Chapter 3

PM2.5 Trends and Scientific Foundation

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Chapter 3: PM2.5 Trends and Scientific Foundation

[Note: The evaluation being conducted to develop this plan is an ongoing work in progress, and will continue to be revised and updated throughout the public process.]

3.1 INTRODUCTION

This chapter provides an overview of recent trends in PM2.5 air quality across the San Joaquin Valley as well as further information important to understanding the scientific nature of PM2.5 formation and concentrations in the Valley. Both the ambient air quality and the emissions inventory play a key role in the regional grid modeling that is used to project pollutant concentrations in the future. A discussion of the challenges standing in the way of further air quality progress in the San Joaquin Valley is included. Finally, the results of the modeling analysis are presented here along with a summary of what reductions will be necessary to reach attainment.

3.1.1 The Nature and Formation of PM2.5

As opposed to ozone (O_3), which is a molecule known to consist of three oxygen atoms, PM2.5 can potentially be composed of any material that is has an aerodynamic diameter of 2.5 microns or less. PM2.5 can be emitted directly as primary PM from various sources or form secondarily through chemical reactions in the atmosphere. Among the chemical precursors that can form secondary PM2.5 are nitrogen oxides (NOx), volatile organic compounds (VOCs), sulfur dioxide (SO2), and ammonia (NH3). In addition, naturally occurring emissions from biogenic sources like plants and forests can also add to the formation of PM2.5.

The resulting ambient PM2.5 mixture can include aerosols (fine airborne solid particles and liquid droplets) consisting of components of nitrates, sulfates, elemental carbons, organic carbon compounds, acid aerosols, trace metals, geological materials, and more. The complex formation and composition of PM2.5 requires a versatile planning effort, where various components of the mass may be targeted for reduction. A control strategy that targets reductions among the precursors of PM2.5 has been shown to have a positive impact in reducing the total formed mass. Direct PM2.5 and a variety of its precursors are tracked and projected within the emissions inventory (see Section 3.3).

3.1.2 PM2.5 Species in the San Joaquin Valley

PM2.5 in the San Joaquin Valley is comprised of an extensive number of species that contribute to the total sum of the mass. This complex mixture is attributable to stationary and mobile sources, as well as area-wide and naturally occurring emissions. Although the list of species contributing to PM2.5 in the Valley is lengthy, the collection can be grouped into larger representative categories. The following is a brief

description of how each of these larger species categories are formed and emitted into the atmosphere.

- **Organic Carbon**

  As one of the major constituents of PM2.5 mass in the San Joaquin Valley, organic carbon is directly linked to emissions sources such as residential wood burning, agricultural burning, cooking, and direct tailpipe emissions from mobile sources. Smaller sources of organic carbon are attributable to road dust and natural biogenic sources.

- **Elemental Carbon**

  Incomplete combustion processes from diesel engines and other sources create elemental carbon, which is also called soot or black carbon.

- **Geologic Material**

  Geologic material consists primarily of road dust that is lifted into the air from passing vehicles as well as soil dust that is entrained into the atmosphere through farming activities and high wind events. This category of species tends to be on the coarse side of the particulate matter spectrum, as opposed to the fine, and represents a small percentage of the overall PM2.5 mass.

- **Trace metals**

  Trace metals appear in soil emissions and combustion from engine wear, brake wear, and similar processes. Fireworks emissions have also been identified as a source of metals that are health impacting.

- **Sea Salt**

  Under meteorological conditions when sea air is transported from the ocean into the San Joaquin Valley, the sodium chloride within the sea spray contributes to the PM2.5 mass. This represents a small portion of the overall mass, and is only a contributor under specific transport conditions.

- **Secondary Organic Aerosol**

  As organic carbon is released into the atmosphere, photochemical reactions can occur that secondarily create organic aerosol, called secondary organic aerosol (SOA).

- **Ammonium Nitrate**

  As nitrogen oxide (NOx) emissions from motor vehicles and stationary combustion sources react through photochemical processes during the day, or reacting with ozone at night, nitric acid is formed. When ammonia emissions react with the formed nitric acid, ammonium nitrate is created.

  Ammonium nitrate is commonly the largest contributor to PM2.5 mass in the San Joaquin Valley, especially in the southern region of the Valley. Stagnant, cold, and damp conditions promote the formation and accumulation of ammonium nitrate. As such, ammonium nitrate is found mostly during winter conditions, transforming from gases to particles and back to gases during periods of higher temperature.

- **Ammonium Sulfate**

  As sulfur oxide (SOx) emissions from combustion sources undergo photochemical reactions in the atmosphere, sulfuric acid is formed. Similar to ammonium nitrate, as sulfuric acid reacts with ammonia emissions, ammonium sulfate is created.

  Unlike ammonium nitrate, ammonium sulfate is formed consistently throughout the year and does not have a peak season. As a comparison, there is much less ammonium sulfate in the San Joaquin Valley atmosphere than ammonium nitrate.

- **Combined Water**

  If a water molecule attaches itself to any of the above species, a combined water species is formed, adding to the total PM2.5 mass.

3.1.3 Air Quality Research

Extensive research on particulate matter in the San Joaquin Valley has been conducted through the San Joaquin Valleywide Air Pollution Study Agency (Study Agency). The Study Agency was established in 1986 with the goal of furthering the understanding of the air quality issues in the region, which would assist regulatory agencies in the development of guidance and strategies on how to achieve air quality standards.

The Study Agency's largest PM2.5 sampling and research campaign occurred from December 1999 to February 2001 under the California Regional Particulate Air Quality Study (CRPAQS). This study collected a robust amount of PM2.5 data from both within and beyond the San Joaquin Valley. This dataset has been widely studied by researchers through particulate matter Study Agency funding of over $20 million. Today, CRPAQS continues to support research and improve understanding of PM2.5 in the Valley.

All of the District's recent air quality plans rely on the results of CRPAQS and other Study Agency efforts. Data collected and analysis conducted through CRPAQS was incorporated into the photochemical modeling analyses of the *2003 PM10 Plan*, the *2006 PM10 Plan*, and the *2008 PM2.5 Plan*. Similarly, research conducted through CRPAQS is being incorporated into photochemical modeling, PM2.5 trends evaluation, and weight of evidence analysis for this plan.

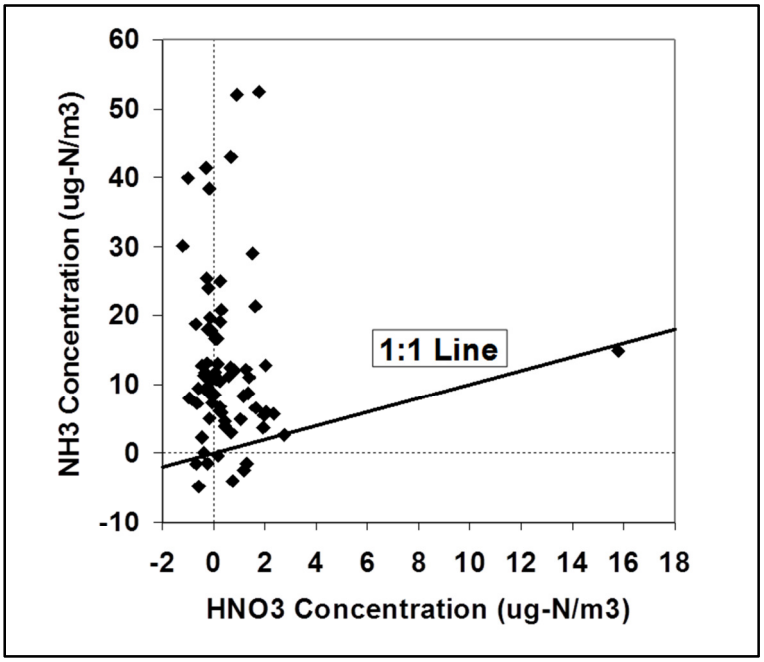
Study Agency work has also been improving air pollutant emissions inventories. For example, recent and current CRPAQS projects have been evaluating emissions from cotton ginning, almond harvesting, and urban sources of ammonia. Emissions inventory improvements provide a more accurate and robust understanding of the magnitude of various sources' contributions to air pollution in the San Joaquin Valley. Some Study Agency work has also been evaluating the effectiveness of various emissions control practices, such as dairy PM controls, urban heat island mitigation, and greenwaste composting controls. Refer to Appendix E for a comprehensive list of projects that have been completed through CRPAQS.

3.1.4 Current Science Regarding Ammonium Nitrate Formation

Studies have shown that winter time PM2.5 in the Valley is predominately comprised of ammonium nitrate, followed by other constituents such as ammonium sulfate, organic carbon, and geologic material[1]. Reducing ammonium nitrate concentrations is thus an effective way to reduce PM2.5 concentrations in the Valley. Ammonium nitrate is formed through a reaction between ammonia and nitric acid. First, nitric acid is formed as NOx undergoes photochemical processes throughout the day. Figure 3-1 displays the amount of ammonia (NH3) and nitric acid (HNO3) that were measured at the Angiola air monitoring site in the San Joaquin Valley during the CRPAQS field study. This shows that ammonia is much more abundant in the region than nitric acid.

[1] Q. Ying, and M. Kleeman. "Regional Contributions to Airborne Particulate Matter in Central California During a Severe Pollution Episode", Atmospheric Environment, 43, 1218-1228, 2009.

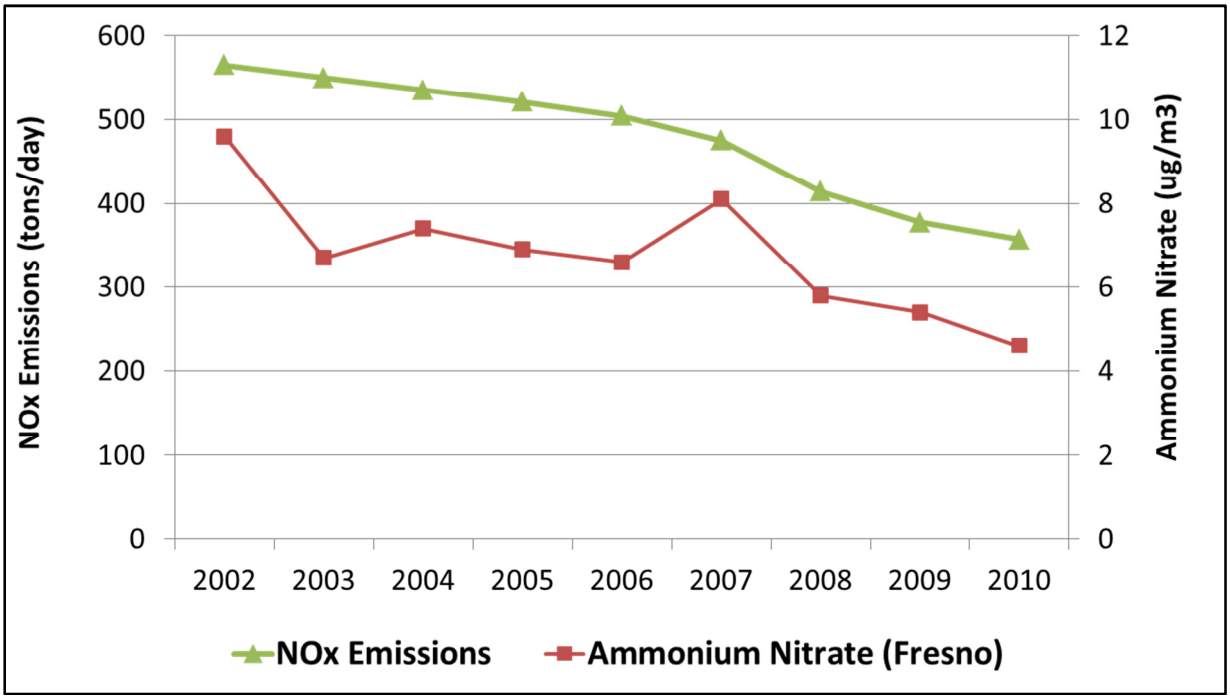
Figure 3-1 Ammonia versus Nitric Acid Measurements at Angiola



PM2.5 can be lowered by reducing nitric acid (i.e., NOx), as shown in Figure 3-2 for the Fresno area. In theory, ammonium nitrate concentrations could also be lowered by reducing ammonia emissions; however, due to the abundance of ammonia emissions compared to NOx in the Valley, research has shown that a massive reduction in ammonia would be required to achieve even a small reduction in ammonium nitrate, and that NOx emissions reductions are the most effective method of reducing ammonium nitrate[2]. The modeling and technical analysis being conducted for this plan will continue to evaluate this issue.

[2] Kleeman MJ, Ying Q, Kaduwela A. "Control strategies for the reduction of airborne particulate nitrate in California's San Joaquin Valley", Atmospheric Environment, 39: 5325-5341, 2005.

Figure 3-2 Connection between NOx and Ammonium Nitrate Reductions



Figures 3-3 and 3-4 illustrate in a simplified manner how ammonia and NOx can react to form ammonium nitrate, and why NOx has been demonstrated to be the most important precursor for reducing ammonium nitrate concentrations. Each ammonium nitrate particle needs a pair of ammonia and NOx to form. Figure 3-3 shows an abundance of ammonia compared to NOx (as exists in the Valley), yet three pairs of ammonia and NOx are able to combine to form three ammonium nitrate particles. In this figure, even if two ammonia particles are reduced, three ammonium nitrate particles will still form, showing the potential ineffectiveness of an ammonia control strategy. Figure 3-4 shows that reducing the atmosphere by one NOx particle effectively reduces the ammonium nitrate formation.

Figure 3-3 Abundance of Ammonia in the San Joaquin Valley

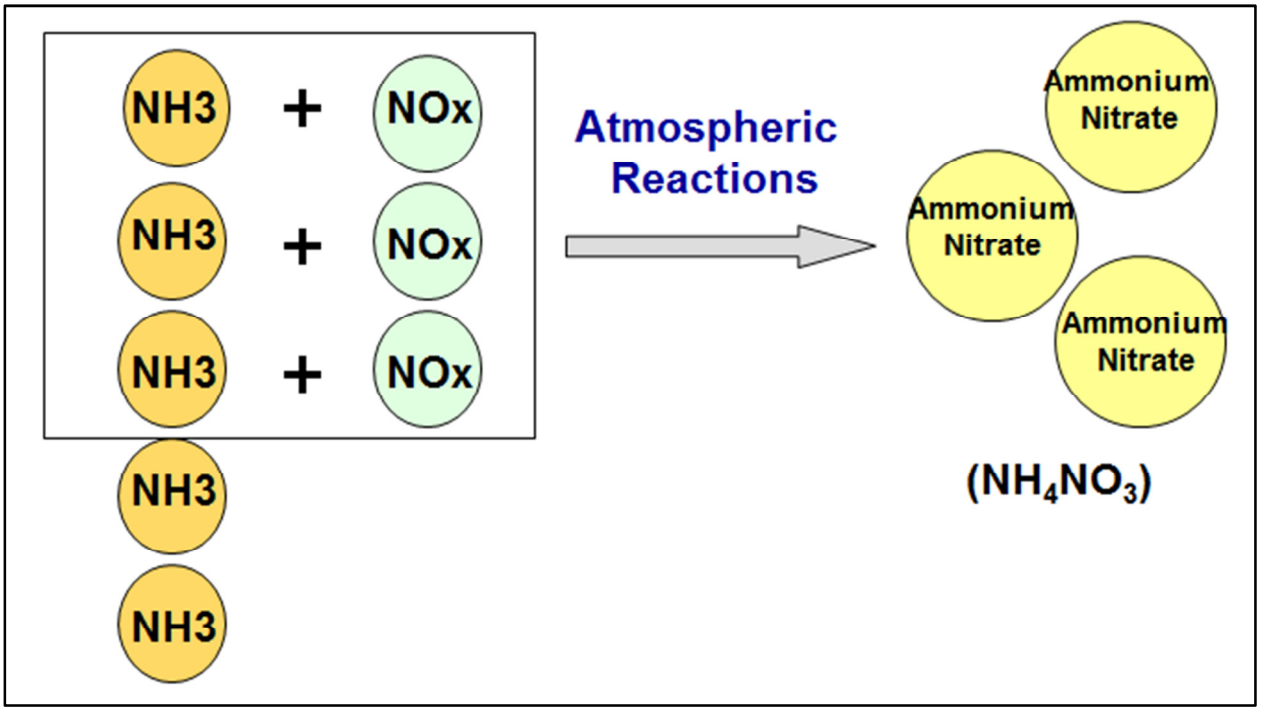
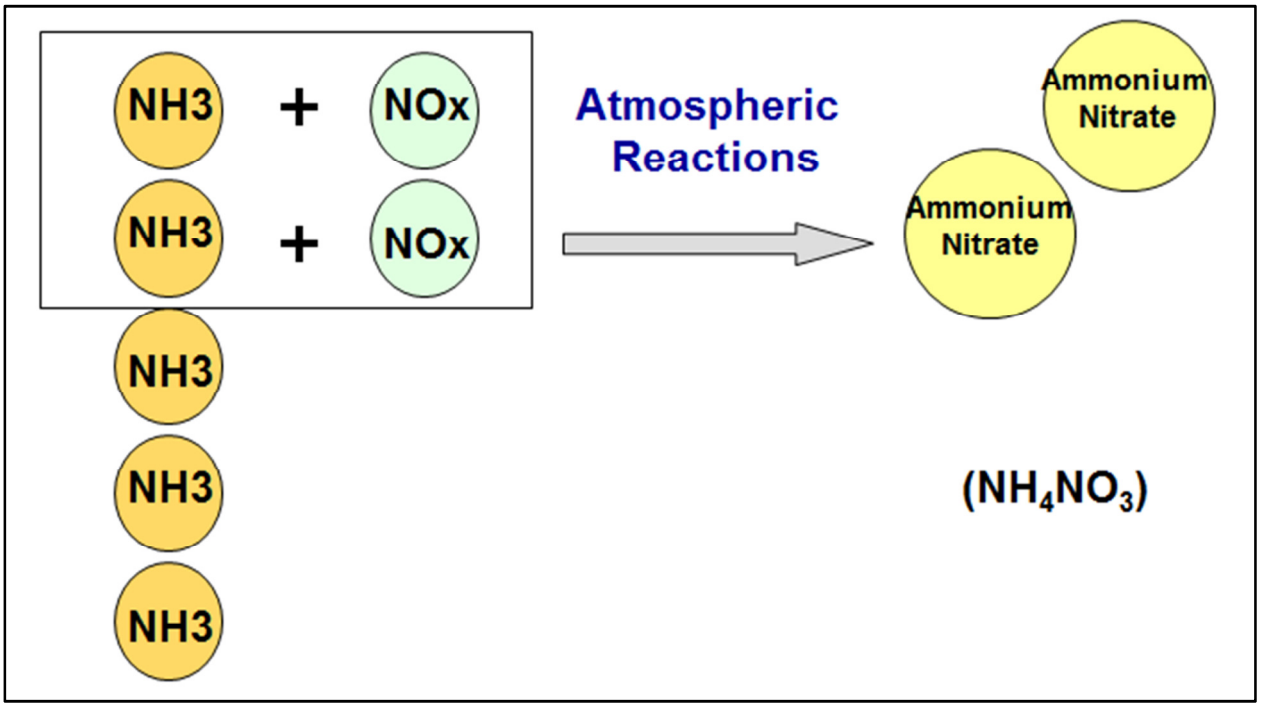


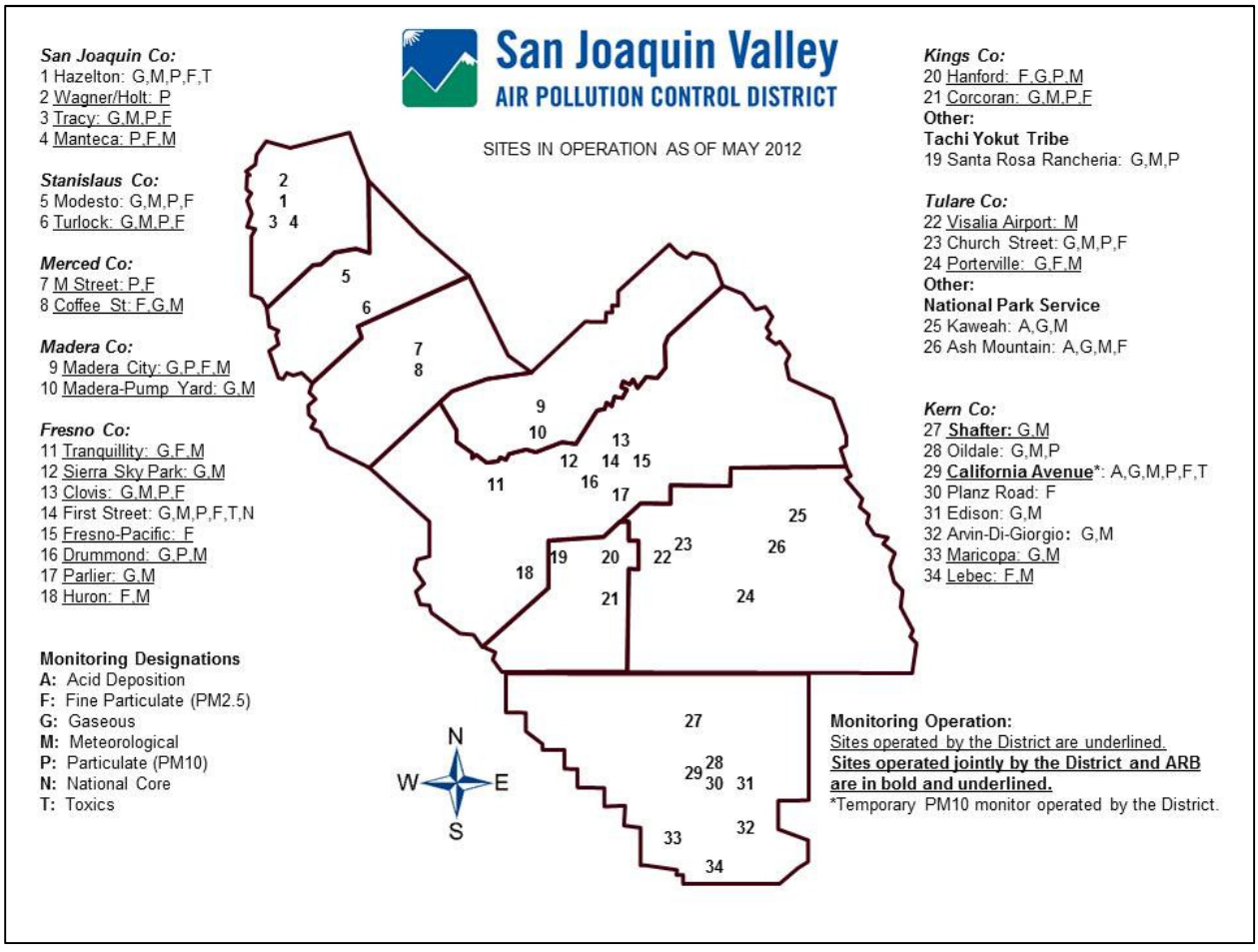
Figure 3-4 NOx Control Reduces Ammonium Nitrate Formation



3.2 ANALYSIS OF PAST AND PRESENT PM2.5 TRENDS

Numerous pollutants and meteorological parameters are measured throughout the San Joaquin Valley on a daily basis. This is accomplished through the operation of an extensive air monitoring network managed by the District and the Air Resources Board (ARB). This network measures progress toward compliance with the National Ambient Air Quality Standards (NAAQS) in addition to providing real-time air quality measurements used for daily air quality forecasts, residential-wood burning declarations, Air Alerts, and the Real-Time Air Quality Advisory Network (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 34 air monitoring stations throughout the Valley, where 21 of these sites measure PM2.5. At each of the PM2.5 sites, PM2.5 samples are taken on a daily filter basis, an hourly real-time basis, or both. Figure 3-5 shows the Valley's air monitoring sites.

Figure 3-5 Air Monitoring Sites within the San Joaquin Valley Air District



PM2.5 is measured and expressed as the mass of particles contained in a cubic meter of air (micrograms per cubic meter, or $\mu g/m^3$). The data collected from the District's network of PM2.5 monitors is used to calculate design values for the 24-hour and annual PM2.5 standards, as outlined in Environmental Protection Agency (EPA) guidance and regulations.[3]

3.2.1 Air Quality Progress

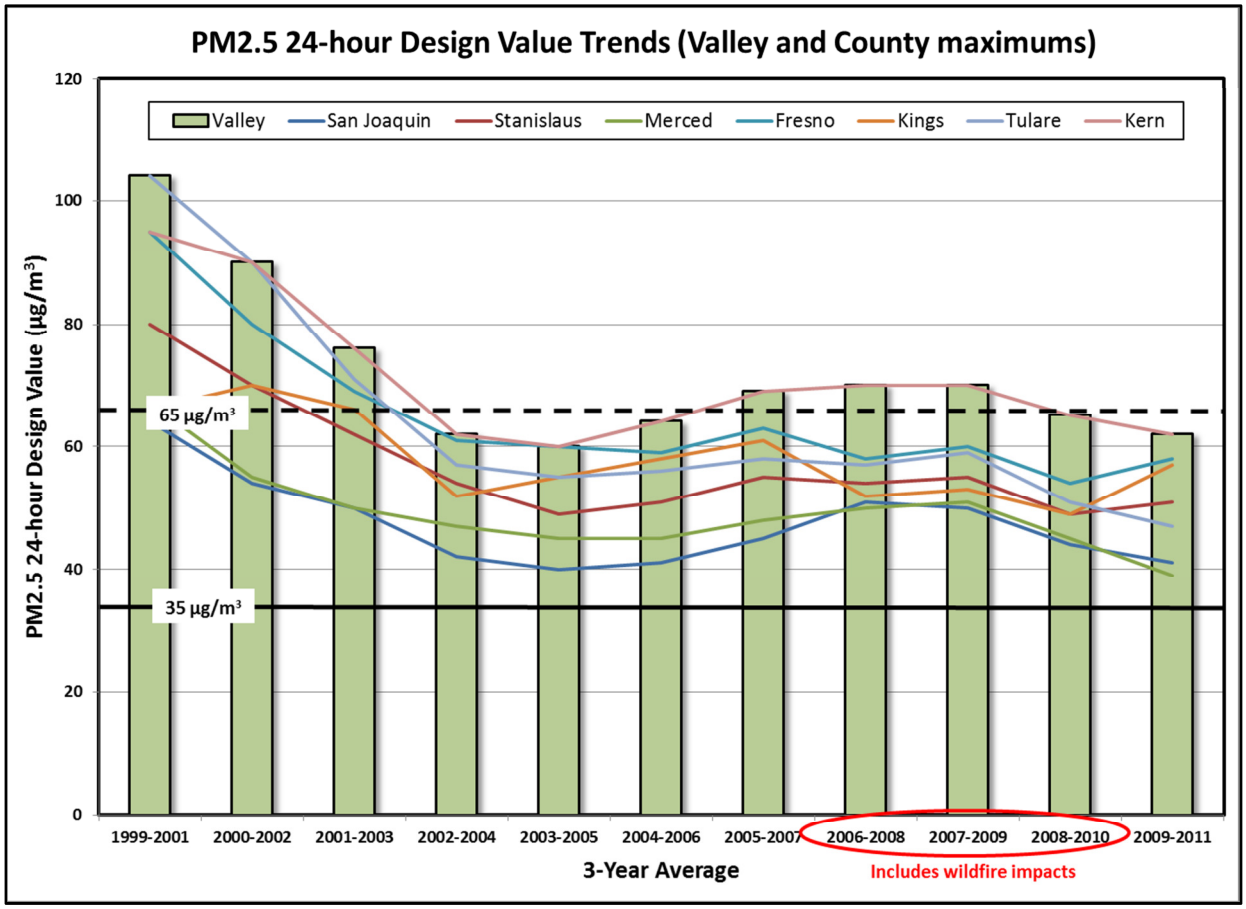
Since 1999, when PM2.5 first began to be measured in the San Joaquin Valley, significant progress has been made in reducing concentrations throughout the region. Most metrics used to measure air quality progress may fluctuate from year to year, due to influential variable factors like meteorology and the economic climate. While short term trends are useful for measuring air quality progress, longer term trends are useful in assessing overall progress of air quality improvement given year-to-year changes.

There are a number of ways that air quality progress can be assessed. The design value is the official method used to determine whether an area is in attainment of a standard, yet other indicators can reveal more about what progress is being made. Comparing the days over the 24-hour average NAAQS threshold from year to year shows the progress in reducing the number of days with the highest concentrations, while quarterly averages can show the movement in larger datasets over time. Comparing the frequency distributions of PM2.5 at an air monitoring site between time periods can show a shift in which concentrations are more commonly occurring now compared to the past. 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 San Joaquin Valley.

Under the 2006 PM2.5 federal standard a region must meet both the 24-hour average standard of 35 $\mu g/m^3$ and the annual average standard of 15 $\mu g/m^3$ in order to meet attainment. Details on how PM2.5 design values are calculated are provided in Appendix A of this plan. As seen in Figure 3-6, the Valley and county maximum 24-hour average PM2.5 design value trends show that significant progress has been made in reducing concentrations. Comparing the Valley maximum 1999-2001 and 2009-11 design values reveals that a 40% reduction in this metric has taken place over this time period. This analysis also reveals a steep reduction in the county maximum design values over the same time period. Note that some of the county design values in 2011 have increased, partly due to the abnormal stagnation and poor air quality in late 2011.

[3] EPA, *Guideline on Data Handling Conventions for the PM NAAQS* (April 1999) and Appendix N of 40 CFR Part 50.

Figure 3-6 Historical PM2.5 24-hour Design Value Trends



Historically, the Bakersfield-Planz air monitoring site has consistently been among the highest PM2.5 design values in the San Joaquin Valley. The following Figures 3-7 and 3-8 show the trend of the 24-hour and annual average design values at Bakersfield-Planz through the 2009-11 time period.

Figure 3-7 Trend of 24-hour Average PM2.5 Design Values at Bakersfield-Planz

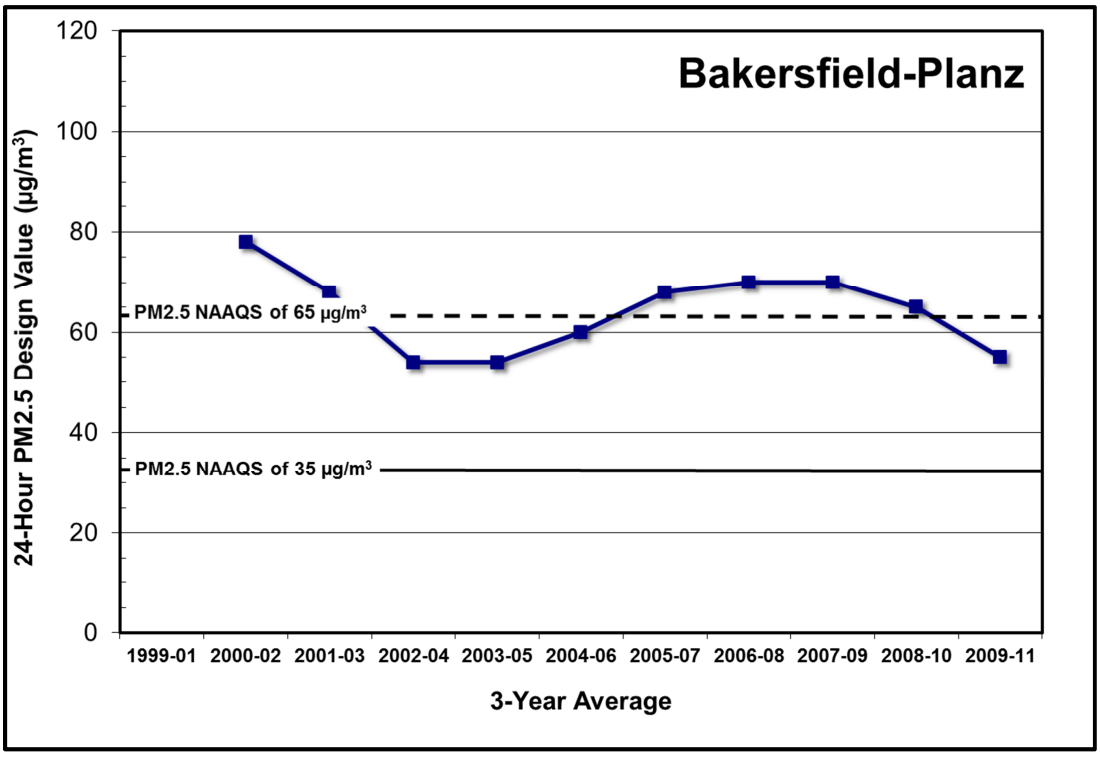
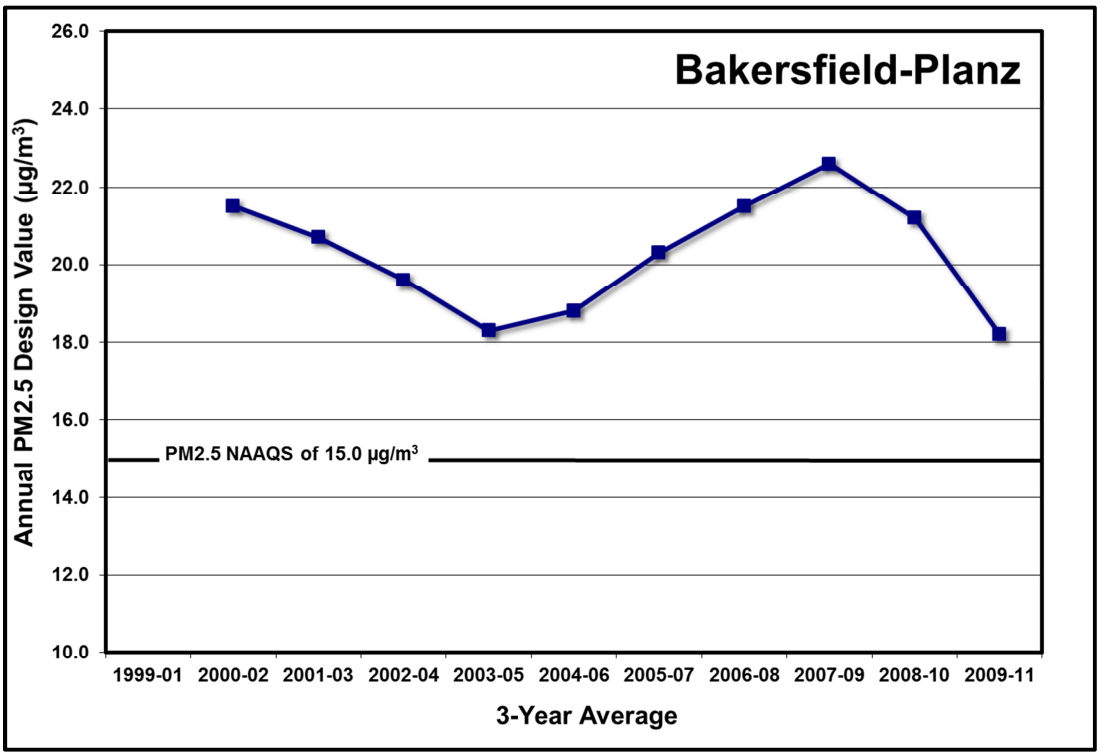


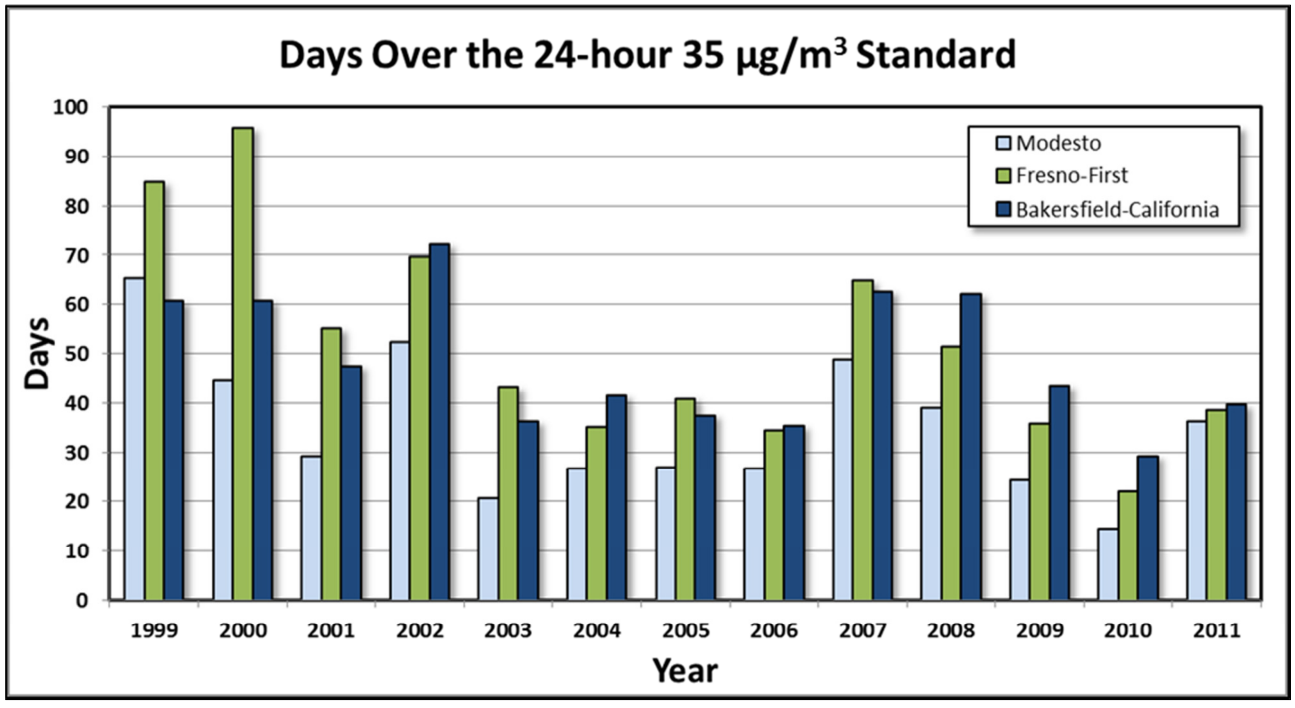
Figure 3-8 Trend of Annual Average PM2.5 Design Values at Bakersfield-Planz



The Bakersfield-Planz air monitoring site is beginning to see a decreasing trend in its design value. As seen in Figure 3-7, this site now has a 24-hour design value below the 1997 24-hour PM2.5 standard of 65 µg/m^3. Notably, the annual average design value in 2009-11 for Bakersfield-Planz has achieved an all-time low for the site at 18.2 µg/m^3 (see Figure 3-8). This downward trends will need to continue at all sites within the District as the San Joaquin Valley strives for attainment of the federal PM2.5 standards.

Another metric used for assessing the trend of PM2.5 is to consider the number of days that concentrations were over the PM2.5 24-hour NAAQS threshold of 35 µg/m^3. Focusing on the long term trend, and as seen in Figure 3-9 below, when comparing 1999 to 2011, the historical sites of Modesto, Fresno-First, and Bakersfield-California have experienced a 46% decrease in days exceeding a concentration of 35 µg/m^3. The year 2011 experienced an increase in days over the NAAQS threshold compared to 2010, however this was predominately due to unfavorable meteorology. Similar meteorology was experienced during the 1999-00 and 2000-01 winter seasons, yet there were a much greater number of days exceeding 35 µg/m^3 during these timeframes. This gives evidence that emissions have been reduced since 1999.

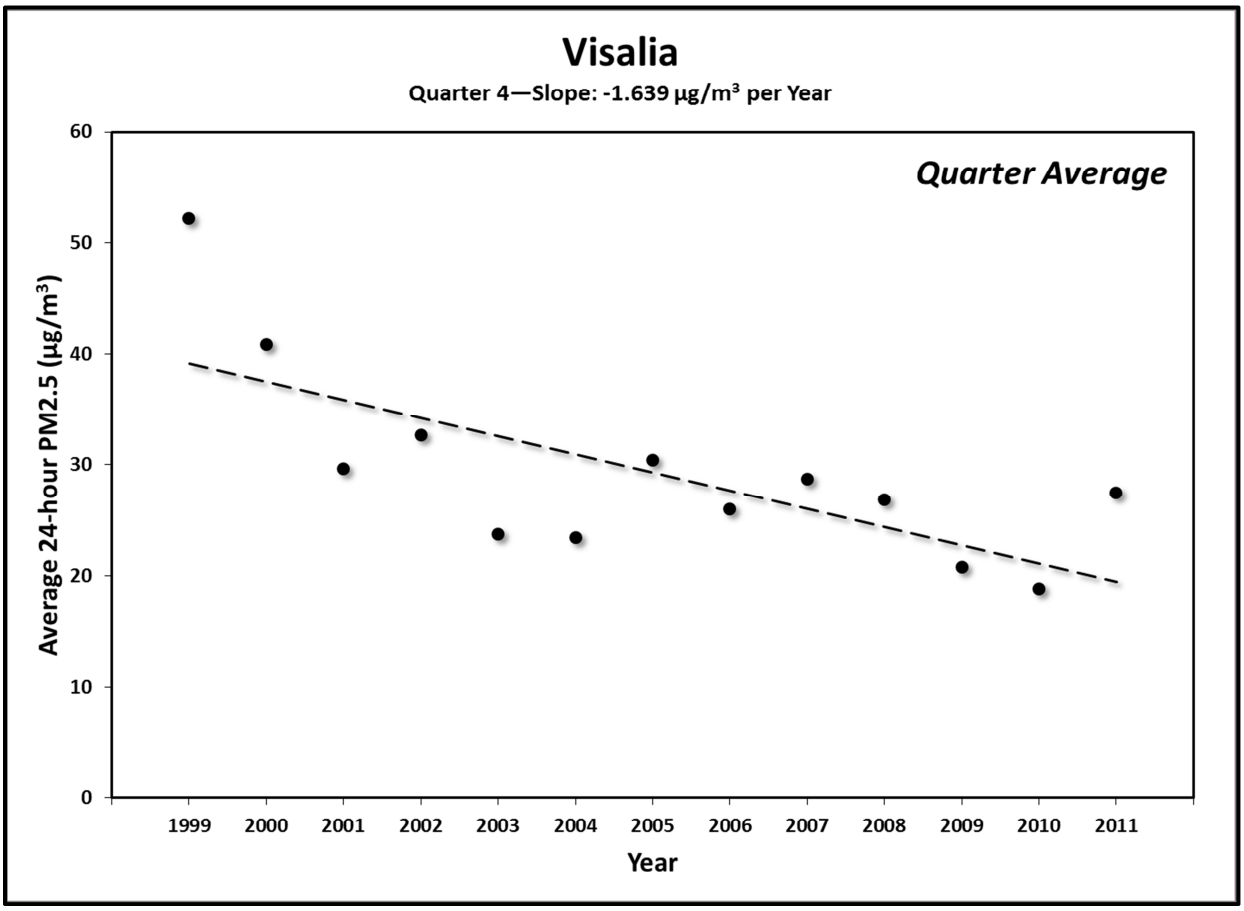
Figure 3-9 Annual Trends in Days over 35 µg/m^3



Since the Valley's highest PM2.5 concentrations occur during the Fall and Winter months, the 1st (January through March) and 4th (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 PM2.5 season is changing over time.

As seen in Figure 3-10, the Visalia site trend is typical of the trend in 4th quarter averages among the PM2.5 sites in the San Joaquin Valley. At this site the 4th quarter average PM2.5 showed a downward trend of 1.64 µg/m³ per year. It will be important for this trend of reductions in the quarterly averages to continue as the District comes closer to attaining the annual average PM2.5 standard of 15 µg/m³, which is calculated on a quarterly average basis. For the expanded results of this analysis, see Appendix A.

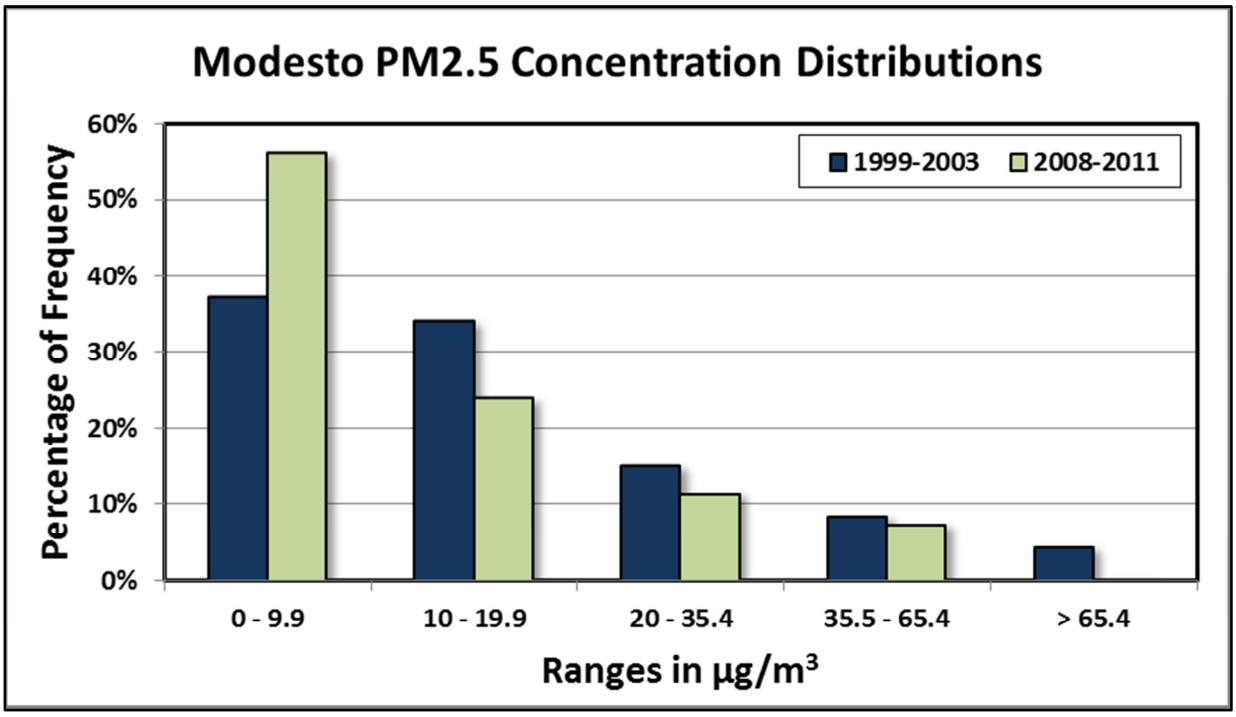
Figure 3-10 Trend of 4th Quarter Average at Visalia



Analyzing the change in the frequency of specific concentrations occurring at an air monitoring site can show how an entire body of data has shifted over time. To display this comparison, frequency distributions were calculated for the four-year timeframes of 1999-2003 and 2008-2011. In this analysis, the spectrum of PM2.5 concentrations was separated into bins so that each observation within each of the four-year time periods would fall into one of these ranges. Figure 3-11 shows the results of this analysis for the Modesto air monitoring site. As can be observed, the frequency of higher concentrations was greater during 1999-2003 when compared to 2008-2011.

Alternatively, lower concentrations were more frequent in 2008-2011 when compared to 1999-2003. This frequency shift toward the lower concentrations shows that progress is being made at reducing exposure to high levels of PM2.5. In addition, Figure 3-11 also reveals a dramatic decrease in the percentage of days that exceeded the 1997 24-hour PM2.5 standard of 65 µg/m^3. Refer to Appendix A for more details on this analysis.

Figure 3-11 Concentration Frequency Distribution Comparison at Modesto



Undoubtedly, PM2.5 air quality has improved since 1999, yet the District still faces difficult challenges in attaining the tightening EPA standards. Continuing the improvement of the San Joaquin Valley's air quality will take involvement and investment from both the regulated community and the general public.

3.2.2 Challenges of the Natural Environment

The San Joaquin Valley, as seen in Figure 3-12, 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, which can rapidly deteriorate dispersion conditions. Often during the winter high-pressure systems can cause the atmosphere to become stable for longer periods of time, where wind flow is calm and air movement is minimized. These stable weather systems can also cause temperature inversions which exacerbate the build-up of pollution.

Figure 3-12 San Joaquin Valley Air Basin

Normally, temperature decreases with increasing altitude, but under the effect of a temperature inversion, the temperature in a portion of the atmosphere will *increase* with altitude, causing warmer air to be above cooler air. As Figure 3-13 displays, this reversal of the "normal" pattern impedes the upward flow of air, causing poor dispersion and trapping emissions near the surface. Since this inversion is often lower than the height of the surrounding mountain ranges, the Valley effectively becomes a bowl with a lid on top trapping emissions near the surface. When dispersion both horizontally (transport flow) and vertically (rising air) are minimized, PM2.5 concentrations can build quickly. These naturally occurring meteorological conditions working against the San Joaquin Valley creates a challenge for the region. Under stagnant air flow and temperature inversions, the Valley needs sharp emissions reductions in order to attain the PM2.5 NAAQS.

Figure 3-13 Atmosphere with/without a Temperature Inversion

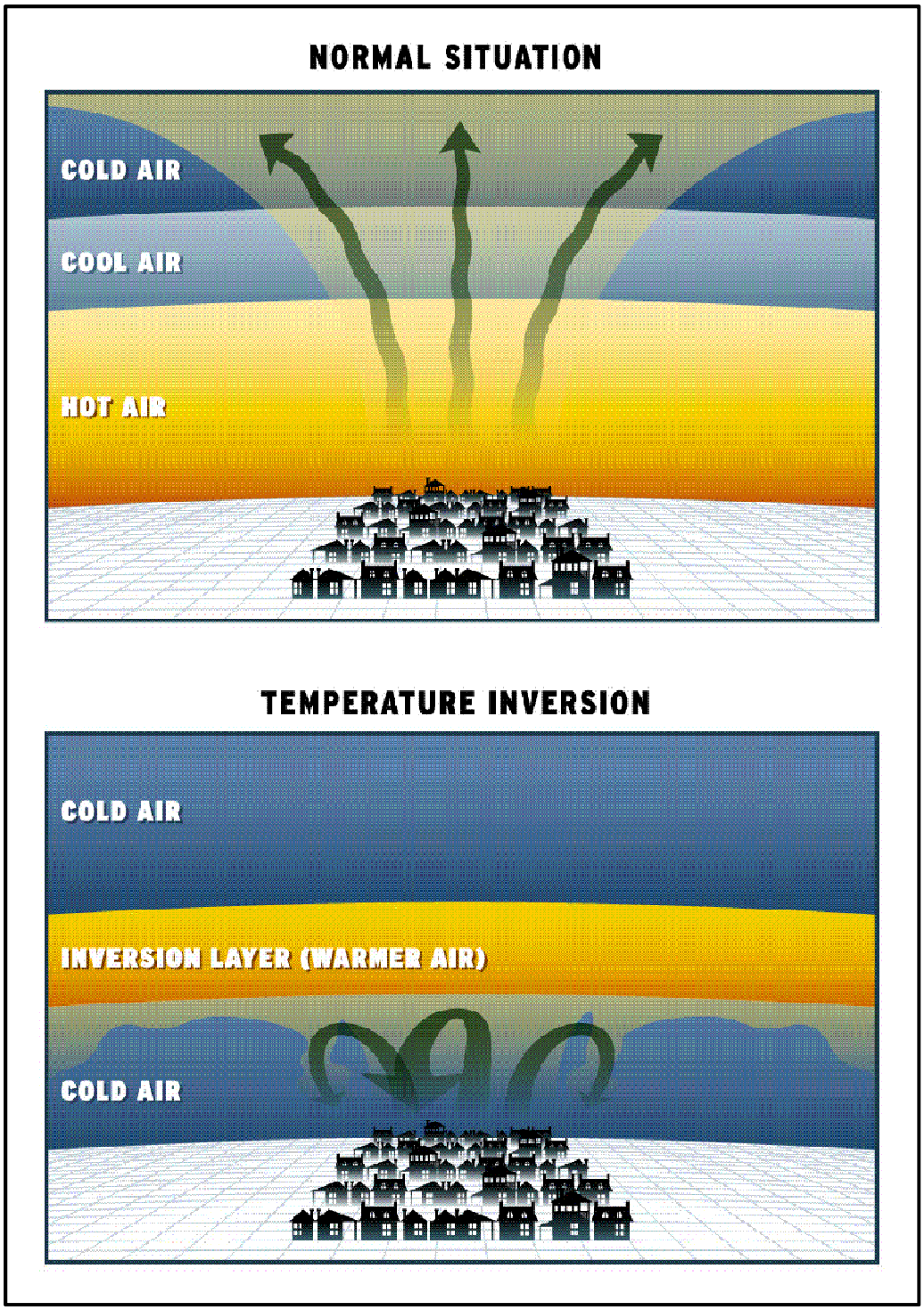
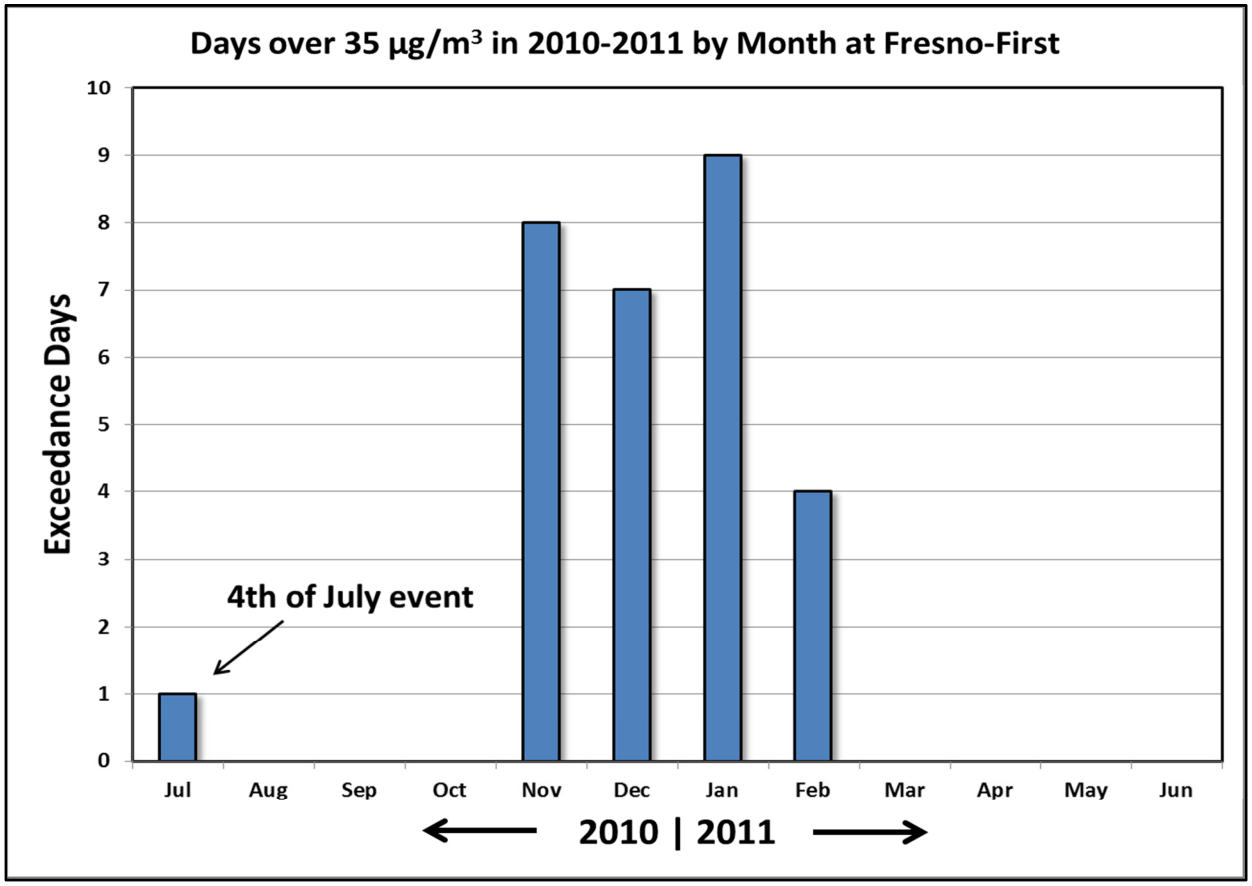


Image taken from:
http://ffden-2.phys.uaf.edu/212_spring2007.web.dir/Amber_Smith/Effects_of_Inversions.htm

Because of frequent stagnant conditions during the winter in the San Joaquin Valley, PM2.5 concentrations tend to be the highest from November to February. As an example, Figure 3-14 below shows the number of days per month during the 2010-11 timeframe when the Fresno-First air monitoring site exceeded the 2006 PM2.5 NAAQS threshold of 35 µg/m^3. Clearly PM2.5 is a problem most heavily experienced during the winter months.

Figure 3-14 Days Over 35 µg/m^3 by Month at Fresno-First from 2010-2011



3.3 THE EMISSIONS INVENTORY FOUNDATION

As reviewed in the previous section, a major indicator of air quality improvement is the trend of ambient pollutant concentrations. However, a more foundational indicator of progress is the emissions inventory. The emissions inventory is an estimate indicating how much direct pollution is going into the air as a result of various activities.

The District uses the emissions inventory to serve as a foundation for the development of control strategies; determine the effectiveness of permitting and control programs; provide input into ambient receptor, aerosol, photochemical, and statistical models; fulfill reasonable further progress requirements; and screen sources for compliance investigations.

3.3.1 Emissions Inventory Categories

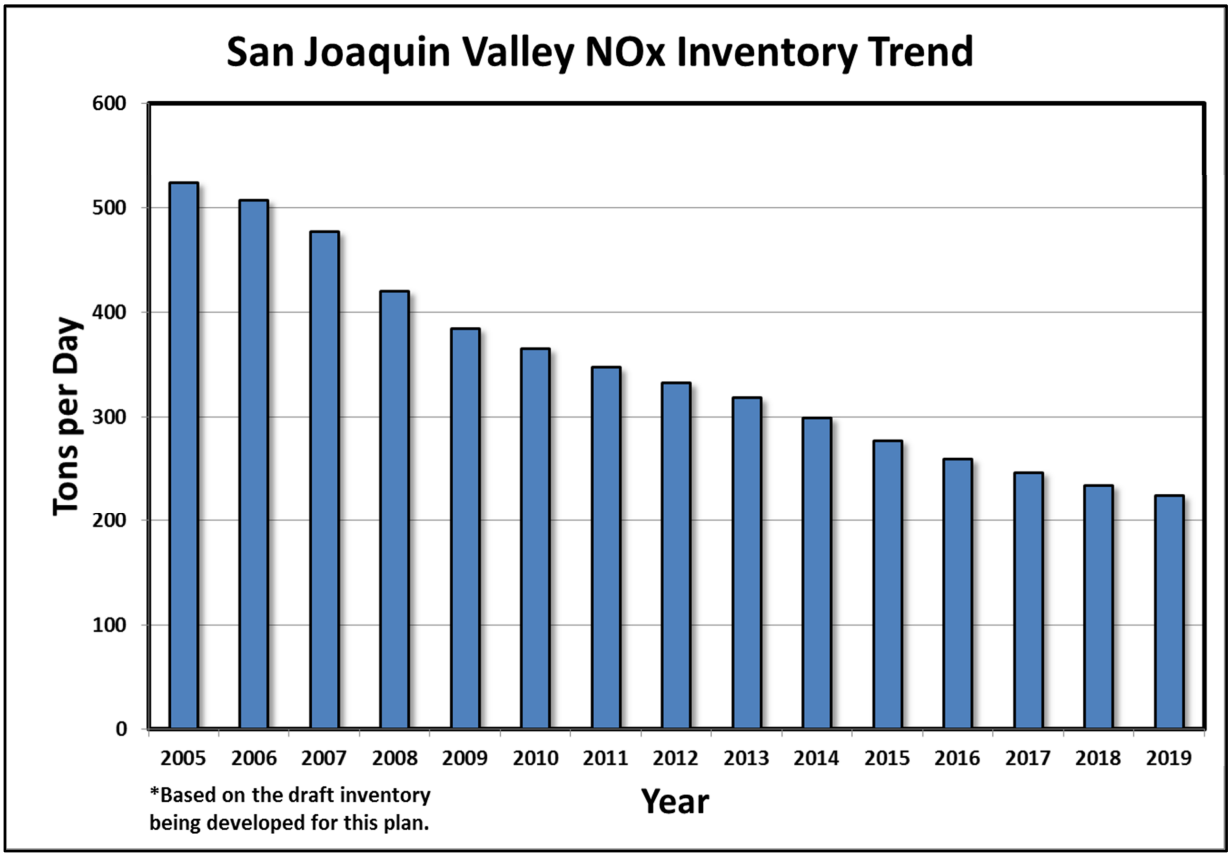
To reduce the Valley's PM2.5 levels further, Chapter 4 of this plan presents a control strategy that is based on an exhaustive evaluation of the emissions inventory of directly emitted PM2.5 as well as relevant PM2.5 precursors. Typically, an emissions inventory is organized by emissions source categories. Source categories consist of several broad groups:

- **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 - 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, fireplaces, tilling, and unpaved road dust.
- **Natural sources** – naturally occurring emissions
  - Geogenic sources, such as petroleum seeps;
  - Biogenic sources, such as emissions from plants;
  - Wildfire sources.

3.3.2 Trends in Reductions of Regional Emissions

The District has made significant progress in reducing direct PM2.5 emissions as well as its precursors. These reductions are the result of many rules and programs put in place by the District and the California Air Resources Board (ARB) that have been effective in the past, and will continue to have a positive effect in the future. Figure 3-15 shows the projected trend of total NOx emissions from 2005 through 2019 based on the draft emissions inventory being developed for this plan. A sharp downward trend from 2005 forward is projected based on current control strategies that will continue to take effect into the future. In light of the District's projected increase in population over this same time period, this anticipated reduction highlights the success of the control measures adopted and enforced by regulatory agencies.

Figure 3-15 NOx Emissions Inventory Trends (2005 through 2019)



Appendix B of this plan contains a more detailed description of the emission inventory as well as detailed tables showing the inventories for directly emitted PM2.5, NOx, SOx, VOC, and ammonia.

3.4 PROJECTED FUTURE AIR QUALITY AND IDENTIFYING THE GOAL

One of the aspects of an attainment plan is to project what the emissions of an area will be like in the future. If these forecast emissions are shown to be in attainment before the deadline, then this provides evidence that the strategic approach taken in this plan to attain the standard will be successful. Regional grid modeling is a method used to forecast air quality years into the future, while accounting for photochemistry, aerosol chemistry, physics, meteorology, and the growth and control of emissions over time based on projected industry trends and current emissions regulations. See Appendix E for details on the modeling approach taken for this plan.

3.4.1 Results of Modeling Analysis

The modeling results showing the projected future PM2.5 concentrations will be included here upon the completion of the analysis. A future draft of this plan will include these details.

3.4.2 Emissions Reductions Target for Attainment

As the modeling analysis is completed as specified in the previous section, the emissions inventory target will also be known. A future draft of this plan will include these details.

3.4.3 Other Analyses Adding to the Weight of Evidence

To add to the evidence that the District is making progress in reducing PM2.5 in the San Joaquin Valley, the ARB and the District are conducting a number of supporting analyses. These analyses may include:

- Positive matrix factorization;
- Chemical mass balance;
- Speciated linear rollback.

The details and results of these supporting analyses will available in future plan drafts.