# Chapter 4

Scientific Foundation and Ozone Modeling Results

2016 PLAN FOR THE 2008 8-HOUR OZONE STANDARD

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### Chapter 4: Scientific Foundation and Ozone Modeling Results

As a pollutant, ozone has been studied and measured in the San Joaquin Valley air basin (Valley) and across the nation for decades. The San Joaquin Valley Air Pollution Control District (District), California Air Resources Board (ARB), U.S. Environmental Protection Agency (EPA), and private partners have invested millions of dollars into the San Joaquin Valley-wide Air Pollution Study Agency (Study Agency) field studies, analyses, and modeling to build a strong scientific foundation for the District's ozone attainment plans. This *2016 Plan for the 2008 8-hour Ozone Standard (2016 Ozone Plan*) evaluates and builds upon existing scientific information to extend the District's ozone air pollution control strategy to attain the increasingly stringent National Ambient Air Quality Standards (NAAQS).

The Study Agency was established in 1985 under a joint-powers agreement between local counties and includes input from air districts, ARB, EPA, public and private industry representatives, and other governmental agencies to create a cooperative and unbiased research program. The Study Agency has developed and funded extensive ozone research specific to the Valley. The Study Agency's main purpose is to further the scientific understanding of regional air quality issues to assist regulatory agencies in attainment strategy and policy development.

This chapter summarizes the contributions to the Valley's 8-hour ozone levels, ozone research, trends in the Valley's 8-hour ozone concentrations, and projections of 8-hour ozone that show attainment of the 2008 standard by 2031. For more information, see Appendix A (Modeling Attainment Demonstration), Appendix B (Modeling Emissions Inventory), and Appendix I (Photochemical Modeling Protocol).

#### 4.1 THE NATURE AND FORMATION OF OZONE

Ozone (O<sub>3</sub>), a molecule of three oxygen atoms, is a product of atmospheric reactions involving volatile organic compounds (VOCs), oxides of nitrogen (NOx), the hydroxyl radical (HO), other radicals, and sunlight. As such, ozone is not emitted directly but, rather, is formed secondarily. Ozone is found in two regions of the Earth's atmosphere: the upper regions of the atmosphere (the stratosphere), where the ozone layer is effective in absorbing the sun's ultraviolet radiation; and ground-level (or tropospheric) ozone. At high concentrations, this ground-level ozone can be harmful to public health and can degrade the environment.

The Valley's ozone levels are a function of geography and natural environment (including meteorology), the production and presence of ozone precursors (e.g. NOx and VOCs), the atmospheric chemistry that controls the ozone life cycle, and the import of non-Valley emissions into the Valley. All of these factors, except geography, vary throughout the year, but during the summer months they combine to account for the Valley's highest annual ozone concentrations.

#### 4.1.1 The Ozone Life Cycle

In a balanced atmosphere, where precursor VOC and NOx emissions are relatively low, ground-level ozone is created and destroyed at the same rate. This regulates diurnal ozone levels and keeps Ozone ( $O_3$ ) at an acceptable background concentration. This ozone life cycle occurs continuously while sunlight is present, but ends at nightfall.

The following reactions summarize the equilibrium ozone life cycle process (see Figure 4-1):

- 1. NO<sub>2</sub> + photon energy from the sun  $\rightarrow$  NO + O
- 2.  $O + O_2 \rightarrow O_3$  (ozone formed)
- 3.  $O_3 + NO \rightarrow NO_2 + O_2$  (ozone breaking down) The  $O_3$  molecule is a very strong oxidizing agent. It is very willing to give away the additional oxygen atom to another molecule and become the more stable  $O_2$ .



Figure 4-1 Ozone Life Cycle

Unfortunately, ideal equilibrium in the Valley is rarely reached as the ozone life cycle becomes

unbalanced in the presence of elevated VOC and  $NO_x$  emissions. Biogenic VOC emissions are especially high during the Valley's summer ozone season. The same photon energy that reacts with  $NO_2$  in the balanced reaction set also reacts with ozone in the presence of water (humidity) to form hydroxyl radicals (HO) that quickly oxidize VOCs to produce peroxy radicals (RO<sub>2</sub>), which in turn react quickly with dissociated NO to form NO2, bypassing the ozone consumption or breakdown process.

The following set of reactions summarizes this alternate chain of events (see Figure 4-2):

- 1. NO<sub>2</sub> + photon energy from the sun  $\rightarrow$  NO + O
- 2.  $O + O_2 \rightarrow O_3$  (ozone formed)
- 3.  $RO_2 + NO \rightarrow RO + NO_2$  (ozone does NOT break down)





The multi-step breakdown of VOCs (mostly naturally occurring or biogenic) regenerates radicals, which work as the fuel, or catalyst, consuming the dissociated NO and driving the ozone production cycle and bypassing the breakdown of  $O_3$ .

This catalytic process is cut off at night, as this removes the photon energy input. Therefore, once the sun sets, ozone levels begin to fall. Figure 4-3 is an example of the diurnal photochemical ozone formation process under unbalanced conditions and shows the concentration of NO, NO<sub>2</sub>, and ozone throughout the hours of a common summer day. The day begins with low ambient levels of NOx (NO and NO<sub>2</sub>) and ozone. As the morning commute begins, motor vehicle traffic directly emits NOx pollutants create a rise in NOx concentration. The influx of NOx emissions between hours four and seven provide the initial startup of the rapid, unchecked photochemical production of ozone beginning at hour five and increasing into the late afternoon. As ozone production increases, NO and NO<sub>2</sub> are quickly consumed by the VOC reactions and these concentrations quickly approach zero. In the early evening, with waning sunlight and decreasing photon energy, ozone production ceases and its concentration rapidly diminishes as NO and NO<sub>2</sub> levels return to normal ambient levels.



Figure 4 - 3 Photochemical Process for a Valley Summer Ozone Day\*

\* Diurnal Photochemical Process (Fresno-Drummond, July 27, 2014)

While biogenic VOC emissions are prevalent throughout the Valley, additional VOC emissions from the combustion of fossil fuels combined with NOx emissions from the same mobile and stationary sources found in metropolitan areas helps give rise to the highest concentrations of ground-level ozone in the Valley.

#### 4.1.2 Relative Roles of VOCs and NOx in Ozone Formation

Both VOC and NOx emissions contribute to the formation of ozone. Under high-NOx and low-VOC conditions, the reaction is more sensitive to the amount of VOCs and is considered a *NOx-rich regime*. Alternatively, when the atmosphere is under high-VOC and low-NOx conditions, the formation of ozone is influenced by a *NOx-limited regime*, which means ozone formation is sensitive to changes in NOx concentration.

Determination of an ozone formation regime requires an understanding of chemical kinetics and the ability to model the spatial and temporal intricacies of the interactions between reactants and products. To date, grid-based photochemical models remain the best available tool to determine relative precursor limitations. Modeling shows that the Valley is a *NOx-limited regime*, especially in projections of future years. For this reason, the District focuses its emissions reductions efforts on NOx reductions, as they are most effective in reducing Valley ozone concentrations.

As proven through extensive modeling and successful reduced ambient ozone levels based on NOx-centric strategies, developing VOC reduction strategies based on a *NOxrich* regime would not be effective in the Valley. While understanding VOC reactivity is an important component of ozone plan analysis, the Valley's ozone formation has transitioned to a NOx-limited regime; therefore, NOx reductions are the most effective way to reduce Valley ozone concentrations.

#### 4.1.3 The Propensities of Different VOCs to Form Ozone

The potential of VOCs to form ozone is specific to the type of VOC. VOCs include many different compounds, each with different properties that contribute differently to ozone formation. These differences in ozone forming potential, or *propensities*, of VOCs are quantified as ozone *reactivities*.

VOC *reactivity scales* have been developed to measure the ozone forming potential of individual VOCs,<sup>1,2,3</sup> of which the most frequently used is the *maximum incremental reactivity* (MIR) scale.<sup>4,5</sup> Incremental reactivity is defined as the amount of additional ozone formation, under optimal NOx conditions, resulting from an addition of a small amount of the given VOC to the system in which ozone is formed, divided by the amount of VOC added. While understanding VOC reactivity is an important component of ozone plan analysis, research and modeling have shown that the Valley has transitioned to a NOx-limited regime; therefore, NOx reductions are the most effective strategy for reducing Valley ozone concentrations.

#### 4.1.4 Trans-Boundary Emissions and Policy-Relevant Background Ozone

As ozone research continues, evidence is mounting that ozone formation is not only affected by precursor emissions originating within the Valley, but is in part affected by trans-boundary emissions; in other words, pollutants are migrating from sources outside the Valley and settling within the Valley. This issue has given rise to the term *United* 

<sup>&</sup>lt;sup>1</sup> Bowman, F. M. & Seinfeld, J. H. (1994). Ozone Productivity of Atmospheric Organics. *Journal of Geophysical Research, 99*, 5309–5324.

<sup>&</sup>lt;sup>2</sup> Bowman, F. M. & Seinfeld, J. H. (1994). Fundamental Basis of Incremental Reactivities of Organics in Ozone Formation in VOC/NOx Mixtures. *Atmospheric Environment, 28*, 3359–3368.

<sup>&</sup>lt;sup>3</sup> Carter, W.P.L (1994). Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air* & *Waste Management Association, 44*, 881–899.

<sup>&</sup>lt;sup>4</sup> Carter, W.P.L (1994). Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air* & Waste Management Association, 44, 881–899.

<sup>&</sup>lt;sup>5</sup> Carter, W.P.L., Pierce, J.A., Luo, D., & Malkina, I.L. (1995). Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmospheric Environment*, *29*, 2499–2511.

*States Background* (USB) ozone, previously referred to as *policy relevant background*, which is defined as the surface ozone concentration that would be present over the U.S. in the absence of North American anthropogenic (human caused) emissions. USB ozone includes emissions from both biogenic (plant life) and trans-boundary sources.

The 1990 amendments to the Clean Air Act (CAA) recognize the potential threat of trans-boundary ozone flow to attainment. While not absolved from implementing reasonably available controls to reduce emission from sources under their control, CAA §179B (International Border Areas), mandates that state, local, and regional authorities will not be penalized or otherwise burdened and held responsible for the impact of pollution emissions from foreign sources: <sup>6</sup>

Notwithstanding any other provision of law, any State that establishes to the satisfaction of the Administrator that, with respect to an ozone nonattainment area in such State, such State would have attained the national ambient air quality standard for ozone by the applicable attainment date, but for emissions emanating from outside of the United States, shall not be subject to the provisions of section 181(a)(2) or (5) or section 185.<sup>7</sup>

As emissions in many other parts of the world increase, both the relative and absolute contributions of international transport to U.S. air quality problems have increased, especially in the western continental United States (U.S.). Evidence collected to date suggests that the incremental contributions of these flows into U.S. regions will affect air quality degradation on the same order of magnitude as the incremental air quality improvements that are expected to result from some of the tightening of the NAAQS.<sup>8</sup> As air districts, especially those along the west coast and in higher elevations in the western U.S., plan for attainment of the 2008 standard, and perhaps more stringent standards in the future, the understanding of such trans-boundary ozone flow will be of great importance.

The volume of research on trans-boundary ozone has grown considerably in the past 10 years. Transport of ozone to North America from Asia along prevailing air currents is now well-established in the scientific literature.<sup>9</sup> Driven by increasing fossil fuel combustion, tropospheric ozone concentrations entering the west coast of the U.S. have

<sup>&</sup>lt;sup>6</sup> Clean Air Act, U.S.C. § 7509a.

<sup>&</sup>lt;sup>7</sup> Carter, W.P.L., Pierce, J.A., Luo, D., & Malkina, I.L. (1995). Environmental Chamber Study of Maximum Incremental Reactivities of Volatile Organic Compounds. *Atmospheric Environment, 29*, 2499–2511. Note: The U.S. Chamber of Commerce and other interested parties have complained that EPA has provided no clear, consistent guidance to state, local, and regional authorities seeking to account for the impact of foreign emissions in calculating attainment of CAA standards.

<sup>&</sup>lt;sup>8</sup> National Research Council. (2009). Global Sources of Local Pollution: An Assessment of Long-Range Transport of Key Air Pollutants to and from the United States. Washington, DC: The National Academies Press, p. 31. Retrieved from <a href="http://www.nap.edu/catalog.php?record\_id=12743#toc">http://www.nap.edu/catalog.php?record\_id=12743#toc</a>

<sup>&</sup>lt;sup>9</sup> Hudman, R. C., Jacob, D. J., Cooper, O. R., Heald, C.L., Park, R.J. ... Ryerson, T. (2004) Ozone Production in Transpacific Asian Pollution Plumes and Implications for Ozone Air Quality in California. *Journal of Geophysical Research: Atmospheres, 109,* D23S10.

increased by about 10 parts per billion (ppb) from the mid-1980s to the mid-2000s.<sup>10</sup> Closely related to this trend, NOx emissions from southern and eastern Asia increased 44% during the 2001 to 2006 timeframe. During the same period, NOx emissions in China rose 55%.<sup>11</sup> In contrast, European ozone precursor emissions decreased by more than 33% from 1990 to 2005 and by a comparable level in the U.S. from 1985 to 2008. Furthermore, a recent study of trans-boundary ozone flows into western North America from 1995 to 2008 found a comparable upward annual trend in ozone (0.80 ppb per year) on those days when air masses transported across the Pacific Ocean had originated in China, India, and Southeast Asia.<sup>12</sup>

Such understanding of trans-boundary flow has direct implications for establishing reasonably accurate USB levels. Air quality agencies will use the USB level to create accurate emission and transport models that form the foundation for cost-effective control measures. For example, if the Valley USB ozone level is underestimated, subsequent emission controls put on local, regional, or state precursor sources may fail to achieve expected ozone reductions. Ongoing research on trans-boundary and USB ozone will be key in future policy decisions and the establishment of subsequent federal ozone standards.

#### 4.2 AIR QUALITY RESEARCH FOCUSED ON OZONE

Because of its unique combination of geography, meteorology, and chemistry, the Valley continues to be one of the most studied airsheds in the world. On a number of academic and professional fronts, including the efforts of the Study Agency, a substantial amount of research has focused on ozone in the Valley. In addition to Study Agency and District sponsored research, many academic groups, independent from the District, regularly study the air quality dynamics of Valley and contribute to the body of shared knowledge. It is this shared knowledge that informs the District's planning process and guides the ultimate success and implementation of its attainment plans.

#### 4.2.1 Central California Ozone Study

The Central California Ozone Study (CCOS) is the most recent major Study Agency field program to analyze ozone in the Valley. CCOS was conducted during the summer of 2000 and included extensive monitoring throughout the Valley and surrounding regions to provide a robust and spatially dense dataset for a large portion of California. Many subsequent research projects have taken advantage of CCOS data to provide a better understanding of ozone in the Valley. The results from these studies have given academics and air quality regulators alike a more robust understanding of Valley ozone

 <sup>&</sup>lt;sup>10</sup> Oltmans, S. J., Lefohn, A. S., Harris, J. M., & Shadwick, D. S. (2008). Background Ozone Levels of Air Entering the West Coast of the U.S. and Assessment of Longer-Term Changes. *Atmospheric Environment, 42*, 6020–6038.
<sup>11</sup> Zhang, Q., Streets, D.G., Carmichael, G.R., He, K.B., Huo, H., Kannari, A. ... Yao, Z.L.. (2009). Asian Emissions in 2006 for the NASA INTEX-B Mission. *Atmospheric Chemistry and Physics, 9*, 5131–5153. Retrieved from http://www.street.org/10/121/2000.pdf

http://www.atmos-chem-phys.net/9/5131/2009/acp-9-5131-2009.pdf <sup>12</sup> Cooper, O.R., Parrish, D.D., Stohl, A., Trainer, M., Nédélec, P., Thouret, V. ... Avery, M.A. (2010). Increasing Springtime Ozone Mixing Ratios in the Free Troposphere over Western North America. *Nature, 463,* 344–348.

formation and have aided in the development of the most effective control strategies in the nation.

#### 4.2.2 PAMS Monitoring

The District participates every year in EPA's enhanced Photochemical Assessment Monitoring Stations (PAMS) program. PAMS sites measure ozone precursors, including NOx and VOC, in addition to a variety of meteorological parameters in serious, severe, or extreme ozone nonattainment areas. The District's current PAMS monitoring network is comprised of two smaller networks focused on the Fresno and Bakersfield metropolitan statistical areas (MSAs) as shown in Figure 4-4. Each of these MSAs include three PAMS sites, with each site filling the role of either a Type 1, Type 2, or Type 3 site:

- Type 1 PAMS sites monitor morning upwind ozone and ozone precursor concentrations
- Type 2 PAMS sites monitor morning ozone and ozone precursor concentrations at the downwind edge of the central business district
- Type 3 PAMS sites monitor peak afternoon ozone concentration downwind of the MSA

PAMS monitoring sites are usually established at existing state and local air monitoring stations (SLAMSs). Table 4-1 summarizes the sites that make up the Valley's PAMS network. There is currently no Type 3 PAMS monitor in the Bakersfield MSA because the Arvin-Bear Mountain air monitoring site was closed in 2010. PAMS monitoring in Arvin will resume once a permanent air monitoring site in the area is established.

#### Table 4-1 San Joaquin Valley PAMS Monitoring Network

MSA	Туре 1	Type 2	Туре 3
Fresno	Madera-Pump	Clovis	Parlier
Bakersfield	Shafter	Bakersfield-Muni	

Valley PAMS monitoring typically occurs each summer from June to August, when ozone concentrations tend to reach annual maximums. Through Valley PAMS monitoring, over 50 VOCs are measured and analyzed. Table 4-2 lists the targeted and measured compounds for the PAMS program.



#### Figure 4 - 4 Locations of the Valley PAMS Monitoring Network

Table 4-2 PAMS VOC Target Species

Hydrocarbons				
Ethylene	t-2-pentene	2,3-dimethylpentane	n-Nonane	
Acetylene	c-2-pentene	3-methylhexane	Isopropylbenzene	
Ethane	2,2-Dimethylbutane	2,2,4-trimethylpentane	n-Propylbenzene	
Propylene	Cyclopentane	n-Heptane	m-Ethyltoluene	
Propane	2,3-dimethylbutane	Methylcyclohexane	p-Ethyltoluene	
Isobutane	2-methylpentane	2,3,4-trimethylpentane	1,3,5-Trimethylbenzene	
1-Butene	3-Methylpentane	Toluene	o-Ethyltoluene	
n-Butane	2-Methyl-1-Pentene	2-methylheptane	1,2,4-trimethylbenzene	
t-2-Butene	n-hexane	3-methylheptane	n-Decane	
c-2-Butene	Methylcyclopentane	n-Octane	1,2,3-trimethylbenzene	
Isopentane	2,4-dimethylpentane	Ethylbenzene	m-Diethylbenzene	
1-Pentene	Benzene	m&p-Xylenes	p-Diethylbenzene	
n-Pentane	Cyclohexane	Styrene	n-Undecane	
Isoprene	2-methylhexane	o-Xylene		
Carbonyls				
Formaldehyde	Acetone	Acetaldehyde		

#### 4.2.3 Transboundary Ozone Research in the Valley

The District began investigating the influence of transboundary background ozone following anomalously high ozone values measured at rural sites. A study by National Oceanic and Atmospheric Administration (NOAA) found evidence of trans-boundary ozone flow from Asia that significantly impacted ground-level ozone monitors in the northern Sacramento Valley. Additionally, daily flows of transboundary ozone were found to be highly correlated with ozone exceedance events in Butte County, CA.

Based on these results, the District awarded the University of California Davis a \$130,000 research grant in 2011 for the installation of a transboundary ozone and PM2.5 monitoring station on Chews Ridge, east of Big Sur (see Figure 4-5). The site sits at 5,200 feet elevation and is the home of Monterey Institute for Research in Astronomy Observatory. The goal of this work was to investigate whether transboundary ozone was mixing downward into the Valley boundary layer and subsequently transported to ambient monitors. The project included bimonthly air flights over the Valley and the Chews Ridge during peak ozone season.



#### Figure 4 - 5 Chews Ridge in Relation to the Valley

In addition, the District awarded a \$100,000 grant to the same UC Davis research team in 2013 to conduct a more intensive flight campaign over the course of the ozone season. A total of four experimental flights lasting three days occurred during periods of ozone buildup. Data collection included north to south Valley transects in the Valley boundary layer and free troposphere as well as spiral transects in the south Valley around Bakersfield. The research design built on previously published research by NOAA scientists in the 2010 CalNEX campaign that estimated Bakersfield ozone enhancements from transboundary flows of 12-23% on peak days.

In partnership with NASA's Air Quality Applied Science Team (AQAST), the District recently organized a scientific conference on transboundary anthropogenic ozone. The *2015 Transboundary Ozone Pollution Conference* provided a forum for researchers to share their latest findings in this field with air quality managers and other atmospheric scientists. Results from the District-funded UC Davis studies were among the many presentations that detailed the growing body of research and knowledge regarding ozone transport. The meeting was successful in guiding the District's policy and attainment strategies while encouraging all air quality entities to continue to fund meaningful research regarding USB ozone levels. All presentations from the conference can be accessed at <u>http://www.valleyair.org/topc</u>.

While the majority of the Valley's ozone pollution is caused by local sources and geological features that trap pollution, many modelers and researchers in attendance at the conference agreed that policy relevant background/baseline ozone levels are higher than originally estimated. While EPA asserts USB in the Valley is roughly 35 ppb,<sup>13</sup> recent field research and the development of updated models show baseline levels higher than 50 ppb. Given the District's unmatched challenges in mitigating ozone pollution, and the recently adopted new federal 8-hour ozone standard of 70 ppb, it is clear that further investigation in understanding and limiting transboundary ozone intrusion is necessary in order for the District to continue to plan for attainment.

<sup>&</sup>lt;sup>13</sup> Zhang et al. (2011) Establishing Policy Relevant Background (PRB) Ozone Concentrations in the United States. Environmental Science & Technology, 45(22), 9484-97.

#### 4.4 MODELING

[This section provided by the California Air Resources Board]

## Modeling 8-Hour Ozone for the SJV's 2016 State Implementation Plan for the 75 ppb 8-Hour Ozone Standard

Photochemical modeling plays a crucial role in the SIP process to demonstrate attainment of air quality standards based on estimated future emissions and for the development of emissions targets necessary for attainment. Currently, the San Joaquin Valley nonattainment area (SJV or the Valley) is designated as an extreme ozone nonattainment area for the 2008 0.075 ppm (or 75 ppb) 8-hour ozone standard and must demonstrate attainment of the standard by 2031. Consistent with U.S. EPA guidelines for model attainment demonstrations (U.S. EPA, 2014<sup>14</sup>), photochemical modeling was used to estimate the future year 2031 ozone (O<sub>3</sub>) design values (DVs) at each monitoring site in the Valley in order to show attainment of the standard by 2031.

The findings of the Valley's model attainment demonstration are summarized below. Additional information and a detailed description of the procedures employed in this modeling are available in the Modeling Attainment Demonstration and Modeling Protocol Appendices of this document.

The current modeling approach draws on the products of large-scale, scientific studies in the region, collaboration among technical staff of State and local regulatory agencies, as well as from participation in technical and policy groups within the region. (See Modeling Protocol Appendix for further details). In this modeling work, the Weather Research and Forecasting (WRF) numerical model version 3.6 was utilized to generate meteorological fields, while the Community Multiscale Air Quality (CMAQ) Model version 5.0.2 was used for modeling ozone in the Valley. Other relevant information, including the modeling domain definition, chemical mechanism, initial and boundary conditions, and emissions preparation can be found in the Modeling Protocol and Modeling Emissions Inventory Appendices.

Based on U.S. EPA modeling guidance (U.S. EPA, 2014<sup>1</sup>), modeling was used in a relative sense to project observed DVs to the future. The year 2012 was chosen as the starting point for the modeling and reference (or baseline) DV calculation based on analysis regarding the conduciveness of recent years' meteorological conditions to enhanced ozone formation (i.e., meteorology in 2012 was particularly favorable for ozone formation and buildup) and the availability of the most detailed emissions inventory. These reference DVs serve as the anchor point for estimating future year projected design values. The year 2031 was the future year modeled in this attainment demonstration since that is the year for which attainment must be demonstrated.

<sup>&</sup>lt;sup>14</sup> U.S. EPA, 2014, Draft Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5 and Regional Haze, available at <u>https://www.epa.gov/ttn/scram/guidance/guide/Draft\_O3-PM-RH\_Modeling\_Guidance-2014.pdf</u>

DVs are the three-year average of the annual 4<sup>th</sup> highest 8-hour  $O_3$  mixing ratio observed at each monitor and are used to determine compliance with the standard. In the attainment demonstration, the U.S. EPA recommends using an average of three DVs to account for the year-to-year variability in meteorology, so DVs were calculated for the three year period ending in 2012, 2013, and 2014 and then the three DVs were averaged. This average DV is called a weighted DV (see the 2<sup>nd</sup> column of Table 4-4 for the weighted DVs utilized in the attainment demonstration modeling).

In order to use the modeling in a relative sense, three simulations were conducted: 1) <u>base year</u> simulation for 2012, which was used to verify that the model reasonably reproduced the observed air quality; 2) <u>reference year</u> simulation for 2012, which was the same as the base year simulation, but excluded exceptional event emissions such as wildfires; 3) <u>future year</u> simulation for 2031, which was the same as the reference year simulation, except projected emissions for 2031 were used in lieu of the 2012 emissions.

Table 4-3 summarizes the 2012 and 2031 SJV anthropogenic emissions used in the attainment demonstration modeling. Overall, anthropogenic NOx was projected to decrease by roughly 60% between 2012 and 2031 from 339.5 tpd to 131.9 tpd. In contrast, anthropogenic ROG was projected to decline by 12% from 337.2 tpd to 296.7 tpd. Biogenic ROG emissions were held constant between all simulations with summer average emissions estimated at 1323 tpd for the Valley.

		NOx			ROG	
Source	2012 [tpd]	2031 [tpd]	Percent Difference	2012 [tpd]	2031 [tpd]	Percent Difference
Stationary	42.4	29.5	-30	85.3	100	+17
Area	4.7	4.9	+4	147	152.7	+4
On-road Mobile	187.7	45.1	-76	60.4	18.3	-70
Off-road Mobile	104.7	52.4	-50	44.5	25.7	-42
Total	339.5	131.9	-61	337.2	296.7	-12
Biogenic		-		13	23	

Table 4-3 Summer emission inventory totals (CEPAM v1.03) for 2012 and 2031. Biogenic emission totals are averaged over May – September, 2012

As part of the model attainment demonstration, the fractional changes in ozone mixing ratios between the model reference year (2012) and model future year (2031) were calculated at each of the monitors following U.S. EPA modeling guidance (U.S. EPA,

2014<sup>15</sup>) and procedures outlined in the Modeling Protocol Appendix. These ratios, called "relative response factors" or RRFs, were calculated based on the ratio of future year modeled maximum daily average 8-hour (MDA8) ozone to modeled reference year MDA8 ozone (Equation 1).

$$RRF = \frac{average MDA8 \text{ ozone }_{future}}{average MDA8 \text{ ozone }_{reference}}$$
(1)

The site-specific RRF was then multiplied by the weighted DV for the corresponding monitor to predict the future year 2031 DVs (Table 4-4). The RRF approach was first applied in the SJV for the 2007 8-hour Ozone SIP<sup>16</sup> and later in the 2013 1-hour Ozone SIP<sup>17</sup>. In both cases, the RRF approach appropriately characterized emission targets for attainment. In the 2007 SIP, attainment was projected to occur in 2023 and all sites are currently on target for attainment of the 84 ppb standard, with many sites already having attained. In the 2013 SIP, attainment of the 124 ppb standard was projected by 2017 and the Valley has already achieved attainment. In addition, two peer-reviewed scientific publications focused primarily on areas outside of California (one from researchers at Rice University<sup>18</sup> and one from U.S. EPA scientists<sup>19</sup>), both found that the RRF approach is highly robust in its ability to predict future DVs.

Table 4-4 shows that all monitoring sites in the Valley are projected to have a future DV less than 75 ppb, so that the entire Valley is projected to attain the 75 ppb 8-hour  $O_3$ standard by 2031 based on the substantial emission reductions from implementation of the current control program. The large projected decrease in DVs from 2012 to 2031 is consistent with recent peer-reviewed, published studies conducted by UC Berkeley researchers<sup>20</sup>, which concluded that cumulative NO<sub>x</sub> controls over time have successfully transitioned the southern and central portions of the SJV into a NO<sub>x</sub>-limited chemistry regime where  $NO_x$  emission reductions are becoming increasingly effective at reducing ozone, while the northern portion of the SJV is currently transitioning to the same chemical regime. This is consistent with analysis on the changes in weekday vs. weekend ozone presented in the Modeling Protocol and Model Attainment Demonstration Appendices, where ozone on weekends is now generally lower than ozone on weekdays (in contrast to higher weekend ozone in the past), which is consistent with the NO<sub>x</sub>-limited chemical regime.

<sup>&</sup>lt;sup>15</sup> U.S. EPA, 2014, Draft Modeling Guidance for Demonstrating Attainment of Air Quality Goals for Ozone, PM2.5 and Regional Haze, available at https://www.epa.gov/ttn/scram/guidance/guide/Draft O3-PM-RH Modeling Guidance-2014.pdf <sup>16</sup> http://www.valleyair.org/Air\_Quality\_Plans/AQ\_Final\_Adopted\_Ozone2007.htm <sup>16</sup> http://www.valleyair.org/Air\_Quality\_Plans/Ozone-OneHourPlan-2013.htm

<sup>&</sup>lt;sup>17</sup> http://www.valleyair.org/Air\_Quality\_Plans/Ozone-OneHourPlan-2013.htm

<sup>&</sup>lt;sup>18</sup> Pegues, A.H., D.S. Cohan, A. Digar, C. Douglass, and R.S. Wilson (2012). Efficacy of recent state implementation plans for 8-hour ozone. Journal of the Air & Waste Management Association, 62, 252-261,

doi: 10.1080/10473289.2011.646049. <sup>19</sup> Foley. K., P. Dolwick, C. Hogrefe, H. Simon, B. Timin, and N. Possiel, (2015), Dynamic evaluation of CMAQ part II: Evaluation of relative response factor metrics for ozone attainment demonstrations. Atmospheric Environment, 103: 188-195, doi:10.1016/j.atmosenv.2014.12.039

<sup>&</sup>lt;sup>20</sup> Pusede, S. E., and R. C. Cohen, 2012, On the observed response of ozone to NO<sub>x</sub> and VOC reactivity reductions in San Joaquin Valley California 1995-present, Atmos. Chem. Phys., 12, 8323-8339.

As part of the attainment demonstration, U.S. EPA also requires analysis of ozone levels outside of the routine monitoring network (i.e., at areas between the monitors) to ensure that all regions within the Valley (even those without a monitor) are in attainment of the standard. This "unmonitored area" analysis combines observation based DVs with model based RRFs and ozone spatial gradients to estimate future DVs in unmonitored areas. Details of how the unmonitored area analysis is performed can be found in the Modeling Protocol and Model Attainment Demonstration Appendices. The unmonitored area analysis in the SJV showed that the areas with the highest future DVs were captured within the existing monitoring network and that all areas are projected to achieve the 75 ppb ozone standard.

Site Name	Weighted Base Year (2012) Design Value [ppb]	RRF	Future Year (2031) Design Value [ppb]
Clovis-N Villa Ave	95.7	0.7729	74
Sequoia and Kings Canyon Natl Park	93.0	0.7038	65
Fresno-Drummond St	92.3	0.7713	71
Parlier	92.0	0.7513	69
Fresno-Garland	90.7	0.7813	70
Arvin-DiGorgio	89.3	0.7242	64
Fresno-Sierra Skypark#2	89.0	0.7685	68
Edison	87.7	0.7398	64
Baker-5558 California Ave	86.7	0.7573	65
Porterville-1839 Newcomb St	86.3	0.7328	63
Hanford-S Irwin St	86.0	0.7538	64
Turlock-S Minaret St	86.0	0.8020	69
Oildale-3311 Manor St	84.7	0.7773	65
Madera-28621 Ave 14	84.7	0.7746	65
Sequoia Natl Park-Lower Kaweah	84.0	0.7302	61
Maricopa-Stanislaus St	83.3	0.7562	63
Shafter-Walker St	83.0	0.7557	62
Visalia-N Church St	82.3	0.7392	60
Merced-S Coffee Ave	81.7	0.8009	65
Madera-Pump Yard	79.3	0.7790	61
Tracy-Municipal Airport	79.3	0.8429	66
Tranquility-32650 West Adams Ave	76.3	0.7937	60
Modesto-14 <sup>th</sup> St	76.0	0.8102	61
Stockton-Hazelton St	68.3	0.8446	57

## Table 4-4 Base year Design Value, modeled RRF, and projected future yearDesign Value by site