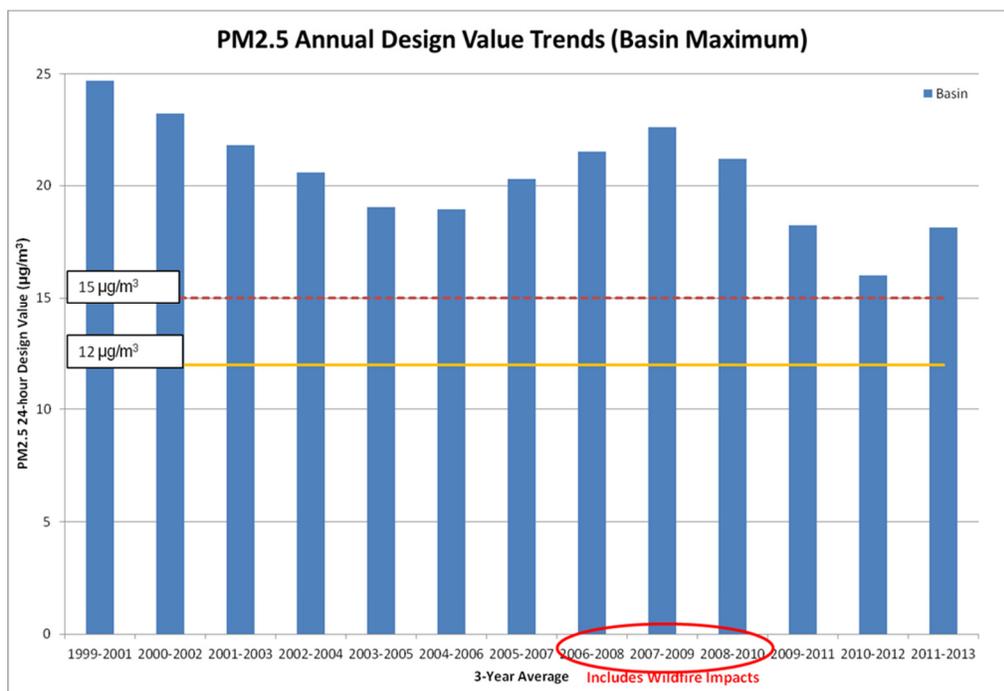
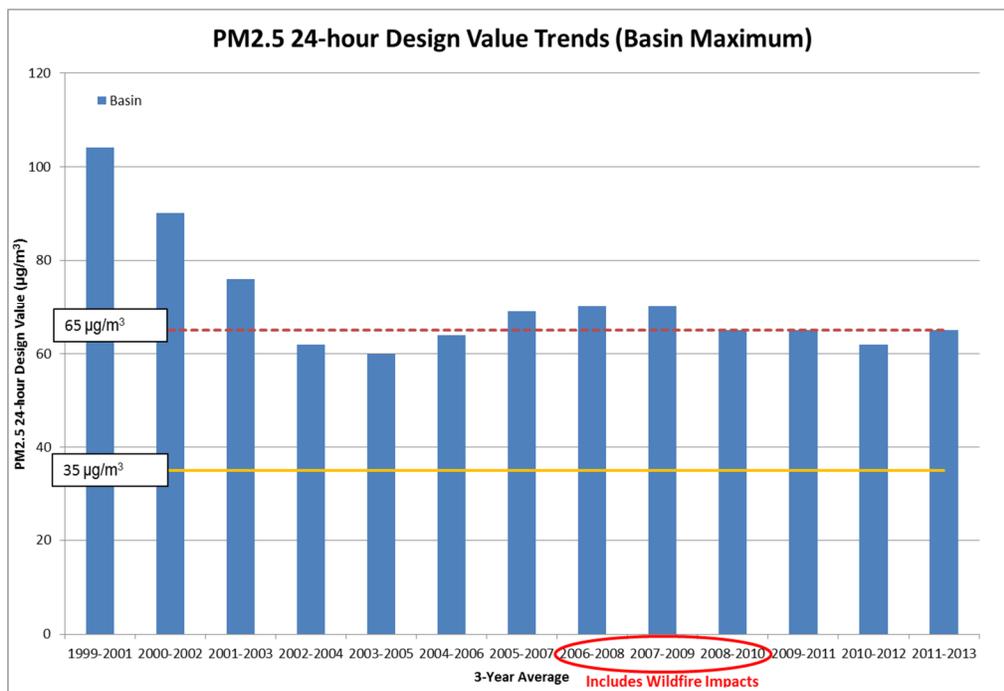
⁴ Interpretation of the National Ambient Air Quality Standards for PM_{2.5}, 40 C.F.R. Pt. 50 Appendix N (2012).

PM2.5 24-hour NAAQS threshold from year to year shows the progress in reducing the number of days with the highest concentrations, while quarterly averages can help to show progress with respect to seasonal peaks in concentration levels. Some of the conclusions from these analyses are included below, followed by a more detailed discussion in Appendix A, which also provides analysis results for a number of other air monitoring sites in the Valley.

Rather than using yearly maximum concentrations for the PM2.5 standards, EPA requires the use of design values for the attainment metric. Design values represent a three-year average and help to smooth out outlier years with exceptional meteorology or exceptional events. Details on how PM2.5 design values are calculated are provided in Appendix A of this plan. As seen in Figure 2-8, the Valley maximum 24-hour and annual average PM2.5 design value trends show that although there is some year-to-year variation significant progress has been made in reducing long-term PM2.5 concentrations. Valley 24-hour design value maximums have decreased by 40% over the 1999–2013 time period.

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Figure 2-8 Historical PM2.5 24-hour and Annual Design Value Trends



Since monitoring began, the Bakersfield-California and Bakersfield-Planz air monitoring sites in Kern County have consistently been among the highest PM2.5 design values in the Valley. Figure 2-9 shows the trend of the 24-hour average design value at Bakersfield-California through 2013, as demonstrated with the 2011-2013 design value (3-year average). Figure 2-10 shows the trend of the annual average design value at

Bakersfield Planz through 2013, as demonstrated with the 2011–2013 design value (3-year average).

Figure 2-9 Trend of 24-Hour Average PM2.5 Design Values at Bakersfield-California

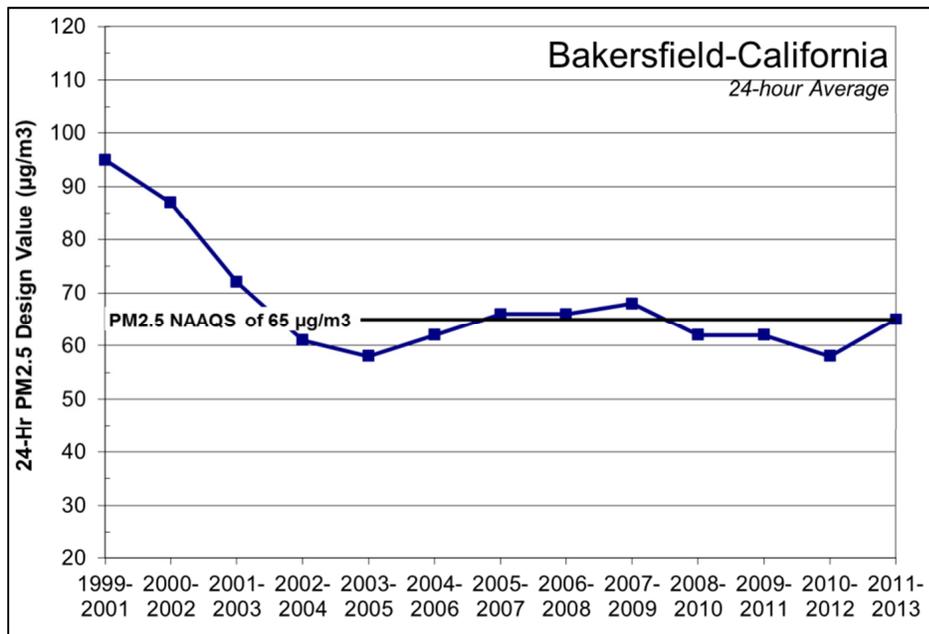
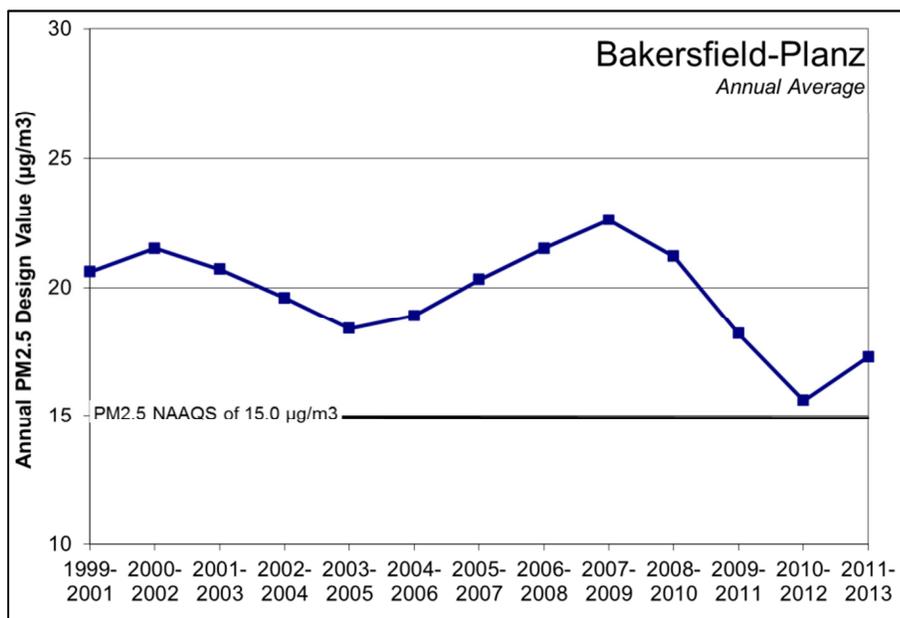


Figure 2-10 Trend of Annual Average PM2.5 Design Values at Bakersfield-Planz



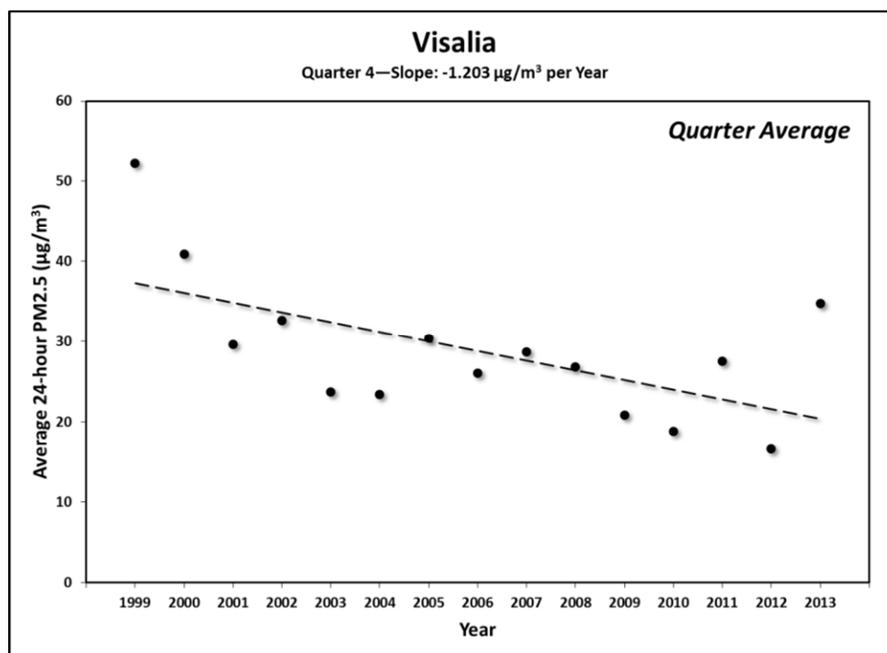
Overall decreasing PM2.5 concentrations at the Bakersfield-California and Bakersfield-Planz air monitoring sites are shown in the design value trends for those sites. The Bakersfield-California site now has a 24-hour design value at or below the 1997 24-hour

PM_{2.5} standard of 65 $\mu\text{g}/\text{m}^3$ (see Figure 2-9). The annual average design value for 2011–2013 continues to trend lower for Bakersfield-Planz at 17.3 $\mu\text{g}/\text{m}^3$ (see Figure 2-10). This downward trend will need to continue at all sites within the Valley as the Valley strives for attainment of increasingly stringent air quality standards.

Since the Valley's highest PM_{2.5} concentrations occur during the fall and winter months, the first (January through March) and fourth (October through December) quarters tend to have the highest average concentrations. Observing the trend in these quarterly averages can shed light on how the peak of the PM_{2.5} season is changing over time.

Data from the Visalia monitoring site (Figure 2-11) is representative of fourth-quarter averages among the PM_{2.5} sites in the Valley. This data also shows a downward trend of 1.20 $\mu\text{g}/\text{m}^3$ per year. The District anticipates continuation of this trend as the Valley gets closer to attaining the annual average PM_{2.5} standard. Refer to Appendix A for the detailed results of this analysis.

Figure 2-11 Trend of Fourth-Quarter Average at Visalia



2.4.3 Impact of Exceptional Drought-Related Weather Conditions on Valley PM_{2.5} Concentrations

In 2012, the Bakersfield-Planz air monitoring site, which is the current peak PM_{2.5} site in the District, recorded an annual average value of 14.7 $\mu\text{g}/\text{m}^3$, below the standard of 15.0 $\mu\text{g}/\text{m}^3$. This site, along with the rest of the District's PM_{2.5} air monitoring sites, was making significant progress towards attaining the 1997 annual PM_{2.5} standard. However, due to the exceptional weather conditions experienced during the winter of

2013-2014, exceedingly high PM2.5 concentrations were experienced, causing a 2013 annual average of 22.8 $\mu\text{g}/\text{m}^3$ for the Bakersfield-Planz site, and an annual design value (2011-2013) of 17.3 $\mu\text{g}/\text{m}^3$ (see Figure 2-10 above).

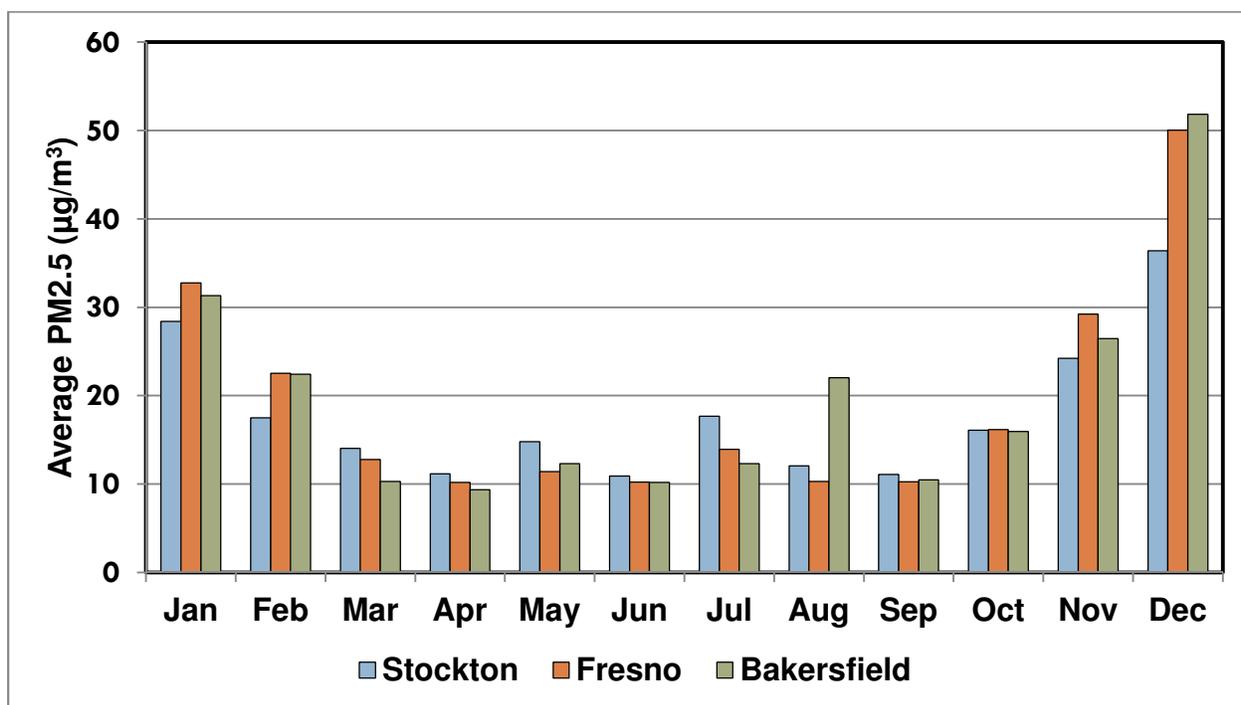
Due to the extreme weather and high values already experienced at this site in the 1st quarter of 2014, the averages for the 2nd, 3rd, and 4th quarters of 2014 would need to be zero for Bakersfield-Planz to reach attainment for the 2012-2014 period (see Chapter 1). In addition, with the high values recorded in 2013 and 2014, attainment during the 2013-2015 period is also impossible (see Chapter 4). The following discusses the magnitude of the weather conditions experienced during the winter of 2013-14, and its impact on the Valley’s ability to attain the 1997 annual PM2.5 standard.

Meteorology during the Winter Season of 2013-2014

This past winter, California Governor Jerry Brown declared a state of emergency due to extreme drought conditions in the state. This emergency declaration was based on record-low precipitation in 2013 and snow pack levels at only 20 percent of the normal amount of snow to provide water for the year. Specifically in the Valley, 2013 represented the driest year since the start of record keeping in 1895. The Valley is currently experiencing an exceptional level of drought not seen in at least 119 years.

Although the Valley has experienced reductions in PM2.5 concentrations over the last 15 years since the pollutant first began to be measured, the winter months of November through February continue to record the peak levels of each year. The following figure displays the relative comparison between the lower concentrations in March through October, and the higher concentrations experienced during the winter.

Figure 2-12 Average PM2.5 by Month in 2013 in Stockton, Fresno, Bakersfield



Stable meteorology during the winter season can increase PM_{2.5} concentrations to high levels by providing strong temperature inversions and low wind speeds. When this occurs, the PM_{2.5} concentrations during the winter months of November to February can climb to very high levels. As seen in Figure 2-13, the winter of 2013-2014 experienced the strongest average atmospheric stability over the last 15 years (period during which PM_{2.5} concentrations have been recorded), creating conducive conditions for the formation and retention of high PM_{2.5} concentrations. This was a result of a persistent, strong high pressure ridge over the eastern Pacific that effectively blocked weather disturbances from entering California, which inhibited dispersion during November, December, and January.

In addition to the historically strong atmospheric stability, the winter of 2013-2014 also experienced record low precipitation totals, with some locations breaking records over 100 years old (see Table 2-2). These unprecedented dry conditions exacerbated the air quality challenge during the winter of 2013-2014. As a result of the extreme meteorology experienced in the Valley, PM_{2.5} concentrations reached peak levels that had not been recorded in over a decade, which in turn has increased the Valley's PM_{2.5} design values, making the journey to attainment of the PM_{2.5} standards even more challenging.

Figure 2-13 Average Atmospheric Stability per Winter Season

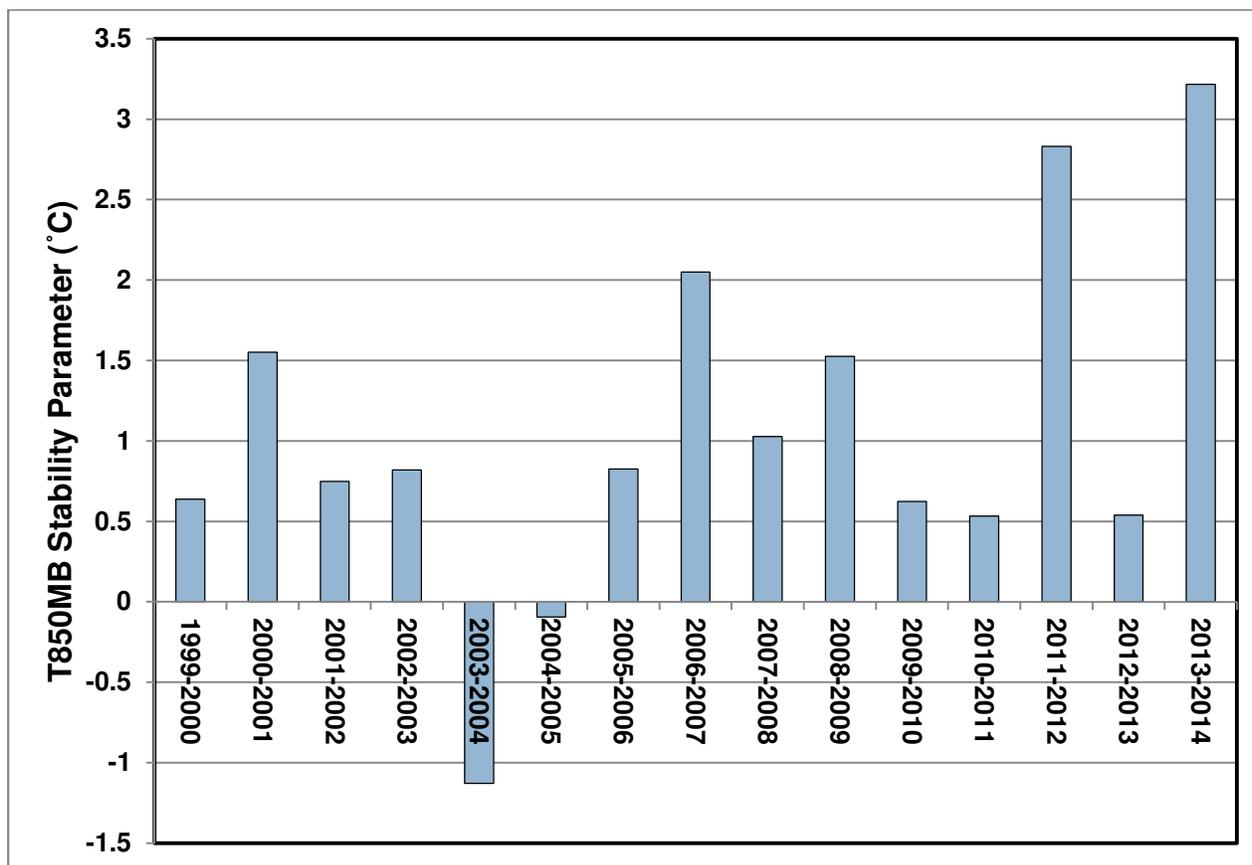


Table 2-2 Calendar Year Rainfall Totals for Select California Cities

City	1981-2010 Average (inches)	2013 Total (inches)	Previous Record Low (inches)	Previous Record Year
Modesto	13.11	4.70	5.70	1929
Merced	12.50	3.79	6.00	2007
Fresno	11.50	3.01	3.55	1947
Visalia	10.93	3.47	4.10	1910
Bakersfield	6.47	3.43	1.87	1959
Sacramento	18.52	5.81	6.67	1976
San Francisco	23.65	5.59	9.00	1917
San Jose	14.90	3.80	6.04	1929
Los Angeles	12.82	3.65	4.08	1953
San Diego	10.34	5.57	3.41	1953

2.5 CONDENSABLE PARTICULATES

Certain high-temperature processes emit gaseous pollutants that rapidly condense into particle form in the ambient air. After January 1, 2011, PM_{2.5} nonattainment areas are to consider these condensable particulates for purposes of establishing the emissions limits for Reasonable Further Progress (RFP), Reasonably available control technology (RACT), and reasonably available control measures (RACM).⁵ In December 2010, EPA revised its “Method 202” stationary source test method to measure condensable particulate matter.⁶

While this issue may be new and more relevant to other regions, the District has historically included condensable particulate emissions in its definition of total particulate emissions, well ahead of federal and other states’ efforts to address this issue. This has included instituting permit requirements for various emissions sources that include condensable particulates as part of total particulate emissions limitations, and associated emissions testing requiring that condensable particulates be measured (including utilizing an EPA-approved modified test method ahead of EPA’s official test method, Method 202). Condensable particulates are thus a part of the total PM_{2.5} inventory, and reductions in condensable particulate matter emissions were included in the District’s evaluation of various emission reduction opportunities for directly emitted PM_{2.5}.

2.6 INSIGNIFICANT PRECURSORS TO PM_{2.5} CONCENTRATIONS IN THE VALLEY

The switch from CAA Subpart 1 to Subpart 4 (see Chapter 1) for PM_{2.5} implementation shifts the precursor presumption for planning purposes. Pursuant to Subpart 1, areas

⁵ 40 CFR 51.1002(c)

⁶ <http://www.epa.gov/ttn/emc/methods/method202.html>

were not required to address volatile organic compounds (VOCs)⁷ and ammonia unless technical demonstration shows that VOC reductions or ammonia reductions contribute to PM_{2.5} attainment. Now, pursuant to Subpart 4 §189(e), areas must address potential precursors of PM_{2.5}, including VOCs and ammonia, unless it is shown that they do not contribute to attainment.

In the Valley, there is extensive scientific research and technical analysis demonstrating that VOC reductions and ammonia reductions do not contribute to PM_{2.5} attainment. As such, the Valley's VOC emissions and ammonia emissions do not need to be reduced to address the federal PM_{2.5} standard. EPA concurs with the conclusion that VOC emissions do not contribute significantly to the formation of PM_{2.5} as stated in their proposed approval of the District's plan to address the 2006 PM_{2.5} standard: *"Based on a review of the information provided by the District and other information available to EPA, we propose to determine that at this time VOC emissions do not contribute significantly to ambient PM_{2.5} levels..."*⁸

Modeling shows that NO_x controls are the most effective approach to reduce PM_{2.5} nitrate concentrations, and once NO_x controls are taken into consideration, VOC emission reductions produce essentially no benefit. In fact, in some instances, VOC emissions reductions may actually lead to an increase in PM_{2.5} nitrate formation. Nitrogen-containing molecules can act as temporary sinks for NO₂. When VOCs are controlled, the reduced availability of certain radicals which are generated from VOCs reduces the amount of NO₂ that is sequestered, thereby increasing the availability of NO₂ and enhancing ammonium nitrate formation.⁹

The extensive research mentioned above and summarized below demonstrates that there is a relative abundance of ammonia compared to nitric acid, and that the amount of nitric acid drives the ultimate formation of ammonium nitrate. Because of this regional surplus in ammonia, even substantial ammonia emissions reductions yield a relatively small reduction in nitrate. Reductions in nitrate concentrations of 30% to 50% were realized through a 50% reduction in NO_x. Modeling a 50% reduction in ammonia, while unrealistic because it's not technologically achievable, would only realize less than 5% reductions in nitrate concentrations. Due to the extensive body of science that clearly shows the much greater efficacy of reducing NO_x emissions relative to ammonia, ammonia reductions have not historically been considered a significant precursor to PM_{2.5} formation in the Valley.

⁷ EPA defines VOCs as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, that participates in atmospheric photochemical reactions to form ozone or particulates. A subset of non-reactive VOCs does not contribute to ozone or particulates and are exempt from regulatory controls. Many VOCs are human-made chemicals used and produced in the manufacture of paints, adhesives, petroleum products, pharmaceuticals. The full EPA definition is available at <http://ecfr.gpoaccess.gov/cgi/t/text/text-idx?c=ecfr&rgn=div8&view=text&node=40:2.0.1.1.2.3.8.1&idno=40>

⁸ Approval and Promulgation of Implementation Plans; Designation of Areas for Air Quality Planning Purposes; California; San Joaquin Valley Moderate Area Plan and Reclassification as Serious Nonattainment for the 2006 PM_{2.5} NAAQS; Proposed Rule, 80 Fed. Reg. 8, pp. 1816-1846. (p. 1826) (2015, January 13).

⁹ Meng, Z., Dabdub, D., and Seinfeld, J.H., 1997, Chemical Coupling Between Atmospheric Ozone and Particulate Matter, *Science*, 277, 116-119.

2.6.1 VOC Contribution to PM_{2.5} Concentrations

VOC emissions have the potential to contribute to the formation of two different PM_{2.5} components: secondary organic aerosols (SOAs) and ammonium nitrate (nitrate). While these components contribute to observed PM_{2.5} concentrations in the Valley, their contribution is minimal. The anthropogenic VOC contribution (those not from biogenic sources) to both components is so minimal, that invoking a VOC-centric control strategy is much less effective than primary PM_{2.5} controls or NO_x controls, as shown through the recent research and modeling.

2.6.1.1 VOC Contribution to SOA Formation

Secondary organic aerosols form when intermediate molecular weight VOCs emitted by anthropogenic and biogenic sources react and condense in the atmosphere to become aerosols. Lighter VOCs also participate in the formation of atmospheric oxidants, which then participate in the formation of SOA. SOAs derived from anthropogenic VOC emissions account for only 1% to 2% of the annual total PM_{2.5} concentrations throughout the Valley.

As part of the attainment demonstration for the District's 2008 PM_{2.5} Plan, ARB used the Community Multi-scale Air Quality (CMAQ) model to show that primary PM_{2.5} emissions are the main contributor to organic aerosols, with SOAs being a small fraction of the total organic aerosol concentration. Furthermore, SOAs are mostly formed during the summer and from predominantly biogenic sources, when total PM_{2.5} concentrations are low. As such, SOAs derived from anthropogenic VOC emission make up only 3% to 5% of the annual average organic aerosol concentrations.

Related to this finding, the California Regional Particulate Air Quality Study (CRPAQS) also found that because of the dominance of primary PM_{2.5} organic matter, overall, a 50% reduction in anthropogenic VOC emissions has limited effect on the modeled PM_{2.5} organic matter.¹⁰ Together, these study results show that for SOAs, further VOC reductions would have very limited effectiveness in reducing PM_{2.5} concentrations.

2.6.1.2 VOC Contribution to Nitrate Formation

Nitrate forms by means of two primary chemical pathways: during the day, NO₂ is oxidized to nitric acid, some of which then reacts with ammonia to form nitrate through interactions with sunlight, VOCs, and background ozone; and during the night, when nitric acid is formed through oxidation of NO₂ (via N₂O₅) by background ozone, which then reacts with ammonia to form nitrate. Several modeling studies^{11,12,13,14} have

¹⁰ Pun, B.K., Balmori R.T.F., & Seigneur, C. (1998). Modeling Wintertime Particulate Matter Formation in Central California, *Atmospheric Environment*, 43, 402-409.

¹¹ Pun, B.K., & Seigneur, C. (1998) *Conceptual Model of Particulate Matter Pollution in the California San Joaquin Valley*. Prepared for Pacific Gas & Electric, Document CP045-1-98.

¹² Pun, B.K. (2004). *CRPAQS Task 2.7 when and where does high O3 correspond to high PM2.5? How much PM2.5 corresponds to photochemical end products?* Prepared for the San Joaquin Valleywide Air Pollution Study Agency.

¹³ Lurmann, F.W., Brown, S.G., McCarthy, M.C., & Roberts, P.T. (2006). Processes Influencing Secondary Aerosol Formation in the San Joaquin Valley during Winter. *Journal of Air and Waste Management Association*, 56, 1679-1693.

investigated the relative veracity of these two mechanisms within the Valley and attempted to determine the specific role and contribution of VOCs on Valley nitrate concentrations. While the specific conclusions were mixed, there was general agreement that the nighttime formation of nitrate in the Valley would not be sensitive to VOC reductions.

Further modeling studies^{15,16,17,18,19,20} evaluated the significance of VOC controls in reducing nitrate concentrations in the Valley. ARB evaluated each of these studies in the context of two key considerations: whether further VOC reduction would provide significant benefits to expedite attainment beyond the District's existing NO_x control program, and what would be the feasible magnitude of any potential VOC reductions beyond the existing and already rigorous VOC control program. Nitrate was only responsive to a 50% reduction in VOCs at very high PM_{2.5} concentrations, concentrations that are no longer reached in the Valley. In contrast, a 50% reduction in NO_x can reduce significantly more nitrate at current PM_{2.5} concentrations, one study²¹ reporting a 38% reduction in nitrate.

Despite the insignificance of VOC emissions with regard to PM_{2.5} concentrations in the Valley, VOC emissions have been reduced and will continue to be reduced through implementation of the *2007 Ozone Plan* and the *2013 Ozone Plan* for the revoked 1-hr Ozone Standard. A more detailed discussion of the VOC influences on PM_{2.5} Concentrations can be found in the *2012 PM_{2.5} Plan*.²²

2.6.2 Ammonia Contribution to PM_{2.5} Concentrations

Early air quality research in the Valley identified ammonium nitrate (nitrate) as a predominant secondary PM_{2.5} species in the region, with high concentrations forming during the winter months.²³ Studies have continued to show that ammonium nitrate is a primary component of wintertime PM_{2.5} in the Valley, followed by other species, such

¹⁴ Ying, Q., Lu, J., & Kleeman, M. (2009). Modeling Air Quality during the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) Using the UCD/CIT Source-Oriented Air Quality Model – Part III Regional Source Apportionment of Secondary and Total Airborne Particulate Matter. *Atmospheric Environment*, 43, 419-430.

¹⁵ Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., & Sylte, W.W. (2000). The Ammonium Nitrate Particle Equivalent of NO_x Emissions for Wintertime Conditions in Central California's San Joaquin Valley, *Atmospheric Environment*, 34, 4711-4717.

¹⁶ Pun, B.K., & Seigneur, C. (2001). Sensitivity of Particulate Matter Nitrate Formation to Precursor Emissions in the California San Joaquin Valley. *Environmental Science and Technology*, 35, 2979-2987.

¹⁷ Kleeman, M.J., Ying, Q., & Kaduwela, A. (2005). Control Strategies for the Reduction of Airborne Particulate Nitrate in California's San Joaquin Valley. *Atmospheric Environment*, 39, 5325-5341.

¹⁸ Meng, Z., Dabdub, D., & Seinfeld, J.H. (1997) Chemical Coupling Between Atmospheric Ozone and Particulate Matter. *Science*, 277, 116-119. DOI:10.1126/science.277.5322.116

¹⁹ Livingstone, P.L., Magliano, K., Güreş, K., Allen, P.D., Zhang, K.M., Ying, Q., ... Byun, D. (2009). Simulating PM Concentrations during a Winter Episode in a Subtropical Valley: Sensitivity Simulations and Evaluation Methods. *Atmospheric Environment*, 43, 5971-5977.

²⁰ Pun, B.K., Balmori R.T.F., & Seigneur, C. (2009). Modeling Wintertime Particulate Matter Formation in Central California. *Atmospheric Environment*, 43, 402-409.

²¹ *Ibid.* 25

²² SJVAPCD. *2012 PM_{2.5} Plan* (2013) http://www.valleyair.org/Air_Quality_Plans/PM25Plans2012.htm

²³ Smith, T.B.; Lehrman, D.E.; Reible, D.D.; and Shair, F.H. (1981). The origin and fate of airborne pollutants within the San Joaquin Valley: Extended summary and special analysis topics. Report No. 2. Prepared for the California Air Resources Board, and by the California Institute of Technology, Pasadena, CA.

as organic carbon, ammonium sulfate, and geologic material.²⁴ In addition, PM_{2.5} speciation data, collected for many years at four Valley urban monitoring locations, also shows nitrate's substantial contribution to the Valley's total PM_{2.5} concentrations, especially on days when peak 24-hour average concentrations are experienced.

2.6.2.1 Ammonium nitrate formation and precursors

Formation of ammonium nitrate is described by Kleeman et al. (2005, pp. 5326-7).²⁵

Particulate ammonium nitrate (NH₄NO₃) forms when the concentration product of gas-phase ammonia (NH₃) and nitric acid (HNO₃) exceeds a saturation point dependent on temperature, relative humidity, and the composition of the pre-existing particles that act as condensation substrate (Wexler and Seinfeld, 1991).²⁶ Ammonia is a relatively stable compound directly emitted to the atmosphere that does not undergo significant chemical reaction on the time scale of interest to regional air quality problems. Nitric acid is an end product of the photochemical transformation of NO_x (NO + NO₂). The majority of the NO_x in the SJV is emitted as NO that is then transformed into various species including NO₂, NO₃, HNO₂, HNO₃, HNO₄, Peroxy Acetyl Nitrate (PAN), Particulate Protein Nitrogen (PPN), particulate nitrate, etc. The sum of NO_x and the entire family of NO_x reaction products is called "reactive nitrogen" (NO_y). The fraction of reactive nitrogen that forms HNO₃ and/or nitrate depends on the concentration of NO_x and VOC as well on meteorological conditions such as temperature, relative humidity, and solar intensity (Aw and Kleeman, 2003; Nguyen and Dabdub, 2002).^{27 28} Measurements taken at the remote Kern Wildlife Station in the San Joaquin Valley show that approximately 22% of the reactive nitrogen exists as particulate (ammonium) nitrate during typical winter conditions (Chow and Egami, 1997).²⁹

Nitrate buildup is a signature outcome of multi-day stagnation periods during the winter (similar buildup is not observed during warmer seasons). The modeled regional variation of nitrate concentrations is shown in Figure 2-14. Higher concentrations of nitrate occur in the southernmost Valley as a result of slower wind speeds and higher levels of reactive nitrogen and ammonia.

²⁴ Ying, Q. & Kleeman, M.J., (2009). Regional Contributions to Airborne Particulate Matter in Central California during a Severe Pollution Episode. *Atmospheric Environment*, 43, 1218–1228.

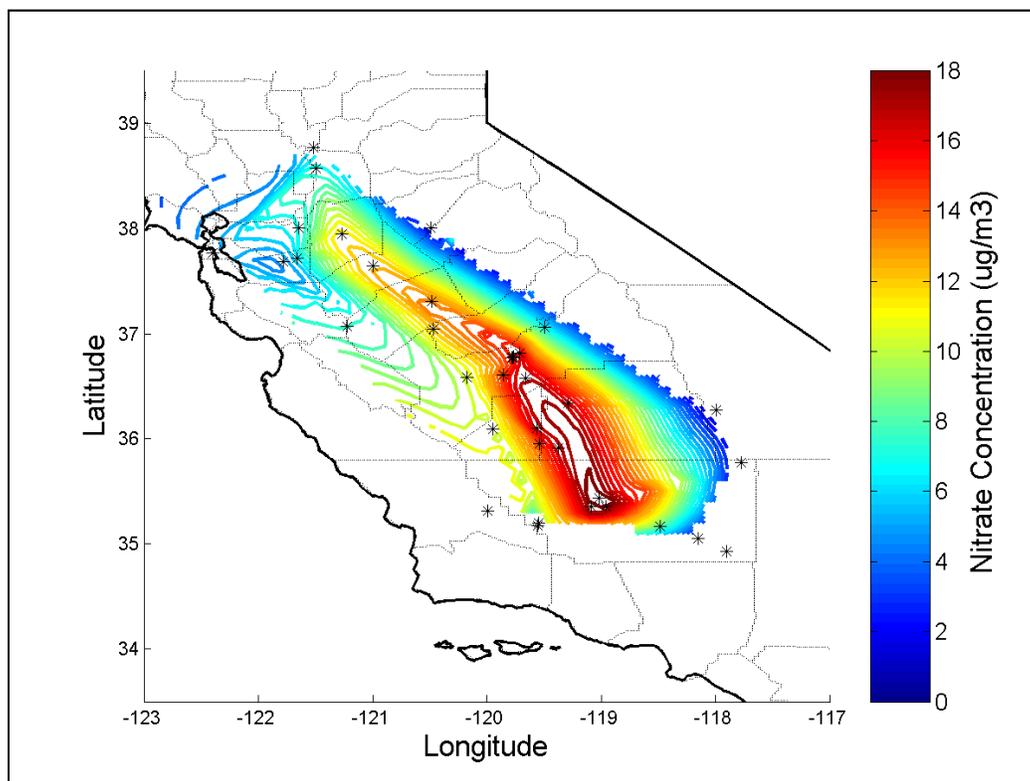
²⁵ Kleeman, M.J., Ying, Q., & Kaduwela, A. (2005). Control Strategies for the Reduction of Airborne Particulate Nitrate in California's San Joaquin Valley. *Atmospheric Environment*, 39, 5325–5341.

²⁶ Wexler, A.S., Seinfeld, J.H. (1991). 2nd-Generation inorganic aerosol model. *Atmospheric Environment Part a-General Topics* 25 (12), 2731–2748.

²⁷ Aw, J., Kleeman, M.J. (2003). Evaluating the First-Order Effect of Intra-Annual Temperature Variability on Urban Air Pollution. *Journal of Geophysical Research-Atmospheres* 108 (D12).

²⁸ Nguyen, K. & Dabdub, D. (2002). NO_x and VOC Control and Its Effects on the Formation of Aerosols. *Aerosol Science and Technology* 36 (5), 560–572.

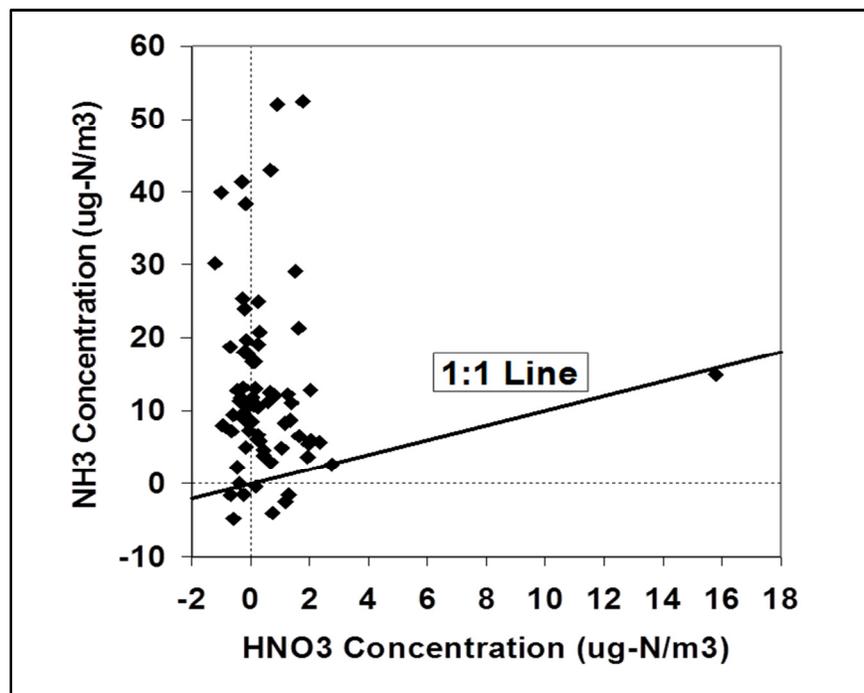
²⁹ Chow, J.C. & Egami, R.T. (1997). San Joaquin Valley Integrated Monitoring Study: Documentation, Evaluation, and Descriptive Analysis of PM₁₀ and PM_{2.5}, and Precursor Gas Measurements. Technical support studies No. 4 and No. 8. Final Report prepared for the California Air Resources Board, Sacramento, CA. Desert Research Institute, Reno, NV.

Figure 2-14 Modeled Regional Distribution of Ammonium Nitrate³⁰

Both nitric acid and ammonia are needed to form ammonium nitrate. The extensive research conducted through California Regional Particulate Air Quality Study (CRPAQS) and subsequent studies, as well as ongoing evaluation and modeling demonstrates that there is a relative abundance of ammonia (NH_3) compared to nitric acid (HNO_3), and that the amount of nitric acid (resulting from NO_x emissions) drives the ultimate formation of ammonium nitrate. Figure 2-15 illustrates this ammonia abundance at the rural Angiola (Fresno County) air monitoring site in the Valley during the CRPAQS field study. Ammonia concentrations are considerably higher than nitric acid concentrations throughout the Valley, including urban areas with concentrated NO_x emissions.³¹ See Appendix G to the *2012 PM_{2.5} Plan* for more information.

³⁰ Chow, J.C., Chen, L.-W.A., Lowenthal, D.H., Doraiswamy, P., Park, K., Kohl, S., Trimble, D.L., & Watson, J.G. (2005). California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) – Initial Data Analysis of Field Program Measurements. Report No. 2497. Prepared for California Air Resources Board, Sacramento, CA, by Desert Research Institute, Reno, NV.

³¹ Magliano, K. L. (2009) Science-Based Policies for Particulate Matter Air Quality Management in California. *International Aerosol Modeling Algorithms Conference*. Davis CA.

Figure 2-15 Ammonia versus Nitric Acid Measurements at Angiola³²

2.6.2.2 Reducing ammonium nitrate

Because of the regional surplus in ammonia, even substantial ammonia emissions reductions yield a relatively small reduction in nitrate. Figures 2-16 and 2-17 provide a simplified illustration of this situation. As seen in Figure 2-18, a comparable modeling analysis based on CRPAQS observational data found a higher disparity between the efficiency of NO_x versus ammonia controls. Reductions in nitrate concentrations of 30% to 50% were realized through a 50% reduction in NO_x. Modeling a 50% reduction in ammonia, while unrealistic because it's not technologically achievable, would only realize less than 5% reductions in nitrate concentrations. Finally, Figure 2-19 provides clear correlative evidence from observed data that NO_x controls are effectively reducing ammonium nitrate, despite an increase in the regional ammonia inventory over the same time period.

³² McCarthy, M. (2005) *The Role of Nighttime Chemistry in Winter Ammonium Nitrate Formation in the San Joaquin Valley*. American Association for Aerosol Research (AAAR), Supersites Conference, February 2005, Atlanta, GA.

Figure 2-16 Abundance of Ammonia in the San Joaquin Valley³³

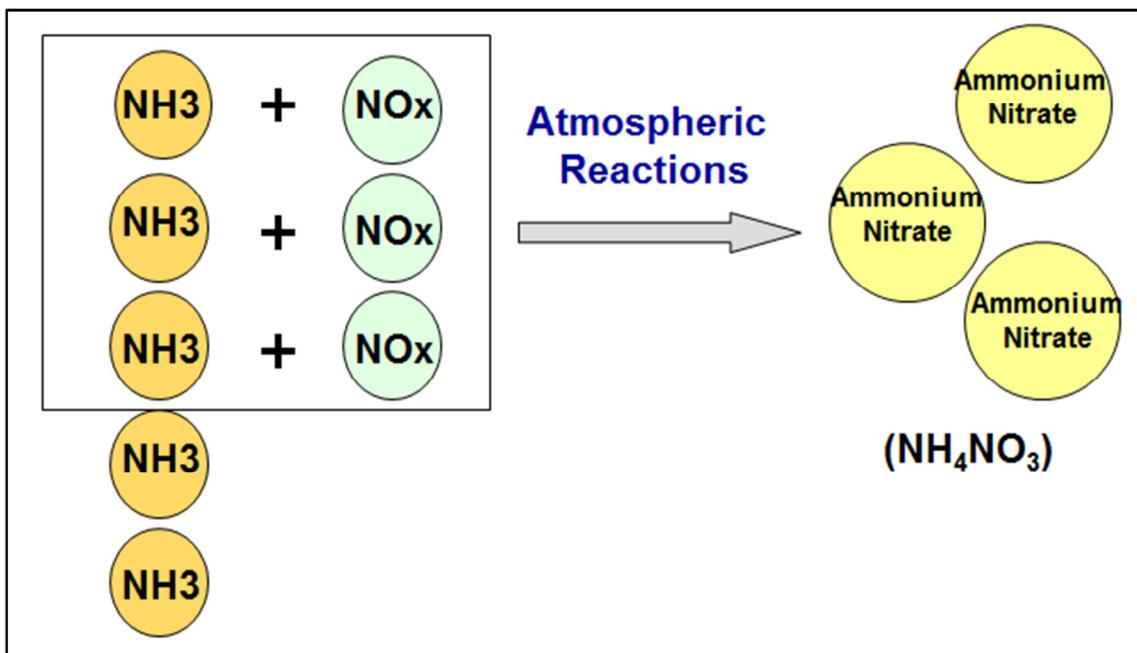
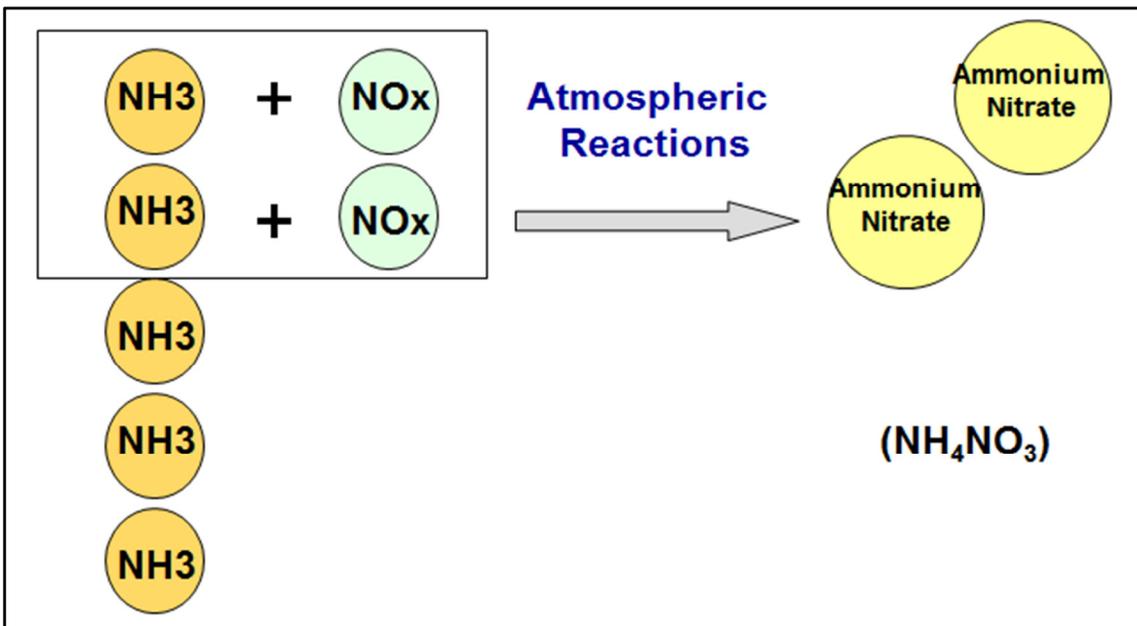


Figure 2-17 NO_x Control Reduces Ammonium Nitrate Most Efficiently



³³ Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., & Sylte, W.W. (2000). The Ammonium Nitrate Particle Equivalent of NO_x Emissions for Wintertime Conditions in Central California's San Joaquin Valley, *Atmospheric Environment*, 34, 4711-4717.

Figure 2-18 Modeled Ammonium Nitrate Response to Ammonia vs. NOx Controls³⁴

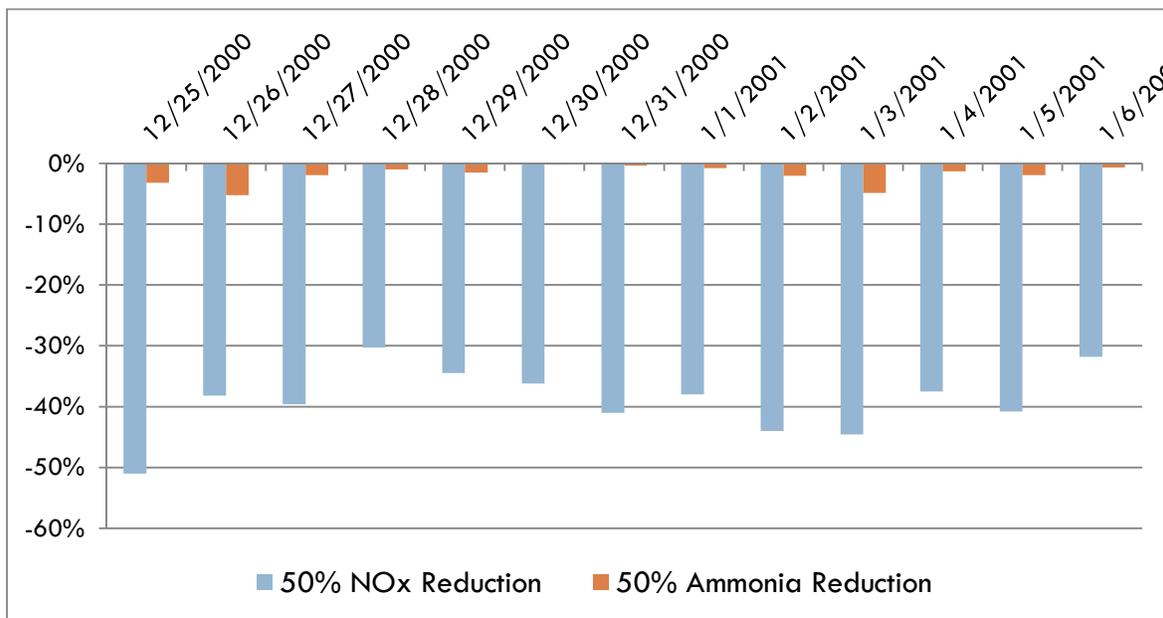
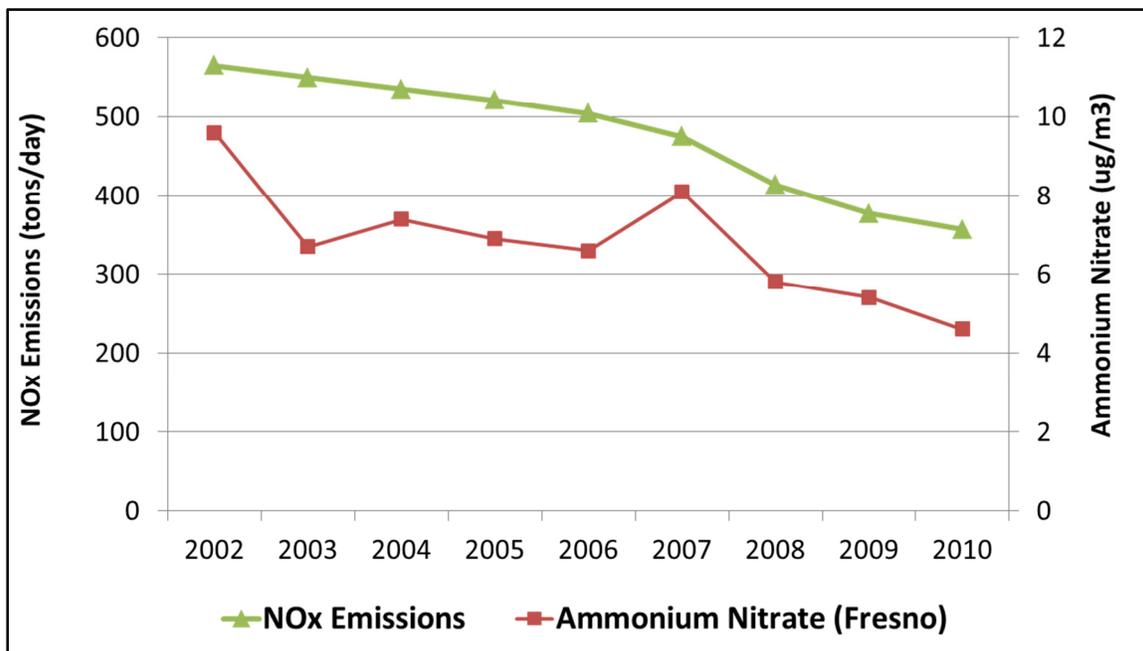


Figure 2-19 Correlation between NOx Reductions and Observed Ammonium Nitrate in Fresno³⁵



³⁴ Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., & Sylte, W.W. (2000). The Ammonium Nitrate Particle Equivalent of NOx Emissions for Wintertime Conditions in Central California's San Joaquin Valley, *Atmospheric Environment*, 34, 4711-4717.

³⁵ Stockwell, W.R., Watson, J.G., Robinson, N.F., Steiner, W., & Sylte, W.W. (2000). The Ammonium Nitrate Particle Equivalent of NOx Emissions for Wintertime Conditions in Central California's San Joaquin Valley, *Atmospheric Environment*, 34, 4711-4717.

Due to this extensive body of science that clearly shows the much greater efficacy of reducing NOx emissions relative to ammonia, ammonia reductions have not historically been considered a significant precursor to PM2.5 formation in the Valley. However, the District and ARB have continued to examine the potential role of ammonia with regard to PM2.5 formation (see Appendices F and G of the *2012 PM2.5 Plan*).

The modeling sensitivity analysis shows that reductions in ammonia emissions achieve insignificant reductions in the PM2.5 design values compared to reductions of direct PM2.5 and NOx emissions. Relative to the other pollutants, ammonia reductions at the Bakersfield-California site are only 2.3% as effective as direct PM2.5 reductions, and only 10% as effective as NOx reductions. Ammonia is not a significant precursor to PM2.5 values in the Valley.

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