



Chapter 4

Scientific Foundation and PM2.5 Modeling Results



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Chapter 4: Scientific Foundation and PM2.5 Modeling Results

The nature of PM2.5 formation in the San Joaquin Valley is highly complex, and attainment of the 2006 National Ambient Air Quality Standard (NAAQS) PM2.5 standard is not a one-size-fits-all effort. Even though ultimate attainment of the 2006 NAAQS is determined by PM2.5 concentrations on the days with the highest concentrations—the worst air quality days—significant differences in regional natural environments and the relative contribution of precursor emissions requires regionally specific modeling and regionally specific control strategies. Also, differences within PM2.5 itself, directly-emitted PM2.5 versus secondary PM2.5 forming in the atmosphere through series of chemical reactions, adds to the complexity inherent in modeling and planning efforts. Within this complexity, the District’s modeling efforts must be able to project PM2.5 concentrations for each square kilometer of the San Joaquin Valley (Valley), not just the areas that currently have air quality monitoring stations.

This complexity is accounted for in the modeling and other scientific analyses conducted for this plan. The District, ARB, and researchers have developed and refined these analytical tools, including regional modeling, over many years. The District’s regional modeling protocol, included as Appendix G to this plan, is over 150 pages and has been reviewed by other air agencies and by atmospheric chemists, atmospheric scientists and other air quality experts. This protocol notes that the Valley is one of the most studied airsheds in the world in terms of the number of publications in peer-reviewed scientific journals and other major reports. Such scientific analyses, and the field studies providing data for these analyses, are the foundation of the modeling efforts for this plan. Public and private sector partnership through the San Joaquin Valleywide Air Pollution Study Agency (Study Agency) provided funding and coordination for many of these studies.

This chapter provides an overview of the scientific foundation for this PM2.5 Plan. It describes Study Agency and other research efforts related to this plan, the nature of PM2.5 in the Valley, and PM2.5 species. It also summarizes the regional modeling effort and the results of the analyses conducted for this plan. These results show which emissions control strategies will most effectively assure attainment of the 2006 PM2.5 NAAQS and improved PM2.5 air quality throughout the Valley.

4.1 AIR QUALITY RESEARCH

The Study Agency has developed and funded extensive research on particulate matter in the Valley. The Study Agency was established in 1985 under a joint-powers agreement between local counties and includes input from districts, the State, EPA, public and private industry representatives, and other governmental agencies to create a cooperative and unbiased research program. The Study Agency’s main purpose is to further the scientific understanding of regional air quality issues to assist regulatory agencies in the development of strategies to attain air quality standards by providing the best available science for policy decisions. In 1992, Study Agency expanded particulate matter research to include PM2.5.

The initial field program for PM₁₀ and PM_{2.5} was the Integrated Monitoring Study (IMS95), which was a two month pilot study that started in December 1995. This short but informative study provided the foundation for successful PM₁₀ and PM_{2.5} monitoring and analysis including the following:

- Evaluating which air monitoring techniques worked best for air quality research projects
- Investigating and improving innovative techniques for identifying airborne particulate matter with atmospheric tracers
- Developing a model for data collection
- Developing a day-specific emission inventory development

While the entire Valley was studied, special attention was given to Corcoran, Fresno, and Bakersfield, which had the highest levels of particulates.

This pilot program led to the Study Agency's largest PM_{2.5} sampling and research effort. The California Regional Particulate Air Quality Study (CRPAQS) commenced in December 1999 and continued through February 2001. The objectives of CRPAQS were to provide an improved understanding of PM emissions, composition, and the dynamic atmospheric processes surrounding them; establish a strong scientific foundation for informed decision making; and develop methods to identify the most efficient and cost-effective emission control strategies to achieve the PM₁₀ and PM_{2.5} standards in Central California. This robust study collected PM_{2.5} data from both within the Valley and from areas outside the Valley that impact Valley air quality. The resulting dataset has been studied by many researchers using Study Agency funding totaling over \$27.5 million. CRPAQS continues to support research and improve the understanding of PM_{2.5} in the Valley.

Results from IMS95 and CRPAQS have helped the District and other agencies understand differences in urban and rural PM episode development, the mechanisms for how nitric acid forms aloft and its contribution to regional ammonium nitrate, the role of NO_x as the limiting precursor for ammonium nitrate formation, and the role of fog on secondary pollutant formation and removal.

This information greatly informed the development of effective PM₁₀ and PM_{2.5} attainment plans for the District. Data collected from these studies have allowed the District, CARB, EPA, and others understand PM_{2.5} creation and movement in the Valley, model future year PM_{2.5} levels, and source apportion PM_{2.5} concentrations to the correct contributing sources. Study Agency projects and results have also been used to improve air pollutant emissions inventories.

The District's *2003 PM₁₀ Plan*, *2006 PM₁₀ Plan*, and *2008 PM_{2.5} Plan* included data and analyses from CRPAQS within the photochemical modeling performed for each plan. Similarly, research conducted through CRPAQS is being incorporated into photochemical modeling, PM_{2.5} trends evaluation, and weight-of-evidence analysis for this plan. Implementation of the plans that use CRPAQS information will result in significantly better visibility, improved health and well-being of the citizens of the Valley,

and eventual attainment of the 2006 PM_{2.5} NAAQS. The District will continue to build on this foundational research and seek additional opportunities to support future research.

4.2 THE NATURE AND FORMATION OF PM_{2.5}

Unlike ozone, which is a fairly simple molecule of three oxygen atoms, PM_{2.5} can be composed of any material that has a diameter of 2.5 microns or less. PM_{2.5} can be emitted directly as primary PM_{2.5} from various sources, or it can form secondarily through chemical reactions in the atmosphere. Among the chemical precursors that can form secondary PM_{2.5} are nitrogen oxides (NO_x), volatile organic compounds (VOCs), sulfur dioxide (SO₂), and ammonia (NH₃). In addition, naturally occurring emissions from biogenic sources, such as plants, can also add to the formation of PM_{2.5}.

The resulting ambient PM_{2.5} mixture can include aerosols (fine airborne solid particles and liquid droplets) consisting of components of nitrates, sulfates, elemental carbon, organic carbon compounds, acid aerosols, trace metals, geological materials, and more. The complex formation and composition of PM_{2.5} requires a robust planning effort, where various components of the mass can be targeted for reduction. A control strategy that targets reductions among the precursors of PM_{2.5} has been shown to have a positive impact in reducing the total formed mass. Both direct PM_{2.5} and its precursors are tracked and projected within the emissions inventory (see Chapter 3). The role of each potential precursor varies by region, and research and photochemical modeling determine which precursor reductions will contribute to a region's attainment.

As discussed in Chapter 2, there is considerable variation in the relative toxicity of the chemical species found in PM_{2.5}. While attainment of the NAAQS is demonstrated through total PM_{2.5} mass reduction (which is the primary goal of District and ARB control strategies), the relative differences in toxicity of species within the total mass provides a justification for new source control measures that specifically target the more toxic species of PM_{2.5}, especially primary PM_{2.5} generated by combustion.

4.3 PM_{2.5} SPECIES IN THE SAN JOAQUIN VALLEY

PM_{2.5} in the Valley is comprised of many species that contribute to the total PM_{2.5} mass. This complex mixture is attributable to stationary, mobile, and area-wide sources, as well as naturally occurring emissions. Although the list of species contributing to PM_{2.5} in the Valley is lengthy, it 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 PM_{2.5} mass in the 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.

Ammonium Nitrate—A portion of nitrogen oxide (NO_x) emissions from motor vehicles and stationary combustion sources react through photochemical processes during the day, or react with ozone at night, to form nitric acid. When ammonia emissions react with the nitric acid, ammonium nitrate is created.

Ammonium nitrate is commonly the largest contributor to PM_{2.5} mass in the Valley, especially in the southern region of the Valley. Stagnant, cool, 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—Sulfur oxide (SO_x) emissions from combustion sources undergo photochemical reactions in the atmosphere, sulfuric acid is formed. Similar to the ammonium nitrate photochemical reaction, sulfuric acid reacts with ammonia emissions to form ammonium sulfate.

Unlike ammonium nitrate, the peak season for ammonium sulfate is the summer. As a comparison, there is much less ammonium sulfate in the Valley atmosphere than ammonium nitrate.

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 and other 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 PM_{2.5} mass.

Trace metals—Trace metals are present in soil dust and are emitted from mobile sources as part of combustion, engine wear, brake wear, and similar processes. Fireworks emissions have also been identified as a source of metals that impact health.

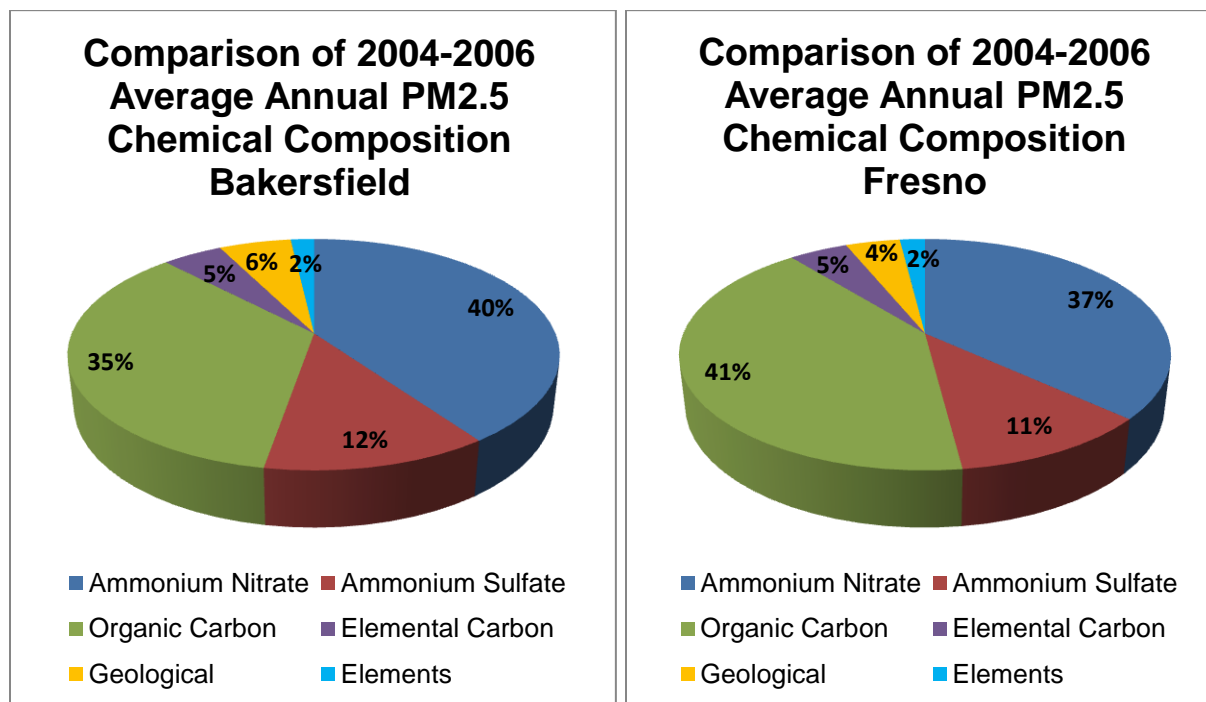
Sea Salt—Sodium chloride within sea spray can contribute to PM_{2.5} mass under meteorological conditions that allow transport of ocean air into the Valley. This represents a small portion of the overall mass and is only a contributor under specific transport conditions.

Secondary Organic Aerosol—As organic carbon is released into the atmosphere, photochemical reactions can occur to create organic aerosol, called secondary organic aerosol (SOA).

Combined Water—If a water molecule attaches itself to any of the above species, a combined water species is formed, adding to the total PM_{2.5} mass.

Figure 4-1 shows the relative chemical composition (major species components) of the average annual PM_{2.5} in Bakersfield and Fresno based on speciation data from 2004–2006.

Figure 4-1 Comparison of 2004–2006 Average Annual PM_{2.5} Chemical Composition



Note: "Elements" includes trace metals, chlorine, and silicon.

4.4 SCIENTIFIC FOUNDATION FOR THE 2012 PM_{2.5} PLAN

As described in Chapter 3, the Valley's climate, topography, and emissions have contributed to a unique set of wintertime PM_{2.5} formation processes resulting in a low regional carrying capacity for PM_{2.5} and secondary precursors. The actual formation and makeup of PM_{2.5} includes a complex mixture of species that have different reaction capabilities and human toxicity.

Meeting the substantial attainment challenge created by the low regional carrying capacity requires new control measures that are feasible and effective based on the combined weight of scientific evidence surrounding the various PM_{2.5} species. For this plan, the development of new control measures is guided by two sources of scientific knowledge: prior research examining the key sources and processes governing PM_{2.5} species formation and substantiated evidence of reductions in ambient concentrations and key species resulting from existing control measures. In combination, this body of knowledge about key sources, their changing inventories, and the unique atmospheric processes found in the region is incorporated into the regional modeling developed for this plan, the results of which are discussed at the conclusion of this chapter.

The following is a review of each of these bodies of evidence with a focus on the predominant PM_{2.5} species of concern: organic carbon compounds (OC) and ammonium nitrate (NH₄NO₃). Prospective controls on these species lie at the heart of the regional modeling exercise discussed at the conclusion of this chapter and hold the key to attaining the 2006 PM_{2.5} NAAQS. Species of lesser importance, including geologic PM_{2.5}, and VOCs are reviewed as well.

4.4.1 Ammonia Contribution to PM_{2.5} Concentrations

Ammonium nitrate contribution to total 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.¹ 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 as organic carbon, ammonium sulfate, and geologic material.² 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 the 24-hour average concentration exceeds the 35 µg/m³ 24-hour PM_{2.5} standard (see Appendix G).

Ammonium nitrate formation and precursors

Formation of ammonium nitrate is described by Kleeman et al. (2005, pp. 5326-7):³

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).⁴ 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

¹ 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.

² 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.

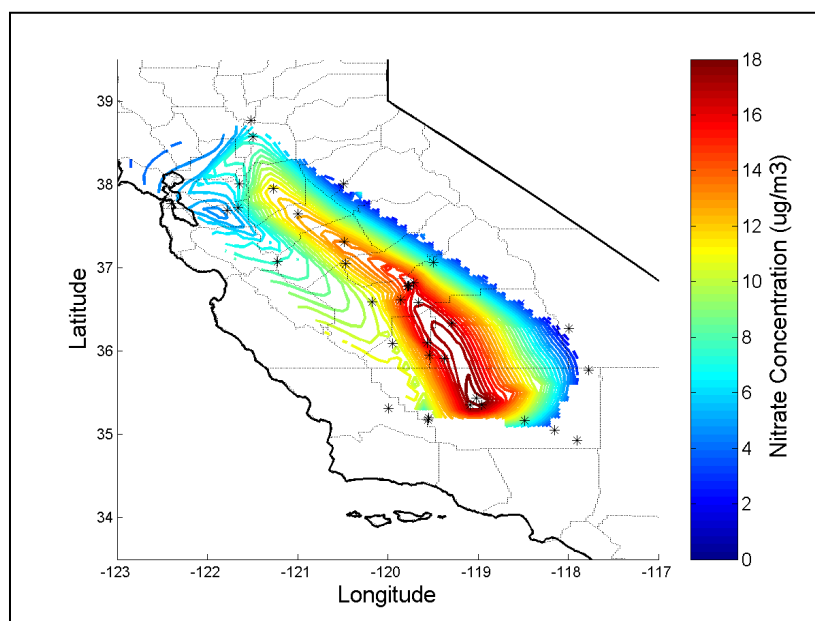
³ Kleeman, M.J., Ying, Q., & Kaduwela, A. (2005). Control Strategies for the Reduction of Airborne Particulate Nitrate in California's San Joaquin Valley. *Atmospheric Environment*, 39, 5325–5341.

⁴ Wexler, A.S., Seinfeld, J.H. (1991). 2nd-Generation inorganic aerosol model. *Atmospheric Environment Part a-General Topics* 25 (12), 2731–2748.

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).^{5 6} 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).⁷

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 4-2. Higher concentrations of nitrate occur in the southernmost Valley as a result of slower wind speeds and higher levels of reactive nitrogen and ammonia.

Figure 4-2 Modeled Regional Distribution of Ammonium Nitrate⁸



Both nitric acid and ammonia are needed to form ammonium nitrate. The extensive research conducted through CRPAQS and subsequent studies, as well as ongoing evaluation and modeling demonstrates that there is a relative abundance of ammonia

⁵ 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).

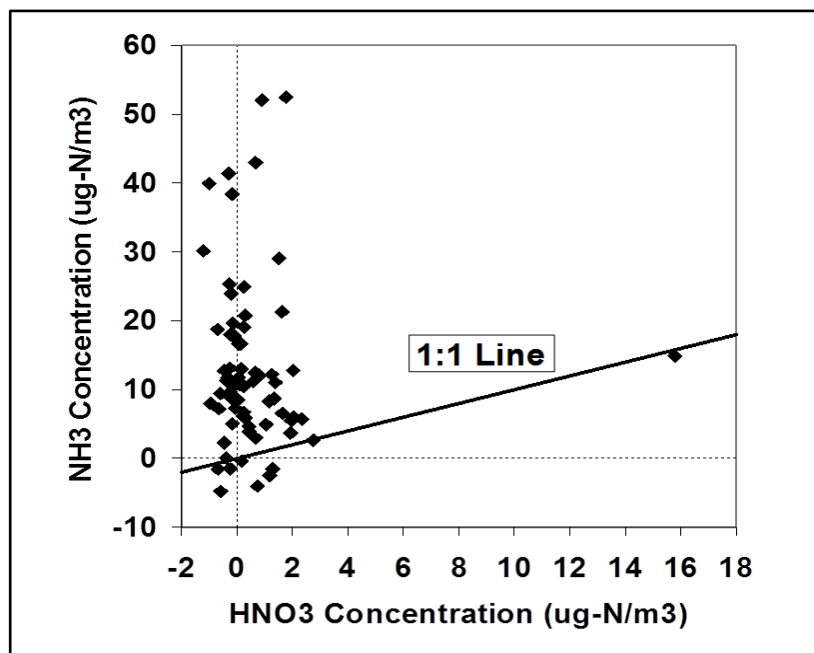
⁶ Nguyen, K. & Dabdub, D. (2002). NO_x and VOC Control and Its Effects on the Formation of Aerosols. *Aerosol Science and Technology* 36 (5), 560–572.

⁷ 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.

⁸ 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.

(NH₃) compared to nitric acid (HNO₃), and that the amount of nitric acid (resulting from NO_x emissions) drives the ultimate formation of ammonium nitrate. Figure 4-3 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.⁹ See Appendix G for more information.

Figure 4-3 Ammonia versus Nitric Acid Measurements at Angiola¹⁰



Reducing ammonium nitrate

Because of the regional surplus in ammonia, even substantial ammonia emissions reductions yield a relatively small reduction in nitrate. Figures 4-4 and 4-5 provide a simplified illustration of this situation. As seen in Figure 4-6, 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, while a 50% reduction in ammonia only realized less than 5% reductions in nitrate concentrations. Finally, Figure 4-7 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.

⁹ Magliano, K. L. (2009) Science-Based Policies for Particulate Matter Air Quality Management in California. *International Aerosol Modeling Algorithms Conference*. Davis CA.

¹⁰ 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 4-4 Abundance of Ammonia in the San Joaquin Valley¹¹

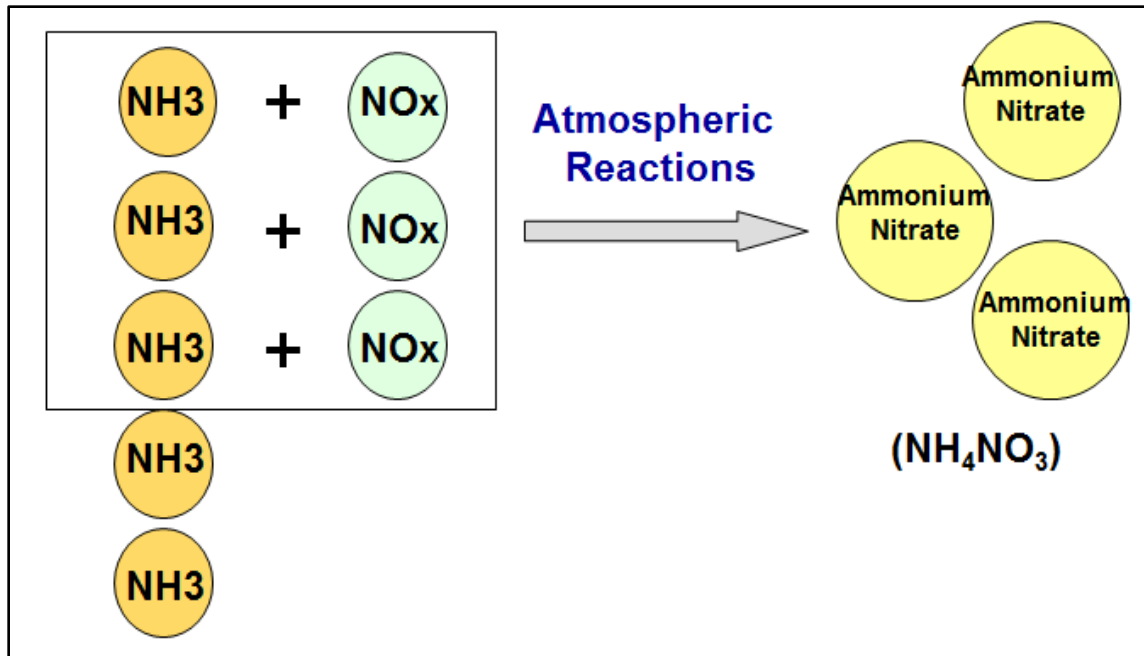
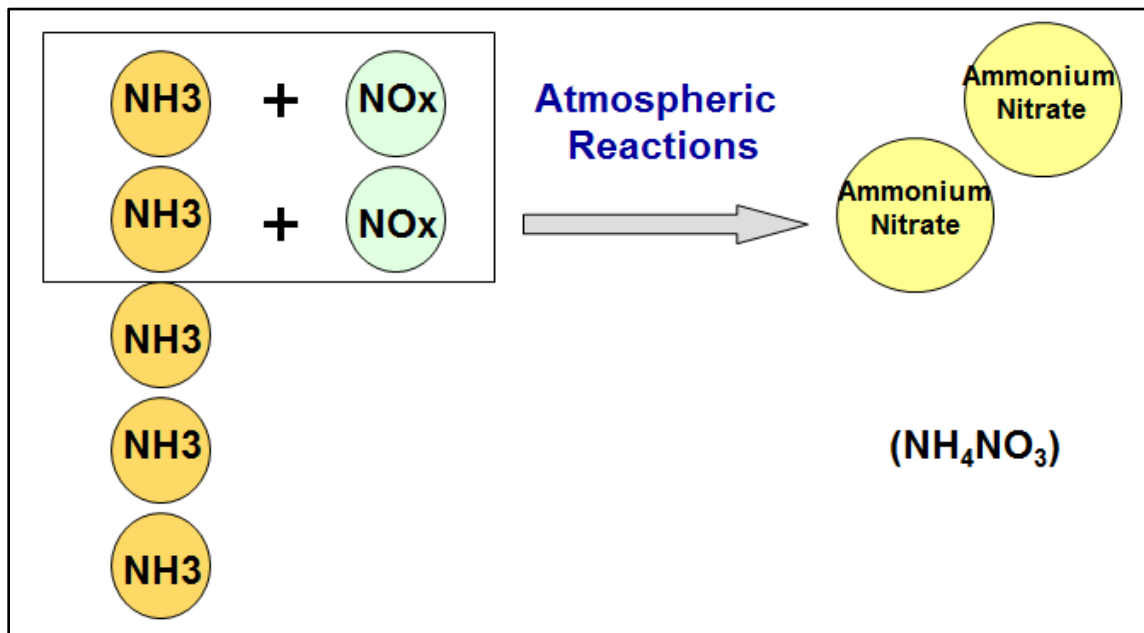


Figure 4-5 NO_x Control Reduces Ammonium Nitrate Most Efficiently



¹¹ Ibid. 9

Figure 4-6 Modeled Ammonium Nitrate Response to Ammonia vs. NOx Controls¹²

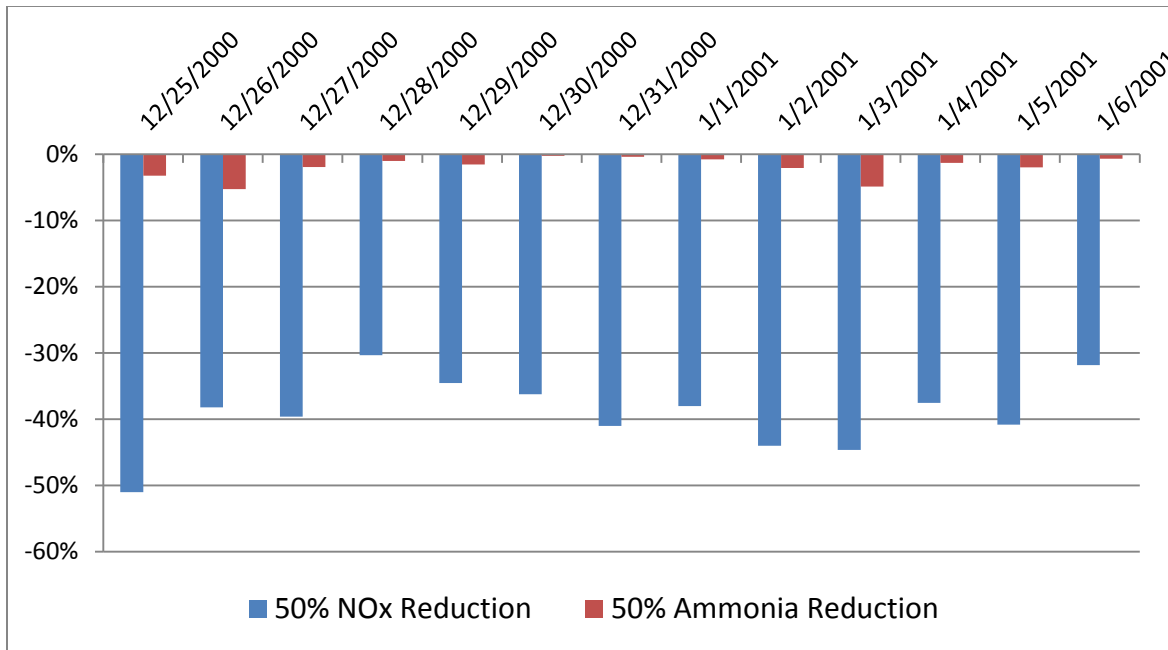
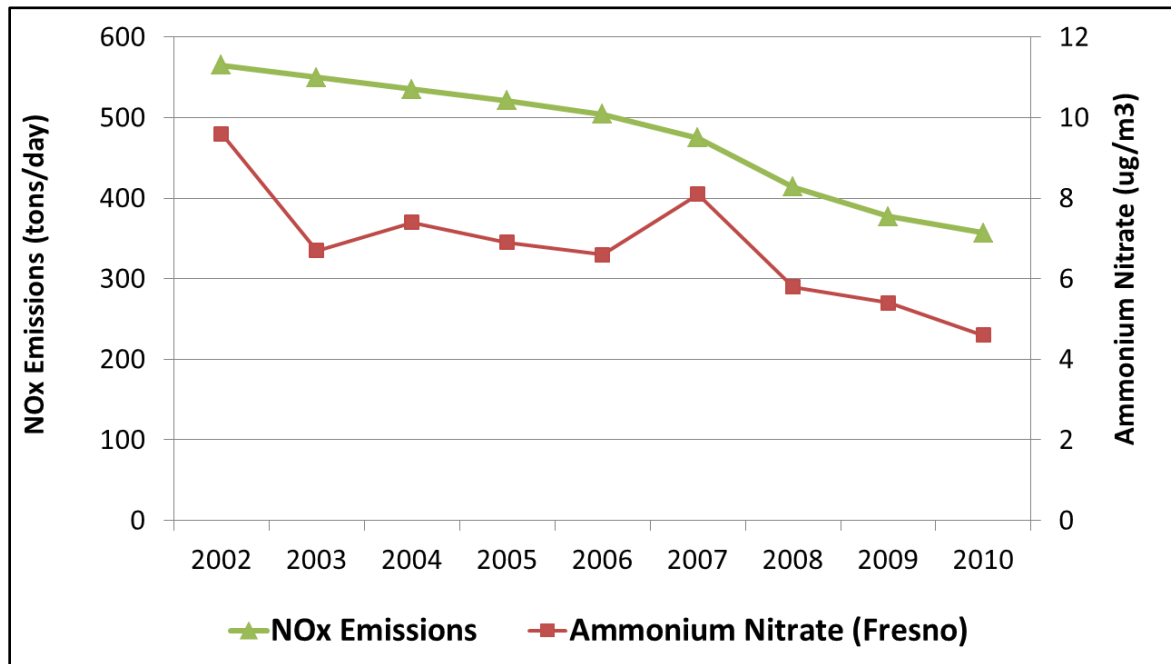


Figure 4-7 Correlation Between NOx Reductions and Observed Ammonium Nitrate in Fresno¹³



¹² Ibid. 9

¹³ Ibid. 9

Due to this 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 San Joaquin Valley. However, the District and ARB have continued to examine the potential role of ammonia with regard to PM_{2.5} formation (see Appendices F and G).

The modeling sensitivity analysis conducted for this plan shows that reductions in ammonia emissions achieve insignificant reductions in the 2019 PM_{2.5} design values compared to reductions of direct PM_{2.5} and NO_x emissions. As Appendix G details:

- A 1 ton reduction in the San Joaquin Valley's total direct PM_{2.5} emissions reduces the Bakersfield-California PM_{2.5} design value by 0.34 µg/m³
- A 1 ton reduction in the San Joaquin Valley's total NO_x emissions reduces the Bakersfield-California PM_{2.5} design value by a 0.08 µg/m³
- A 1 ton reduction in the San Joaquin Valley's total ammonia emissions reduces the Bakersfield-California PM_{2.5} design value by a mere 0.008 µg/m³

Relative to the other pollutants, ammonia reductions at the Bakersfield-California site are only 2.3% as effective as direct PM_{2.5} reductions, and only 10% as effective as NO_x reductions.

Furthermore, it would therefore take an unreasonable tonnage of ammonia reductions to reduce PM_{2.5} mass a significant amount. Since, as noted above, 1 ton of reduction in ammonia achieves a 0.008 µg/m³ reduction in the PM_{2.5} design value, it would take a total ammonia reduction of 125 tons per day for the San Joaquin Valley to achieve only a 1 µg/m³ reduction in the PM_{2.5} design value. Based on the total ammonia emissions inventory for the San Joaquin Valley in the year 2019, this would equate to a 34% reduction of the total tonnage. Thus, current technical analyses demonstrate that ammonia reductions would not significantly contribute to the Valley's attainment of the 2006 PM_{2.5} standard, so ammonia emissions do not need to be reduced under this plan.¹⁴

In the Reasonably Available Control Measures (RACM) analysis in Chapter 9, the District analyzed the amount of emissions reductions necessary to advance attainment by one year, from 2019 to 2018. The 2018 design value for Bakersfield-California is at least 1 µg/m³ higher than the attainment level. As discussed in Chapter 5, the amount of ammonia reductions that could advance attainment by one year is an infeasible amount, since there are no control strategies that exist or have been identified which could achieve such large reductions.

In contrast, each ton of NO_x reduced yields a summer ozone benefit and a winter reduction in nitrate. Additionally, NO_x controls on mobile sources are largely based on new generation Tier IV engines (diesel) that generate OC at much lower rates. Given that the OC fraction of Valley PM_{2.5} is a primary driver of respiratory and cardiovascular

¹⁴ Clean Air Fine Particle Implementation Rule [PM_{2.5} Implementation Rule]. 72 Fed. Reg. 79, pp. 20586–20667 at p. 20590 (2007, April 25). Retrieved from <http://www.gpo.gov/fdsys/pkg/FR-2007-04-25/pdf/E7-6347.pdf#page=1>

effects of PM_{2.5} exposure, the health benefits of mobile source NO_x controls are considerable.

4.4.2 VOC Contribution to PM_{2.5} Concentrations

Volatile organic compound¹⁵ (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.

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 Multiscale 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.¹⁶ Together, these study results show that for SOAs, further VOC reductions would have very limited effectiveness in reducing PM_{2.5} concentrations.

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.

¹⁵ 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>

¹⁶ Pun, B.K., Balmori R.T.F., & Seigneur, C. (1998). Modeling Wintertime Particulate Matter Formation in Central California, *Atmospheric Environment*, 43, 402-409.

Several modeling studies^{17,18,19,20} have 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^{21,22,23,24,25,26} 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 NOx 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 PM2.5 concentrations, concentrations that are no longer reached in the Valley. In contrast, a 50% reduction in NOx can reduce significantly more nitrate at current PM2.5 concentrations, one study²⁷ reporting a 38% reduction in nitrate.

Despite the insignificance of VOC emissions with regard to PM2.5 concentrations in the Valley, VOC emissions have been reduced and will continue to be reduced through implementation of the *2007 Ozone Plan*.

4.4.3 Geologic Contribution to PM2.5 Concentrations

Geologic dust is not a major PM2.5 emission source in the Valley. As shown in Figure 4-1, based on speciation data from 2004–2006, geologic dust accounts for between 4% and 5% in Fresno and Bakersfield, respectively. In addition, studies have shown that geologic dust, by itself, has relatively low toxicity.

¹⁷ 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.

¹⁸ 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.

¹⁹ 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.

²⁰ Ying, Q., Lu, J., & Kleeman, M. (2009). Modeling Air Quality during the California Regional PM10/PM2.5 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.

²¹ 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.

²² 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.

²³ 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.

²⁴ 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

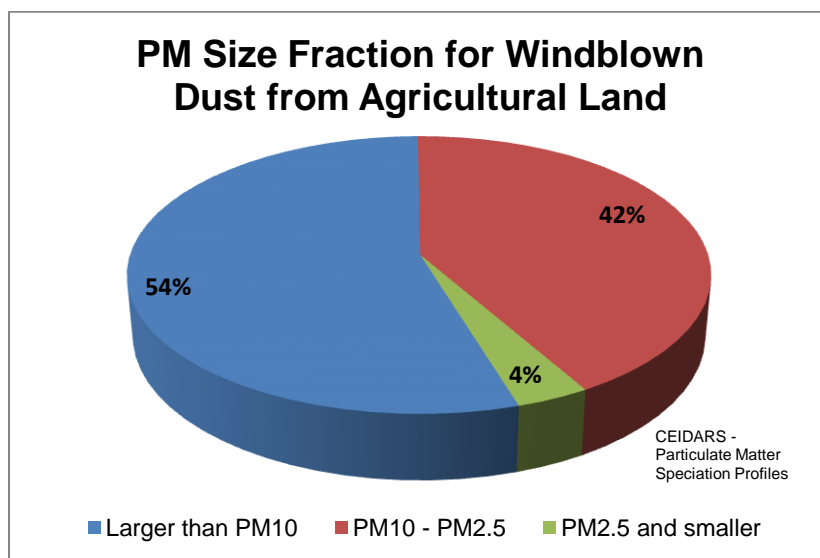
²⁵ Livingstone, P.L., Magliano, K., Güreş, K., Allen, P.D., Zhang, K.M., Ying, Q., ... Byun, D. (2009). Simulating PM Concentrations during a Winter Episode in a Subtropical Valley: Sensitivity Simulations and Evaluation Methods. *Atmospheric Environment*, 43, 5971-5977.

²⁶ Pun, B.K., Balmori R.T.F., & Seigneur, C. (2009). Modeling Wintertime Particulate Matter Formation in Central California. *Atmospheric Environment*, 43, 402-409.

²⁷ *Ibid.* 25

Fugitive dust rules were critical in the District's attainment of the PM₁₀ NAAQS. However, PM_{2.5} from geologic dust makes up a very small portion of overall geologic dust fraction. The California Emission Inventory and Reporting System (CEIDARS) published particulate matter speciation profiles in 2009. As shown in Figure 4-8, for windblown dust from agricultural land, there was only a 4% geologic source contribution of PM_{2.5}.

Figure 4-8 PM Size Fraction for Windblown Dust from Agricultural Land



Geologic dust emissions are lowest in the winter when the majority of the District's PM_{2.5} 24-hour exceedances occur. The Valley receives the majority of its precipitation during the winter, and the emissions inventory methodologies assume that as little as 0.01 inches of rainfall on any day suppresses geologic dust for 24 hours. Based on precipitation data from airports throughout the Valley, 71% of the days with at least 0.01 inches of precipitation occur during the winter months. Additionally, U.S. Forest Service and National Park unpaved roads, another source of geologic dust, are inaccessible or snow packed, during the winter, thus reducing emissions during those months.

Not only is the geologic dust contribution to the total PM_{2.5} mass extremely low, the overall toxicity of geologic dust, which consists mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metals, is relatively low. As discussed in Chapter 2, geologic PM_{2.5} by itself is not a major threat to human health.

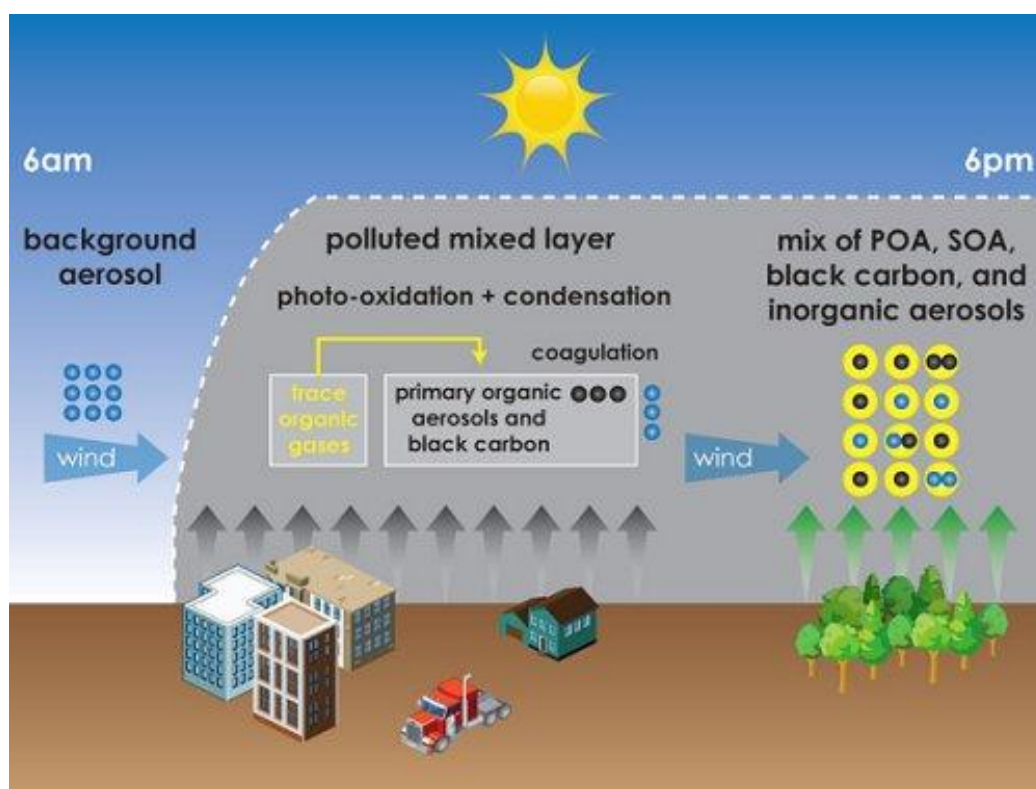
4.4.4 Organic Carbon Formation: Summary of Research Findings

Carbon-based aerosols contained within the PM_{2.5} fraction include organic carbon (OC), elemental carbon (EC), and carbonate minerals; however, it is the OC species that are particularly relevant to reducing the most negative health effects of PM_{2.5}. Chapter 2 of this plan discusses the chemical complexity and resultant capacity of organic carbon species to impact cardiovascular and respiratory functioning. This section provides a brief overview of organic carbon aerosol (OA) atmospheric

chemistry, a review of its implications for human exposure and health effects within the context of the District's Risk-based Strategy, and the primary sources of OA, including hydrocarbon combustion, residential wood combustion (RWC), motor vehicles operation, and meat charbroiling.

Organic Aerosol in the Environment. Organic aerosols (OA) and ammonium nitrate are the two largest contributors to PM_{2.5} mass in the Valley; however, the chemical complexity is very different between these two species. Many anthropogenic and biogenic sources of OA produce hundreds of primary organic aerosol (POA) species and hundreds of secondary organic aerosol species (SOA), which emerge from chemical aging and photolysis (photo-oxidation). The basic sources and processes that govern the dynamic relationship between POA and SOA are shown in Figure 4-9.

Figure 4-9 POA and SOA Formation Processes and Atmospheric Interactions²⁸

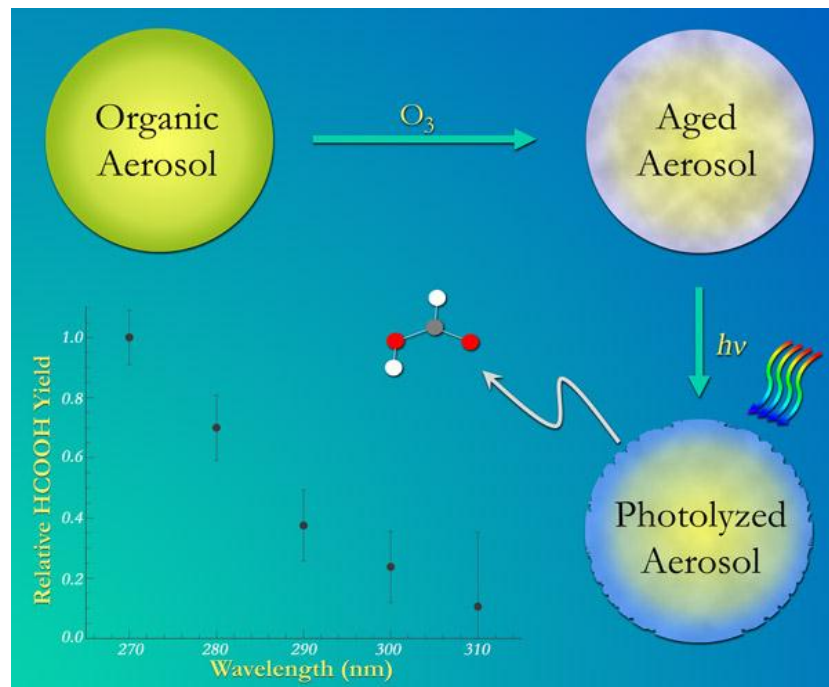


Primary Organic Aerosol Formation, Aging, and Photolysis. As opposed to SOAs, which appear in the atmosphere as a result of VOC chemical reactions, primary organic aerosols (POA) are released directly into the atmosphere by their sources. Most anthropogenic POA originates from the combustion of hydrocarbons (primarily coal, petroleum fuels, natural gas, and biomass) and the charbroiling of meat. Such particles are typically coated by an outer layer of fairly hydrophobic organic material. Over several hours or days, this layer is slowly oxidized by hydroxides (OH), ozone, and nitrogen oxides in a process known as *chemical aging*. As shown in Figure 4-10, these

²⁸ U.S. Department of Energy, Pacific Northwest National Laboratory: A Chemistry Tale of Two Carbons. (2012, August). Retrieved from <http://www.pnl.gov/science/highlights/highlight.asp?id=1193>

particles are subsequently subject to photolysis (chemical decomposition induced by light energy), which results in the creation of a breakdown product, HCOOH--formic acid, with a yield dependence on the reacting energy wavelength.

Figure 4-10 POA Aging and Photolysis²⁹



Volatility of POA and Impact on SOA Formation. Volatility is a key construct necessary for understanding the chemical transport and fate of OA. A traditional assumption in chemical transport models (CTMs) has been that POA is emitted to the atmosphere as non-volatile compounds and remains in a non-reactive state. In fact, a substantial fraction of POA is semi-volatile, including one of the most important categories from a public health perspective, polycyclic aromatic hydrocarbon (PAH). In this case, PAH species range from the totally condensed coronene to completely volatile naphthalene. As such, all OA can be categorized along a volatility continuum according to their partitioning coefficient, i.e. that mass fraction that is condensed in a given air volume under standard atmospheric conditions.³⁰ As POA species evolve through oxidation, their partitioning coefficient changes as well, leading to movement into the aerosol state or back to gas, depending on current chemical composition, relative dilution, and atmospheric conditions. These new findings have made it clear that POA, once volatilized, can and does contribute to subsequent SOA species.

VOCs and SOA Formation. Until the 1950s, scientists assumed that smoke dominated by carbon black was the primary source of organic aerosol into the environment. By

²⁹ University of California, Irvine, Department of Chemistry: Photochemistry of Organic Aerosols. (2012). Retrieved September 17, 2012 from <http://aerosol.chem.uci.edu/research/photochemistry.htm>

³⁰ Donahue, N.M., Robinson, A.L. & Pandis, S.N. (2009). Atmospheric Organic Particulate Matter: From Smoke to Secondary Organic Aerosol. *Atmospheric Environment* 43, 94-106.

1952, however, Hagen-Smit had discovered, while studying Los Angeles smog, that non-volatile SOA was being formed from the oxidation of VOCs generated by motor vehicles.³¹ Further laboratory studies conducted two decades later proved that oxidation of organic vapors can create products with low volatility that ultimately condense to form a fraction of tropospheric OA.³² Just as VOCs react in the presence of NO_x and sunlight to form ozone, VOC reactions with oxidants, i.e. ozone, OH, and NO₃, often lead to partitioning from gas to a particle phase forming secondary organic aerosols. Many biogenic and anthropogenic volatile compounds yield less-volatile products, in effect driving the process of SOA formation.³³

Despite exponential growth of global fossil fuel combustion since the late nineteenth century, SOAs resulting from the oxidation and condensation of VOCs emitted naturally from vegetation still exceeds production from anthropogenic sources.³⁴ In fact, Zimmerman et al. have estimated that global terpenes (the primary category of biogenic VOC) released by plants are approximately eight times the volume of total anthropogenic emissions of non-methane hydrocarbons.³⁵ Recent studies have quantified the contribution that VOC emissions from natural vegetation and crops is making to the formation of ozone and SOAs, with natural vegetation being the largest contributor.³⁶ This suggests that a substantial fraction of the haze found in Valley foothills is the result of SOA formed by the oxidation and photolysis of biogenic VOCs.

On an annual average basis, secondary organic aerosols derived from anthropogenic VOC emissions account for only 1% to 2% of the annual total PM_{2.5} concentrations throughout the Valley. ARB air quality modeling exercises conducted as part of the District's 2008 PM_{2.5} Plan attainment demonstration analysis using the CMAQ model showed that primary PM_{2.5} emissions are the main contributor to organic aerosols and SOA contribute to only a small extent. Furthermore, SOA are mostly formed during the summertime, when total PM_{2.5} concentrations are low, and are mainly derived from biogenic emission sources. As a result, annual average SOA derived from anthropogenic VOC emissions are a small part of the organic aerosol concentrations (3% to 5%).

Key POA Sources and Species of Concern in the Valley. Within the Valley and globally, biomass and fossil fuel combustion are the most important sources of POA.³⁷

³¹ Haagen-Smit, A.J. (1952). Chemistry and Physiology of Los Angeles Smog. *Analytical Chemistry* 44, 1342–1346.

³² McMurry, P.H. & Grosjean, D. (1985). Photochemical Formation of Organic Aerosols: Growth, Laws, and Mechanisms. *Atmospheric Environment* 19, 1445–1451.

³³ Donahue, N.M., Robinson, A.L., Stanier, C.O., & Pandis, S.N. (2006). Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics. *Environmental Science & Technology* 40(8), 2635–2643.

³⁴ Duce, R.A., Mohnen, V.A., Zimmerman, R., Grosjean, D. Grosjean, Cautreels, W., ... & Wallace G.T. (1983). Organic Material in the Global Troposphere, *Reviews of Geophysics*, 21(4), 921–952.

³⁵ Zimmerman, P.R., Chatfield, R.B., Fishman, J, Crutzen, P., & Hanst, P.L. (1978). Estimates of the Production of CO and H₂ from the Oxidation of Hydrocarbon Emissions from Vegetation. *Geophysical Research Letters*, 5(8), 679–682.

³⁶ Goldstein, A.H. & Karlik, J.F. (2011). Flux Measurements of Biogenic Precursors to Ozone and Particulate Matter in the Central Valley. Final Report, Contract No. 06-329. Prepared for the California Air Resources Board and the California Environmental Protection Agency. August 16, 2011. Available at <http://www.arb.ca.gov/research/apr/past/06-329.pdf>

³⁷ Lioussé, C., Penner, J.E., Chuang, C., Walton, J.J., Eddleman, H., & Cachier, H. (1996). A Global Three-Dimensional Model Study of Carbonaceous Aerosols. *Journal of Geophysical Research*, 101(D14), 19,411–19,432.

Unlike SOA, which tends to be more evenly distributed between source and non-source areas, POA is concentrated in areas near emissions sources, e.g. urban areas, freeways, railways, and shipping ports. In the case of fossil fuels, motor vehicles are the primary source of POA in urban areas. Rogge et al. conducted a series of speciation studies in the Los Angeles basin and found that motor vehicle exhaust contributed 21% of the POA in that area, characterized by a variety of cyclic and polycyclic compounds, with PAH being the most significant in terms mass contribution and potential public health impacts.³⁸ In addition, meat charbroiling was also found to contribute 21%, with residential wood combustion contributing up to 30% in winter.^{39,40} Finally, 16% was contributed from road dust, tires, and brake dust.⁴¹

The source contribution percentages from the Los Angeles research are comparable to POA source contributions in the Valley, with the exception of POA from wood smoke. In the case of residential wood combustion (RWC), a Fresno PM_{2.5} speciation study based on the use of levoglucosan as a tracer for wood smoke collected during the CRPAQS winter-intensive study in 2000–2001 concluded as follows: “Combined, the emissions from wood smoke, meat charbroiling, and motor vehicles appear to contribute 65–80% to measured OC, with wood smoke, on average, accounting for approximately 41% of OC and approximately 18% of PM_{2.5} mass.”⁴²

The contribution of OC as a fraction of the total PM_{2.5} mass has decreased over the last nine years as shown in Figure 4-11. This provides evidence that more stringent controls on POA from motor vehicles and RWC control measures put in place by ARB and the District over that time period have been effective in reducing emissions. The District’s stringent RWC controls were implemented just prior to the 2003–2004 winter season and were further strengthened prior to the 2008–2009 winter season. Overall, the total winter PM_{2.5} concentration has decreased since the 1999–2000 winter season (Figure 4-12). Reductions in potassium levels, a key indicator species for wood combustion, provide further evidence of reductions in winter season wood combustion (Figure 4-13).

³⁸ Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., & Simoneit, B.R.T. (1993). Sources of Fine Organic Aerosol, 2, Noncatalyst and Catalyst-Equipped Automobiles and Heavy-Duty Diesel Trucks. *Environmental Science & Technology*, 27(4), 636–651.

³⁹ Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. (1991) Sources of fine organic aerosol, 1, Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 25, 1112–1125.

⁴⁰ Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. (1998) Sources of fine organic aerosol, 9, Pine, oak and synthetic log combustion in residential fireplaces, *Environ. Sci. Technol.*, 32, 13–22.

⁴¹ Rogge, W. F., L. M. Hildemann, M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. (1993) Sources of fine organic aerosol, 3, Road dust, tire debris, and organometallic brake lining dust—Roads as sources and sinks, *Environ. Sci. Technol.*, 27, 1892–1904.

⁴² Gorin, C, J. Collett, and P. Herckes. (2006) Wood Smoke Contribution to Winter Aerosol in Fresno, CA. *Journal of the Air and Waste Management Association* 56: 1584-1590 (quote on p. 1584).

Figure 4-11 Valley Trend of OC Mass as a Fraction of PM2.5 Mass

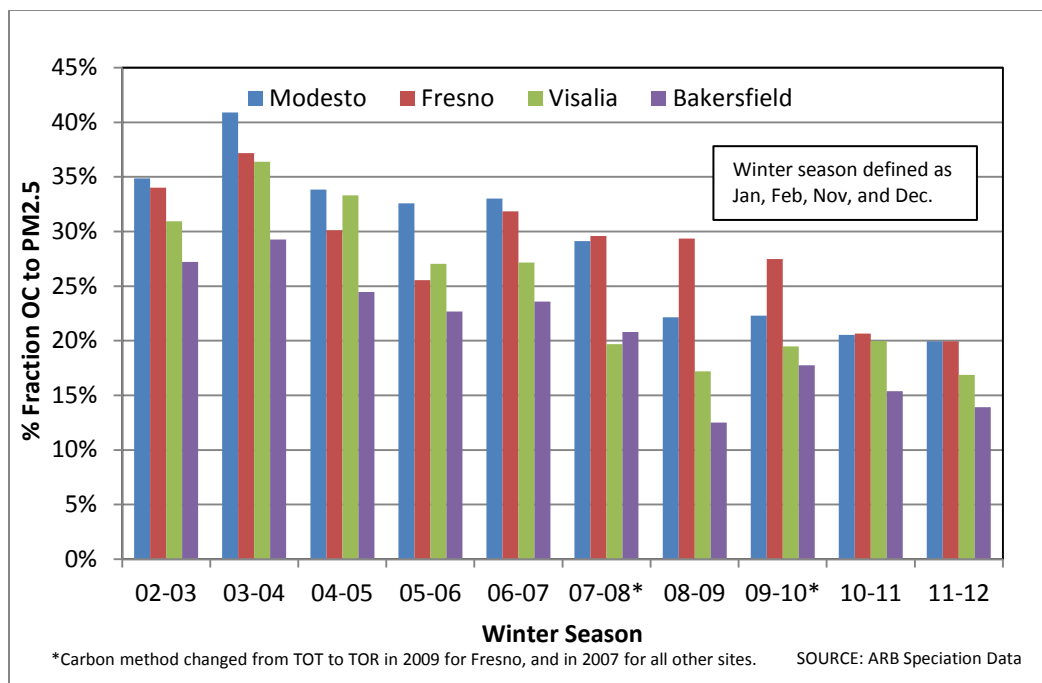


Figure 4-12 Winter Season Trend of Valley Average Daily PM2.5 Mass

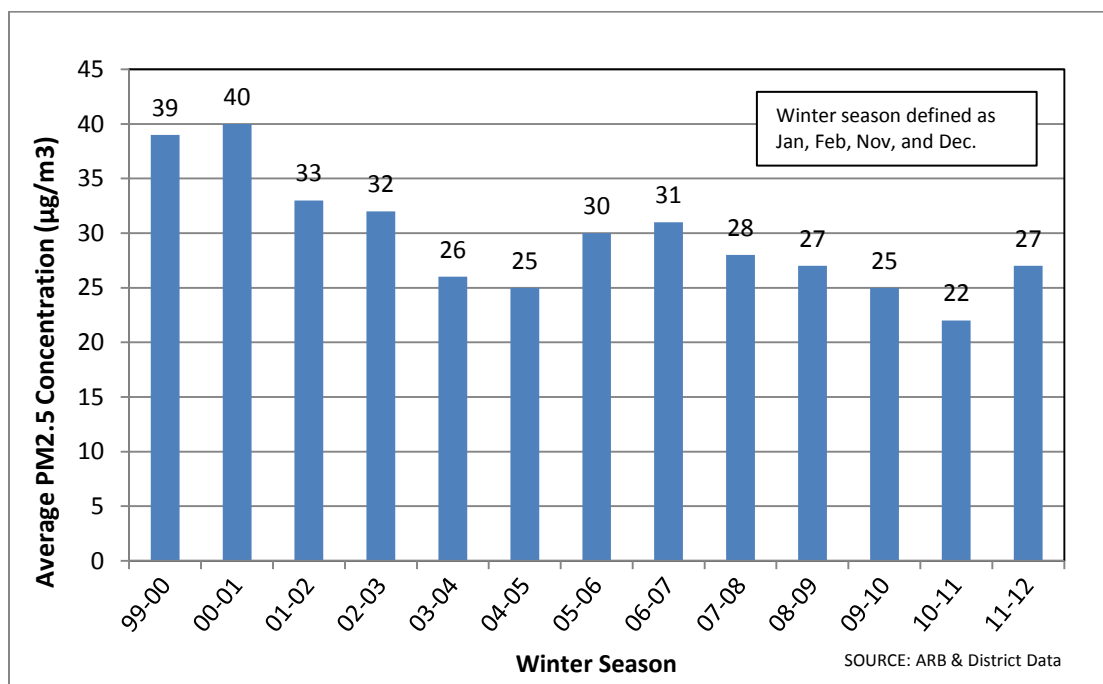
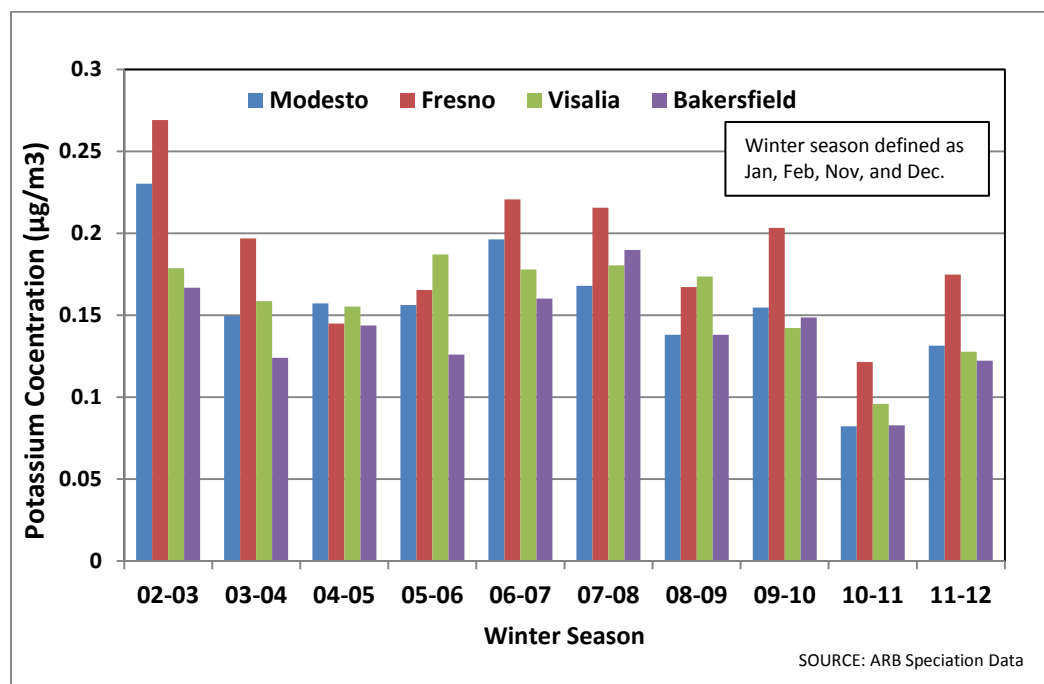


Figure 4-13 Average Winter Season Potassium Concentration in the San Joaquin Valley



4.4.5 Controlling Organic Aerosol under the Risk-Based Strategy

While reducing ammonium nitrate concentrations through NO_x reductions is important for attainment, strategies that reduce organic aerosols provide opportunities for not only addressing the standard, but also providing much greater relative health benefits.

Relevance to attainment. New controls on the creation of primary organic aerosol via combustion processes hold the promise of a win-win outcome—providing substantial reductions in health risk as well as making a significant reduction in PM_{2.5} mass. The attainment strategy discussed below, therefore, is centered on POA reduction based on scheduled emission controls by ARB on motor vehicles, especially heavy duty trucks, combined with further restrictions on RWC, new controls on commercial charbroiling, and incentives for zero-emission lawn care equipment.

Species toxicity of POA and SOA. As discussed on Chapter 2, both combustion POA, such as PAH, and downstream SOA species have been implicated in a wide range of health effects, including cardiovascular and respiratory inflammation and carcinogenesis. Unlike other aerosol precursors such as NO_x and VOCs that are currently being reduced through ongoing ozone control measures, reductions in POA (and the subsequent SOA that is produced by downstream oxidation and photolysis of POA) necessitates direct controls on primary emission sources. From a public health perspective, reductions in POA mass will result in a compounding of risk reduction that significantly exceeds the proportional contribution of those controls to PM_{2.5} mass reduction. This is because the chemical aging of SOA is responsible for some of the most toxic OA species such as quinones.

Particle size and deposition. POA generated by combustion as well as the SOA that emerges from the chemical processing of POA and VOC condensation are largely concentrated in the ultrafine (PM_{0.1}) and fine (PM_{2.5}) particle size categories. Inhalation of these particles results in deposition in the alveolar and thoracic zones of the lungs with potential impacts spanning the cardiovascular, immune, nervous, and respiratory systems. Individuals with pre-existing health conditions and those subject to high concentrations in urban areas or near high-volume roadways are especially vulnerable to inhalation of concentrated POA and SOA species that result from POA processing.

Proximity to ultrafine particles. POA is highly concentrated in freshly emitted ultrafine particles (UFP), or those particles less than 0.1 microns (PM_{0.1}). Because of their ability to pass through protective epithelium in the lung,⁴³ enter the brain via the olfactory bulb,⁴⁴ and enter the bloodstream in the alveolar region,⁴⁵ UFP-induced health effects are disproportionately high relative to their mass. In the case of POA, however, their ability to penetrate past the body's normal particle defense mechanisms is magnified by the relative toxicity of POA species, PAH in particular. In the case of combustion POA, its chemical toxicity has been shown to be magnified by the presence of metals, including iron, vanadium, and nickel.⁴⁶

Population intake fraction. POA emitted by internal combustion engines, residential wood combustion, and meat charbroiling is highly concentrated in urban areas where population density is greatest. Whether inhaled as freshly-emitted UFP or as larger fine particles, the net effect is a much larger intake fraction for these sources relative to comparable emission sources located in less populated, rural areas. Furthermore, heavy concentrations of vehicular POA from roadways located near urban neighborhoods may result in intake fractions that are an order of magnitude greater than outlying suburban areas within the same metro area. This elevated health risk from elevated POA exposure is especially relevant to health impacts from RWC, particularly given that UFP from wood combustion results in sustained high levels of indoor UFP during nocturnal inversions.⁴⁷ This high level of sustained exposure to PAH-laden UFP places the exposed individuals at risk to immune system sensitization and heightened vulnerability to subsequent exposure.⁴⁸

⁴³ Donaldson, K., V. Stone, A. Clouter, L. Renwick, and W. MacNee. (2001) Ultrafine Particles. *Occupational Environmental Medicine* 58: 211–216.

⁴⁴ Oberdorster, G., Z. Sharp, V. Atudorei, A. Elder, R. Gelein, and W. Kreyling. (2004) Translocation of Inhaled Ultrafine Particles to the Brain. *Inhalation Toxicology* 16:437–445.

⁴⁵ Delfino, R.J., S. Constantinos, and S. Malik. (2005) Potential Role of Ultrafine Particles in Associations between Airborne Particle Mass and Cardiovascular Health. *Environmental Health Perspectives* 113 (8): 934-946.

⁴⁶ Chen, L., and M. Lippmann (2009) Effects of Metals within Ambient Air Particulate Matter (PM) on Human Health. *Inhalation Toxicology* 21: 1–31.

⁴⁷ Thatcher, T., and T. Kirchstetter (2011) Assessing Near-Field Exposures from Distributed Residential Wood Smoke Combustion Sources. Report prepared for the California Air Resources Board. California State Polytechnic University; Lawrence Berkeley National Laboratory. September.

⁴⁸ Li, N., Harkema, J.R., Lewandowski, R.P., Wang, M., Bramble, L.A., Gookin, G.R., Ning, Z., Kleinman, M.T., Sioutas, C., and Nel, A.A. (2010) Ambient Ultrafine Particles Provide a Strong Adjuvant Effect in the Secondary Immune Response: Implication for Traffic-Related Asthma Flares. *American Journal of Physiology: Lung and Cell Molecular Physiology* 299 (3): L374-83.

4.4.6 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).⁴⁹ In December 2010, EPA revised its “Method 202” stationary source test method to measure condensable particulate matter.⁵⁰

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}.

4.5 PROJECTED FUTURE AIR QUALITY AND IDENTIFYING THE GOAL

[This section was prepared by the California Air Resources Board (ARB)]

Consistent with EPA guidelines, ARB modeled air quality to predict future PM_{2.5} concentrations at each monitoring site in the Valley. This modeling shows attainment of the 24-hour PM_{2.5} standard by 2019 based on implementation of the ongoing control program in all counties except Kern and Kings. In Kern and Kings Counties, additional focused emission reductions are needed to provide for attainment. Additional analyses confirmed that attainment is predicted throughout each county (i.e. in each modeled grid cell; see Appendix G - Appendix 6). This section summarizes these efforts and results. Additional information is available in Appendices F and G. Additional technical information can be found on ARB’s website:

<http://www.arb.ca.gov/planning/sip/sjvpm25/24hrsivpm25.htm>

4.5.1 Modeling Overview

The modeling analysis includes new emission reductions each year between now and 2019 from implementation of a combination of adopted ARB and District programs. As a result, most sites in the northern and central Valley are expected to attain before

⁴⁹ 40 CFR 51.1002(c)

⁵⁰ <http://www.epa.gov/ttn/emc/methods/method202.html>

2019. As required by EPA, the modeling replicates the base year 2007 meteorological conditions for each calendar day in the year 2019. The 2007 meteorological conditions included several periods of time especially conducive to the formation of PM_{2.5}. However, that modeling indicated that only two areas (Corcoran and Bakersfield) would not attain with the new emission reductions from adopted measures with implementation between now and 2019.

ARB staff then modeled a scenario with an enhanced wood-burning curtailment program, which would be designed to prevent wood burning on days that may lead up to a PM_{2.5} exceedance. The predicted design values for each site from this modeling scenario are shown in Table 4-1.

Table 4-1 2019 Modeled 24-hour PM_{2.5} Design Values with Enhanced Residential Wood-Burning Curtailment Program

Monitoring Site	Design Value (µg/m ³)
Bakersfield - California	35.7
Bakersfield - Planz	32.9
Corcoran - Patterson	32.1
Visalia - N. Church	29.4
Fresno - Hamilton	28.6
Fresno - First	30.5
Clovis	28.6
Merced	22.6
Modesto	24.7
Stockton	21.4

Additional emissions reductions from Rule 4901 bring Corcoran (Kings County) into attainment, and brings Bakersfield (Kern County) closer to attainment. As a result of implementation of the ongoing control program, coupled with the enhanced wood-burning curtailment measure, ammonium nitrate concentrations are predicted to decrease by over 45%, and combustion-related carbon concentrations by approximately 65%. Like the rest of the Valley, PM_{2.5} concentrations at the Bakersfield-California site are also projected to significantly decrease as emissions are further reduced. While adoption of a more stringent wood-burning curtailment program brings the Bakersfield-California site very near attainment, further reductions are still needed and will be provided through a measure to achieve additional emission reductions from commercial cooking operations. The final attainment demonstration for the Bakersfield-California design site is provided in Table 4-2 below:

Table 4-2 Attainment Demonstration—Bakersfield-California Design Value Site

2007 Design Value ($\mu\text{g}/\text{m}^3$)	2019 Design Value with Wood Burning Program Enhancement ($\mu\text{g}/\text{m}^3$)	2019 Final Design Value ($\mu\text{g}/\text{m}^3$)
66	35.7	35.4

Note: The benchmark for attainment is a design value that is equal to or less than $35.4 \mu\text{g}/\text{m}^3$

As noted above, the design value in column 2 of Table 4-2 reflects the implementation of ongoing control programs, as well as implementation of an enhanced residential wood burning curtailment program. The final design value reflects the combined impact of further reductions in commercial cooking, as well as a small increase in motor vehicle emissions resulting from updated vehicle activity data from Valley Metropolitan Planning Organizations (MPOs). Based on a modeling sensitivity run, implementation of further controls on commercial cooking in Kern County is expected to result in a $0.6 \mu\text{g}/\text{m}^3$ reduction in the baseline design value. The revised MPO activity data represents approximately 1% of Valley-wide NO_x emissions. Based on modeling sensitivity runs, this is estimated to result in a design value increase of $0.2 \mu\text{g}/\text{m}^3$. In aggregate, the modeling demonstrates that with the total plan control strategy, including adopted control measures as well as new control measures in Kings and Kern Counties, the modeled Bakersfield-California design value meets EPA's attainment target of less than or equal $35.4 \mu\text{g}/\text{m}^3$.

4.5.2 Measuring the Benefit of Control Measure Reductions

In order to determine where to focus the remaining emission reductions needed to bring Bakersfield-California into attainment, ARB staff conducted additional modeling sensitivity runs to assess the relative efficacy of further reductions of different PM_{2.5} precursors. The current 24-hour PM_{2.5} standard modeling demonstrates that on a relative basis the greatest benefits are achieved from reductions in sources of directly emitted PM_{2.5}, followed by NO_x, based on EPA's relative response factor procedure. ARB also conducted Kern County-specific model sensitivity runs for NO_x and PM_{2.5} to evaluate the specific benefits of emission reductions focused on the nonattainment sub-area. The Kern County sensitivity runs demonstrated that

- One ton per day of directly emitted PM_{2.5} reductions provides a $1.0 \mu\text{g}/\text{m}^3$ improvement in the Bakersfield-California design value; and
- One ton per day of NO_x reductions provides for a $0.12 \mu\text{g}/\text{m}^3$ improvement in the Bakersfield-California design value.

Therefore, to bring Bakersfield-California into attainment, this plan's control strategy focuses on opportunities to further reduce direct PM_{2.5} and NO_x emissions. As discussed above, ARB and the District are proposing two control measures with a potential emphasis on Kern County that would provide for attainment in 2019. In

addition, benefits from incentive programs will be used for contingency purposes. Incentive programs provide an effective means to accelerate fleet turnover and the conversion to cleaner engine technologies. Both ARB and the District are committed to pursuing the needed funding, as well as targeting the incentive programs to those areas and sources that will provide for expeditious attainment. The role of incentive funding also highlights the need for continued legislative reauthorization of incentive funding mechanisms such as the Carl Moyer program. See Chapter 9 for more information.

4.5.3 Modeling Requirements

Following EPA guidance and procedures, the attainment demonstration was conducted through a modeled attainment test. Photochemical modeling relates measured PM_{2.5} levels to modeled PM_{2.5} concentrations, using precursor emissions and meteorology in the region to simulate future PM_{2.5} levels based on changes in emissions. This modeling is used to identify the most expeditious attainment date, the relative benefits of controlling different PM_{2.5} precursor pollutants, and the magnitude of emission reductions needed from each pollutant.

This is the first time that modeling has been applied to demonstrate attainment for the 24-hour PM_{2.5} standard using revised procedures recently issued by EPA⁵¹. This requires modeling of the most severe air quality days, which relies on the proper characterization of episodic daily emissions. Developing day-specific emission estimates and forecasting what those emissions will be on episodic days in the future is a complex process that is further described in Appendix F of this plan. The following sections summarize the photochemical modeling performed and results.

Under the Clean Air Act, areas are presumed to have five years from the date of nonattainment designation to attain the standard, with a potential five-year attainment date extension. In the case of the 24-hour PM_{2.5} standard, this corresponds to attainment dates of 2014 and 2019. The benchmark for attainment is a design value that is equal to or less than 35.4 µg/m³.

4.5.4 Base and Future Years for Modeling

As required by EPA, ARB conducted a speciated modeled attainment test (SMAT). The SMAT is necessary because of the multiple constituents that form PM_{2.5} and their different relative responses to emission reductions. This test provides a method to link PM_{2.5} constituents with the appropriate emission sources. SMAT requires base and future years for the modeling. The base year is used for two purposes: to validate that the model is working properly and is able to replicate observed air quality and meteorological data, and as the starting year for projections of emissions and air quality predictions. For this effort, 2007 was chosen as the base year and 2019 as the attainment year for the modeling. The design values recorded in 2007 were some of the highest in recent years. In addition, analysis of the impacts of meteorology on PM_{2.5} levels in the Valley over the last ten years indicate that the 2007 meteorology

⁵¹ U.S. EPA. (2011, June 28). *Memorandum: Update to the 24 Hour PM_{2.5} NAAQS Modeled Attainment Test*. Air Quality Modeling Group, U.S. EPA, Research Triangle Park, North Carolina.

was one of the most conducive to PM_{2.5} formation. Thus, the selection of 2007 represents a health-protective approach to the attainment demonstration modeling.

4.5.5 Air Quality and Meteorological Models

The Mesoscale Meteorological Model version 5 (MM5)⁵² was used to generate the three-dimensional meteorological fields used for this effort. MM5 is a mesoscale, limited-area, non-hydrostatic numerical model developed by Penn State and the National Center for Atmospheric Research (NCAR). It uses a terrain-following, Lambert Conformal, sigma coordinate system. MM5 has been improved on an ongoing basis over the last two decades by contributions from a broad scientific community and has been maintained by NCAR along with necessary meteorological and geographical input data. Based on the complexity of terrain in northern and central California, the MM5 model represents an appropriate tool for resolving dynamics and thermodynamics using nesting capabilities. ARB has also been using the MM5 model over the last two decades, since it has been widely used and tested for various meteorological regimes over the world and has been supported by NCAR.

The Community Multiscale Air Quality (CMAQ) Modeling System was used for the air quality modeling. The CMAQ model, a state-of-the-science “one-atmosphere” modeling system developed by EPA, was designed for applications ranging from regulatory and policy analysis to understanding of the atmospheric chemistry and physics. It is a three-dimensional Eulerian modeling system that simulates ozone, particulate matter, toxic air pollutants, visibility, and acidic pollutant species throughout the troposphere⁵³. The CMAQ model has undergone peer review every few years and was found to be state-of-the-science⁵⁴. The CMAQ model is regularly updated to incorporate new mechanisms, algorithms, and data as they become available in the scientific literature⁵⁵. In addition, the CMAQ model is well documented in terms of its underlying scientific algorithms as well as guidance on operational uses.⁵⁶

⁵² Grell, G. A., Dundhia, J., and Stauffer, D. R., 1994, A description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5), National Center for Atmospheric Research, Boulder, CO, USA, NCAR/TN-398+STR, 122pp.

⁵³ UNC, 2010, Operational Guidance for the Community Multiscale Air Quality (CMAQ) Modeling System Version 4.7.1., available at http://www.cmascenter.org/help/model_docs/cmaq/4.7.1/CMAQ_4.7.1_OGD_28june10.pdf

⁵⁴ Aiyyer, A., Cohan, D., Russell, A., Stockwell, W., Tanrikulu, S., Vizuete, W., and Wilczak, J., 2007, Final Report: Third Peer Review of the CMAQ Model, submitted to the Community Modeling and Analysis System Center, University of North Carolina, Chapel Hill.

⁵⁵ For example, Foley, K.M., Roselle, S.J., Appel, K.W., Bhave, P.V., Pleim, J.E., Otte, T.L., Mathur, R., Sarwar, G., Young, J.O., Gilliam, R.C., Nolte, C.G., Kelly, J.T., Gilliland, A.B., and Bash, J.O., 2010, Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7, *Geoscientific Model Development*, 3, 205-226.

⁵⁶ For example:

Binkowski, F.S. and Roselle, S.J., 2003, Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component, 2. Model description, *Journal of Geophysical Research*, 108, D6, doi:10.1029/2001jd001409.

Byun, D.W. and Ching, J.K.S., 1999, Science Algorithms of the EPA Models-3 Community Multiscale Air Quality (CMAQ) Modeling System, EPA/600/R-99/030, available at <http://www.epa.gov/AMD/CMAQ/CMAQscienceDoc.html>

Byun, D.W. and Schere, K.L., 2006, Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system, *Applied Mechanics Review*, 59, 51-77.

4.5.6 Modeling Domains

Meteorological Modeling Domains: The MM5 meteorological modeling domain consists of three nested grids of 36 km, 12 km, and 4 km with uniform, horizontal-grid spacing. The coarse 36 km grid (D01) provides synoptic-scale conditions to the 12 km grid (D02), which in turn provides the same to the 4 km grid (D03). The two coarse grids were run simultaneously, and the D03 grid was run independently using the output of its coarser, parent D02 grid as input. The D03 grid is intended to resolve the fine details of atmospheric motion and is used to feed the air quality modeling simulations. The vertical layer structure consists of 30 layers.

Air Quality Modeling Domains: The principle determinants of the extent of the air quality modeling domain are the nature of the PM_{2.5} problem and the scale of the emissions that impact the nonattainment area. The modeling domain used for this plan is shown in Figure 4-14. This is the same modeling domain used for the previous annual PM_{2.5} plan, which has been approved by the EPA.⁵⁷ This domain provides the high-resolution modeling results that are used in SMAT. This domain fully encompasses the Valley 24-hour PM_{2.5} non-attainment area. Consistent with EPA guidance⁵⁸, the modeling also includes a larger outer domain to provide for boundary conditions and initial inputs to the nonattainment area domain. The coarse domain extends from the Pacific Ocean in the west to Eastern Nevada in the east and runs from the U.S.-Mexico border in the south to the California-Oregon border in the north.

Carlton, A.G., Bhave, P., Napelenok, S.L., Edney, E.O., Sarwar, G., Pinder, R.W., Pouliot, G.A., and Houyoux, M., 2010, Model representation of secondary organic aerosol in CMAQv4.7, *Environmental Science Technology*, 44, 8553-8560.

Foley, K.M., Roselle, S.J., Appel, K.W., Bhave, P.V., Pleim, J.E., Otte, T.L., Mathur, R., Sarwar, G., Young, J.O., Gilliam, R.C., Nolte, C.G., Kelly, J.T., Gilliland, A.B., and Bash, J.O., 2010, Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling system version 4.7, *Geoscientific Model Development*, 3, 205-226.

Kelly, J.T., Bhave, P., Nolte, C.G., Shankar, U., and Foley, K.M., 2010a, Simulating emission and chemical evolution of coarse sea-salt particles in the Community Multiscale Air Quality (CMAQ) model, *Geoscientific Model Development*, 3, 257-273.

UNC, 2010, Operational Guidance for the Community Multiscale Air Quality (CMAQ) Modeling System Version 4.7.1., available at http://www.cmascenter.org/help/model_docs/cmaq/4.7.1/CMAQ_4.7.1_OGD_28june10.pdf

⁵⁷ Approval and Promulgation of Implementation Plans; California; 2008 San Joaquin Valley PM_{2.5} Plan and 2007 State Strategy, 76 Fed. Reg. 134, pp. 41337–41363. (2011, July 13). (to be codified at 40 CFR Part 52)

AND Approval and Promulgation of Implementation Plans; California; 2008 San Joaquin Valley PM_{2.5} Plan and 2007 State Strategy; Final Rule. 76 Fed. Reg. 217, pp. 49896–49926. (2011, November 9). (to be codified at 40 CFR Part 52)

⁵⁸ U.S. EPA, 2007, Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM_{2.5}, and Regional Haze, EPA-454/B07-002.

Figure 4-14 Air Quality Modeling Domain

For the coarse portions of nested regional grids, EPA guidance suggests a grid cell size of 12 km if feasible, but not larger than 36 km. For the fine scale portions of nested regional grids, it is desirable to use grid cells about 4 km.⁵⁹ The defined modeling domains for the 24-hour PM_{2.5} plan are consistent with the guidance.

EPA guidance does not require a minimum number of vertical layers for an attainment demonstration, although typical applications of “one- atmosphere” models (with the model top at 100 mb) employ 12 to 21 vertical layers. For the present plan, 15 vertical layers are used in the CMAQ model, extending from the surface to 100 mb, consistent with the number of vertical layers used for the previous annual PM_{2.5} plan. The majority of the layers are in the planetary boundary layer.

Model Performance Evaluation: As recommended by EPA, the model performance evaluation consists of a number of metrics to evaluate performance for PM_{2.5} mass as well as PM_{2.5} components. These metrics include mean fractional bias (MFB), mean fractional error (MFE), normalized mean bias (NMB), and normalized mean error (NME). In addition, the evaluation includes other statistics such as mean bias, mean error, and the correlation coefficient whenever they provide meaningful information. Various forms of graphics are created to visually examine comparison of the model predictions to observations. Model performance goals are based on EPA guidance as well as performance recommendations proposed in peer-reviewed journal articles.⁶⁰

Emission Inventory Preparation and Gridding: The process of preparing base-year emission inventories and future-year emission forecasts is described in appendices to

⁵⁹ *Ibid.*

⁶⁰ For example, Boylan, J.W. and Russell, A.G., 2006, PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models, *Atmospheric Environment*, 40, 4946-4959. AND U.S. EPA, 2007, *Guidance on the Use of Models and Other Analyses for Demonstrating Attainment of Air Quality Goals for Ozone, PM_{2.5}, and Regional Haze*, EPA-454/B07-002.

this plan. The gridding process, in which county-level emissions are allocated spatially and temporally, as well as chemically- and size-resolved, is described in the Modeling Protocol prepared for this effort (Appendix F). Development of the base-year emission inventories and the future-year forecasts involved a comprehensive review of the methodologies used to estimate key emission categories. As noted earlier, modeling of the 24-hour PM_{2.5} standard requires detailed information on the timing and locations of emission sources on the most severe air quality days. This poses a unique challenge to translate regional, annual emission estimates into the temporal and spatial resolution needed for 24-hour modeling. Special attention was paid to determining the sources and pollutants that had the largest effect on PM_{2.5} concentrations in the portions of the Valley with the highest concentrations, and focusing emissions improvement efforts on these areas. An iterative process was used as a means to refine the spatial, temporal, and chemical characteristics of modeling emission inputs to better reflect observed conditions expected at a local, 24-hour scale. Model-simulated concentrations were compared with chemical species present in the ambient monitoring data, maps of emission sources known to surround the monitoring stations, and temporal trends in the monitoring data. This led to updates in the spatial, temporal, and chemical allocation of the gridded emissions used in the modeling.

Attainment Demonstration Modeling Results: The SMAT process produces future year design values by monitoring site for comparison to the applicable ambient air quality standard. The first step in the future year modeling is to model the 2019 forecasted emissions. This modeling run includes all adopted regulations plus an enhanced wood burning curtailment program along with estimated population and economic growth. The modeled, future year projected design values are presented in Table 4-1.

Precursor Sensitivity Modeling Runs: Ambient PM_{2.5} is comprised of many different constituents and as a result, there are multiple precursor pollutants that lead to PM_{2.5} formation (directly emitted PM_{2.5}, NO_x, SO_x, VOCs, and ammonia). EPA's PM_{2.5} implementation rule specifies that a precursor is considered "significant" for control strategy development purposes when a significant reduction in the emissions of that precursor pollutant leads to a significant decrease in PM_{2.5} concentrations. Such pollutants are known as *PM_{2.5} attainment plan precursors*.⁶¹ The EPA's implementation rule also establishes a presumption that PM_{2.5}, NO_x, and SO_x are attainment plan precursors, while VOCs and ammonia are not. For the annual PM_{2.5} plan, PM_{2.5}, NO_x, and SO_x were identified and approved as the only attainment plan precursors by EPA. Results of the annual PM_{2.5} modeling showed that of these three pollutants, reductions in directly emitted PM_{2.5} was the most effective—reducing one ton of directly emitted PM_{2.5} was approximately nine times more effective than reducing one ton of NO_x. The evaluation of the 24-hour PM_{2.5} attainment plan precursor focus is on the two winter quarters when peak PM_{2.5} concentrations occur in the Valley. Because annual average concentrations are heavily influenced by winter time levels, results for the 24-hour PM_{2.5} standard are expected to be similar to those for the annual standard.

⁶¹ Clean Air Fine Particle Implementation Rule; Final Rule. 72 Fed. Reg. 79, pp. 20586–20667. (2007, April 25). (to be codified at 40 CFR Part 51)

In order to identify the PM_{2.5} attainment plan precursors and better understand the effectiveness of emission reductions for primary PM_{2.5} and precursors, the model is typically exercised with varying combinations of precursor reductions from anthropogenic sources. The results of these runs are plotted on isopleth diagrams, also referred to as carrying capacity diagrams. These carrying capacity diagrams shows the level of emissions that the atmosphere can “carry” and still demonstrate attainment. These diagrams help show what combinations of precursor emissions reductions (including which precursors are most effective to reduce as well as the magnitude of reductions needed) might lead to attainment, informing the development of a corresponding control strategy. The carrying capacity diagrams presented in Figures 4-15 through 4-24 show that NO_x and directly-emitted PM_{2.5} are the most effective precursors to reduce to improve 24-hour PM_{2.5} design values.

Assessment of Grid Cell Concentrations: Modeling must demonstrate that the standard is attained in every modeling grid cell. In the Valley, the extensive monitoring network captures population exposure. Demonstration of attainment at these monitors, combined with the modeling grid cell evaluation will ensure that all regions in the Valley are in compliance with the 24-hour PM_{2.5} standard. EPA recommends combining interpolated spatial fields and modeled gradients to generate the gradient adjusted spatial fields for PM_{2.5}. Future year estimates for all grid cells are created by applying the grid specific relative reduction factors to the gradient adjusted spatial fields. This analysis confirms that all areas of the Valley will reach attainment with this plan’s control strategy.

Figure 4-15 Bakersfield-California Carrying Capacity Diagrams

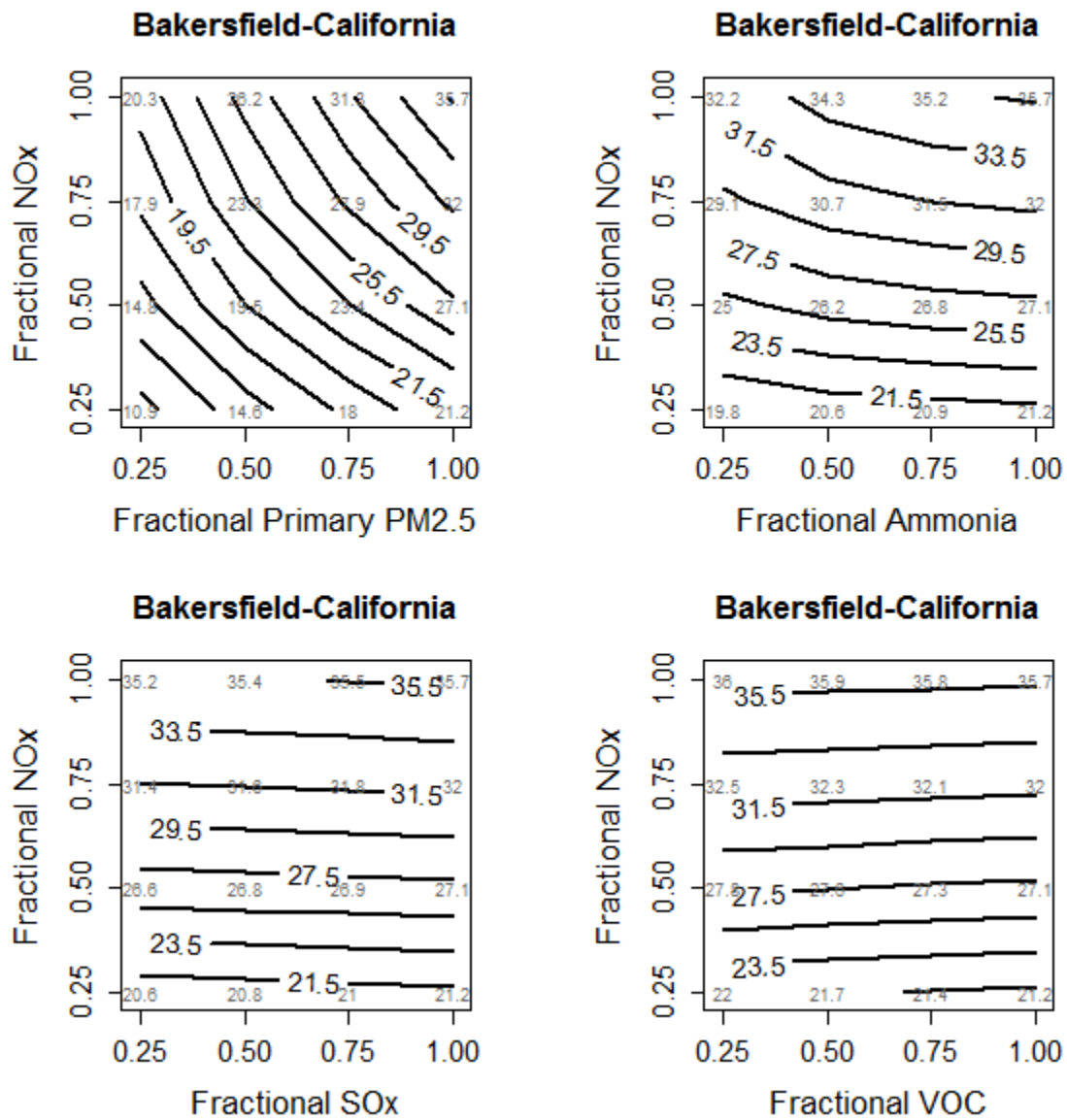


Figure 4-16 Bakersfield-Planz Carrying Capacity Diagrams

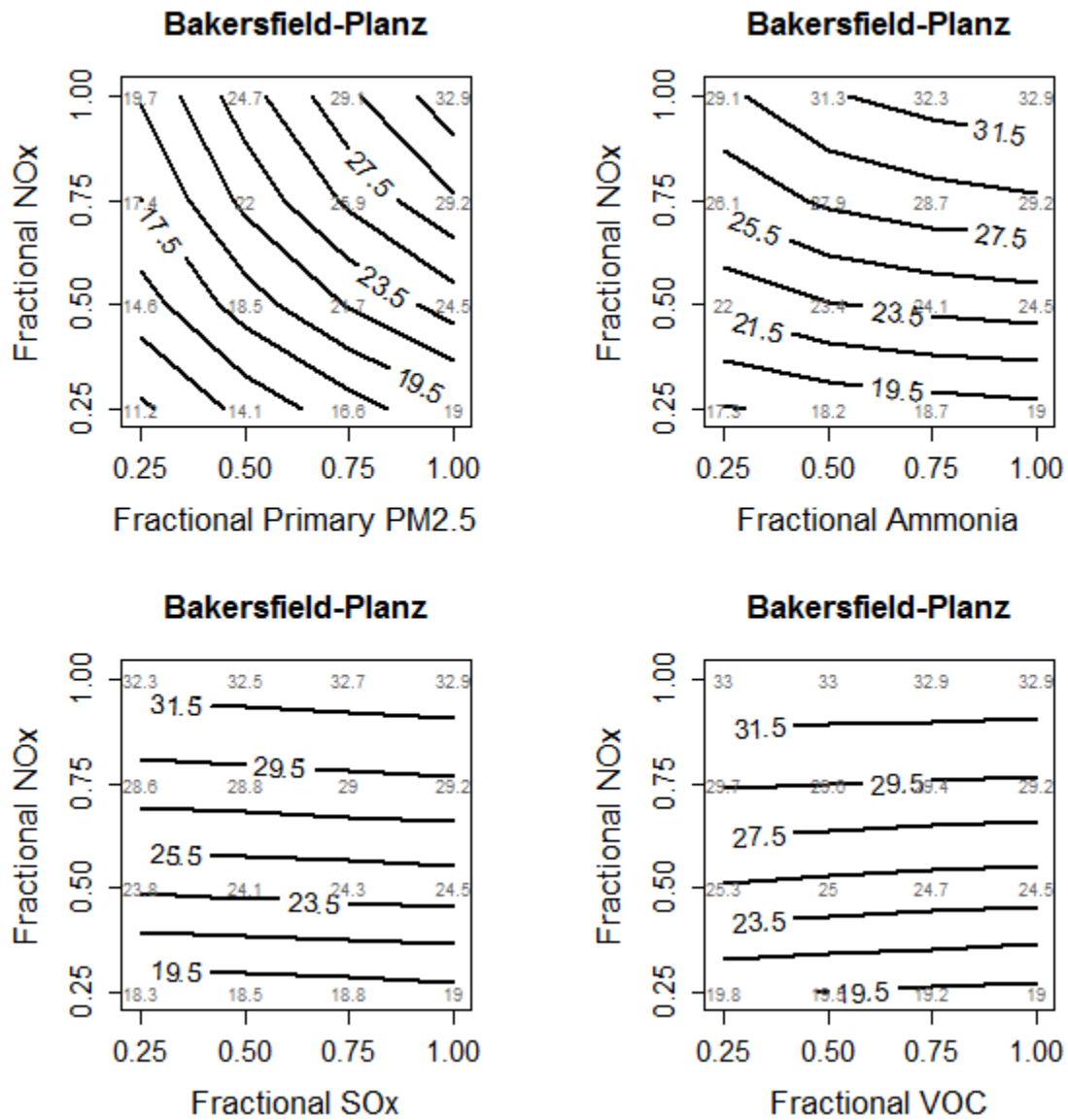


Figure 4-17 Fresno-1st Carrying Capacity Diagrams

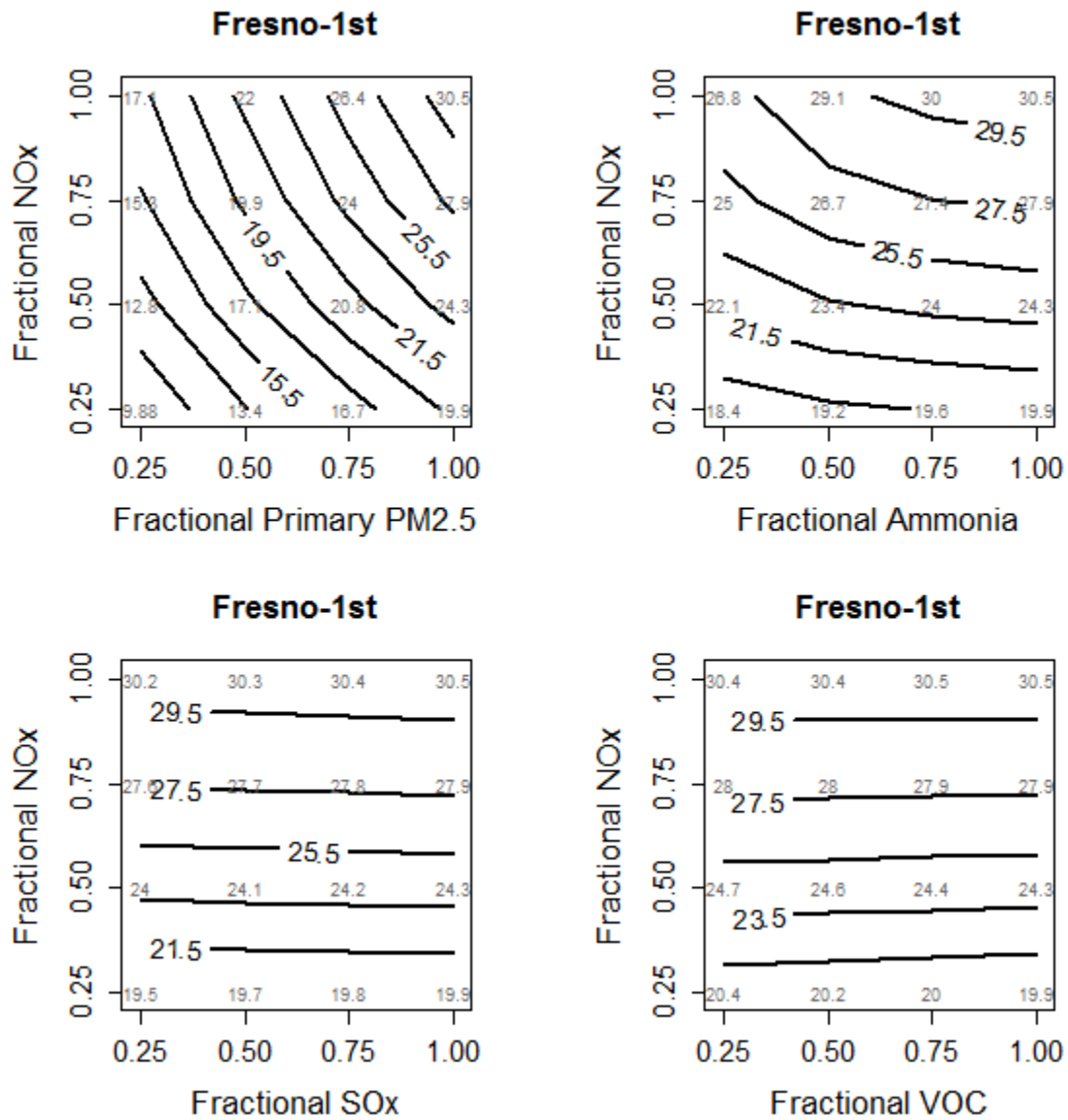


Figure 4-18 Fresno-HW Carrying Capacity Diagrams

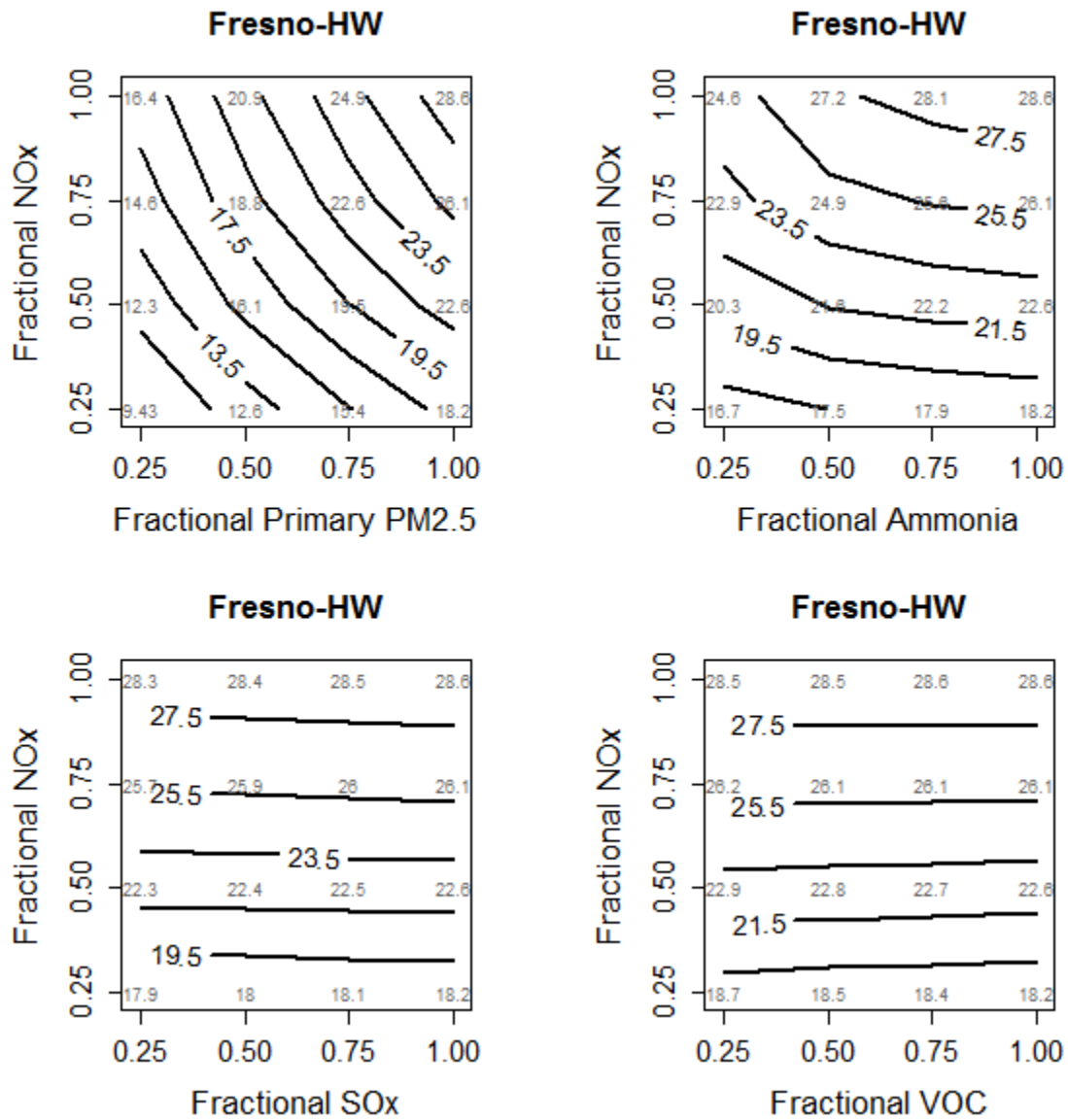


Figure 4-19 Clovis Carrying Capacity Diagrams

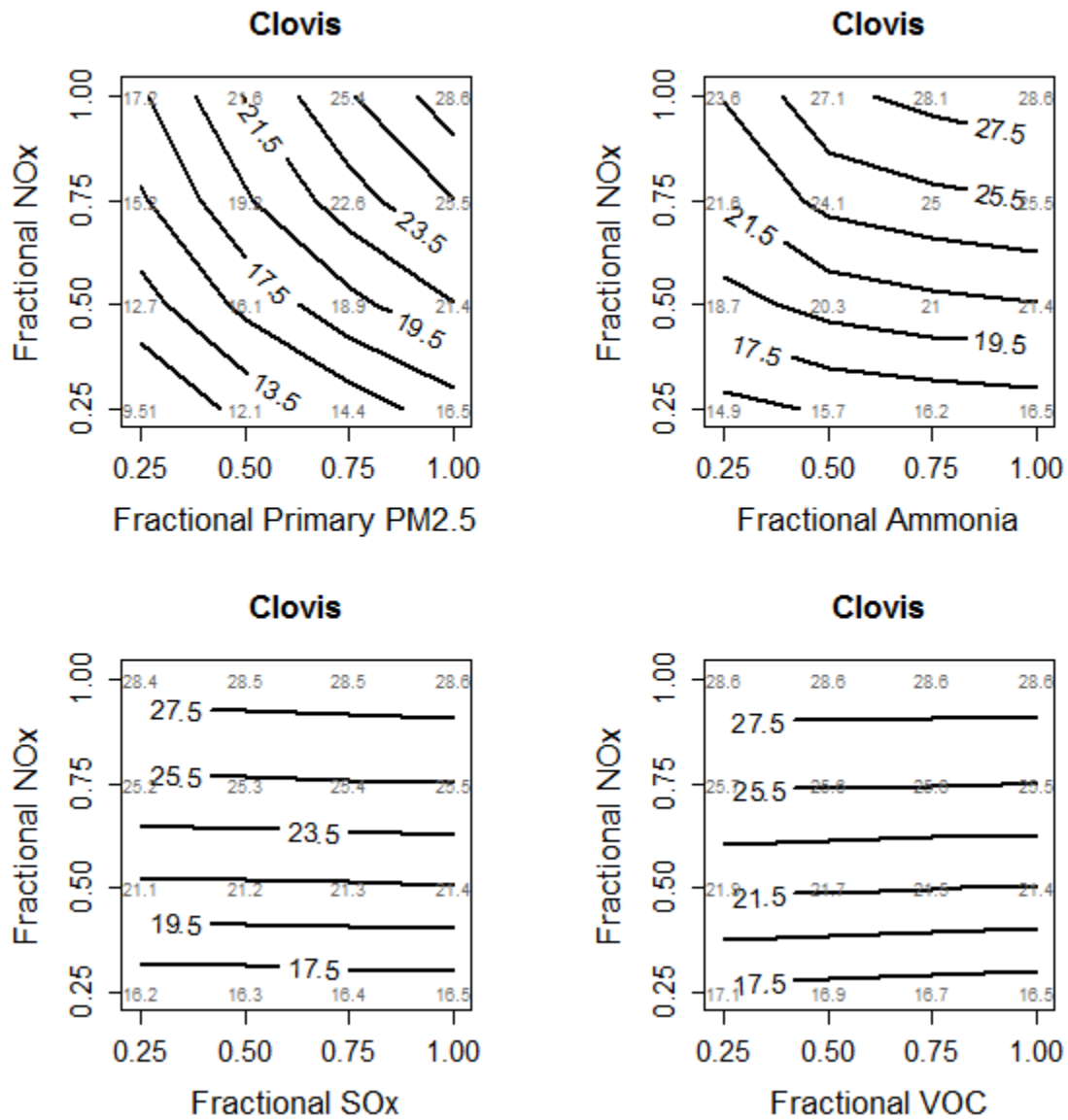


Figure 4-20 Modesto Carrying Capacity Diagrams

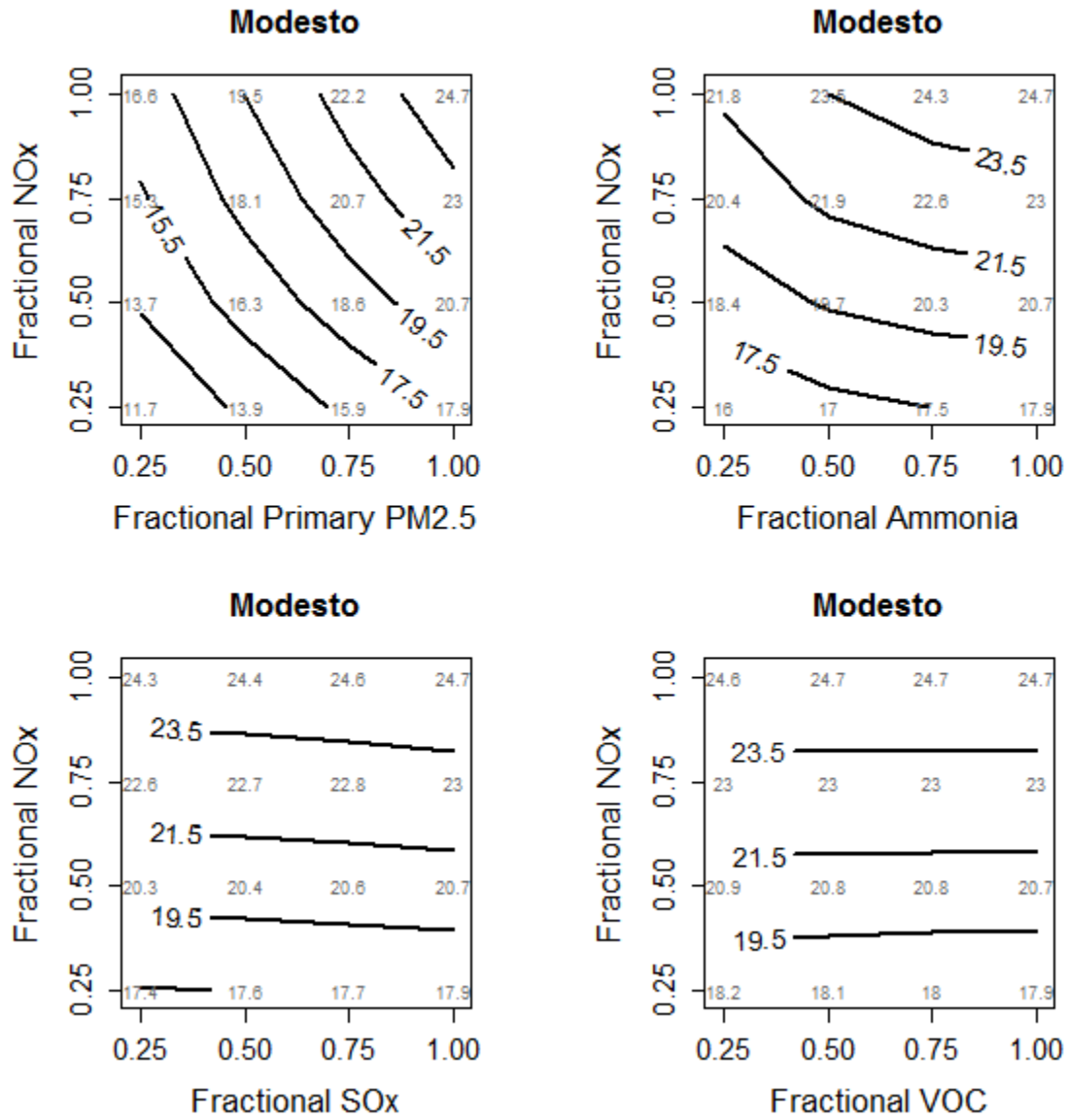


Figure 4-21 Merced Carrying Capacity Diagrams

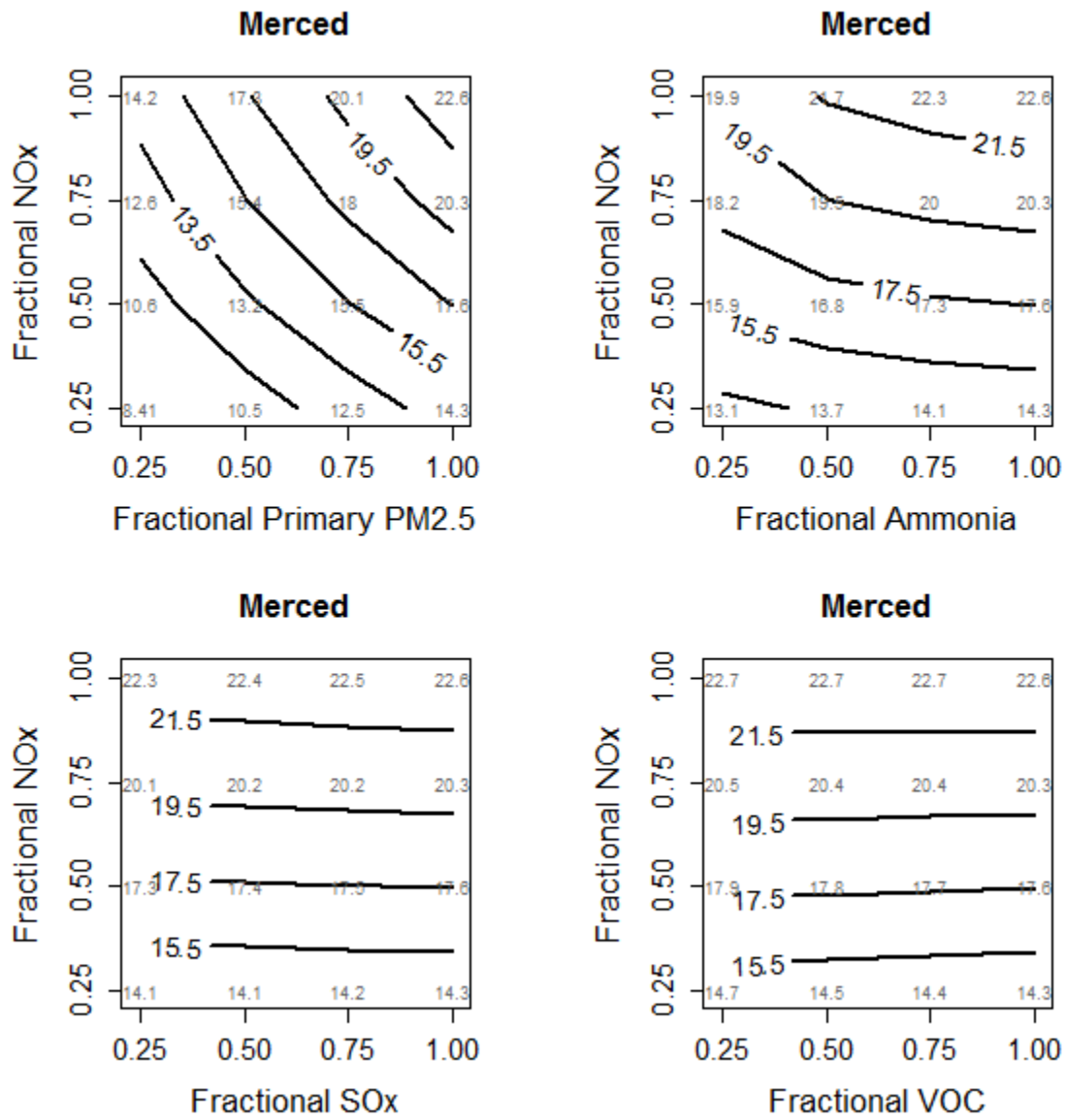


Figure 4-22 Stockton Carrying Capacity Diagrams

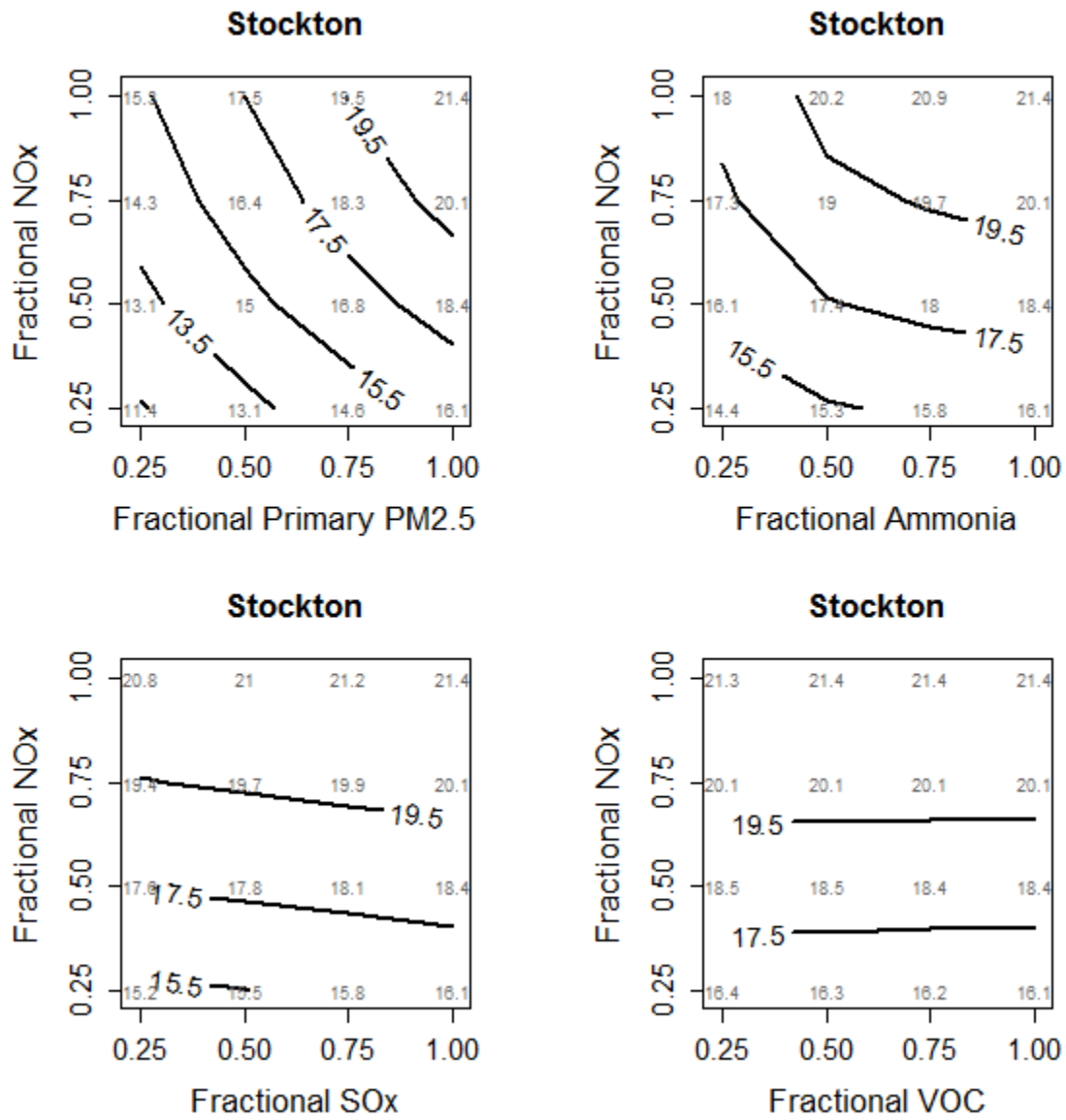


Figure 4-23 Visalia Carrying Capacity Diagrams

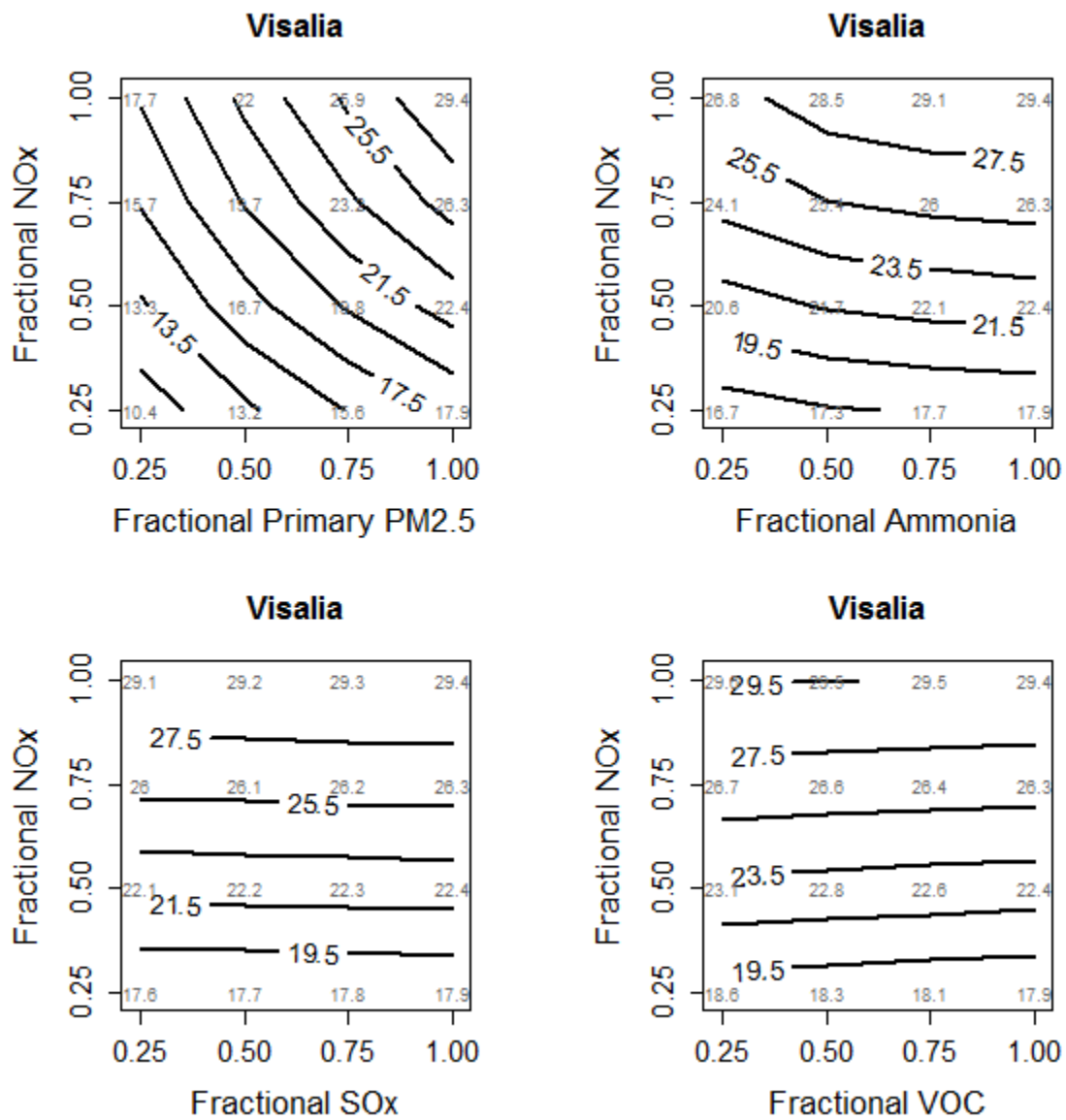


Figure 4-24 Corcoran Carrying Capacity Diagrams

