SJVUAPCD

Chapter 4

Scientific Foundation and Ozone Modeling Results

DRAFT *2016 PLAN FOR THE 2008 8-HOUR OZONE STANDARD*

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Chapter 4: Scientific Foundation

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), 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 more 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 (Ambient Air Quality Data), Appendix B (Emissions Inventory), and Appendix D (Photochemical Modeling Support Documents).

4.1 THE NATURE AND FORMATION OF OZONE

Ozone (O_3), 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 (UV) 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.

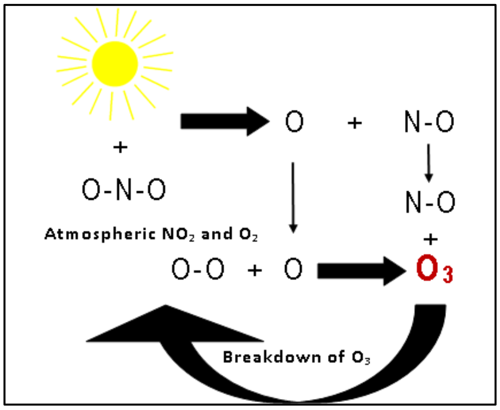
4.1.1 The Ozone Life Cycle

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_2 + photon energy from the sun → NO + O
2. O + O_2 → O_3 (*ozone formed*)
3. O_3 + NO → 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

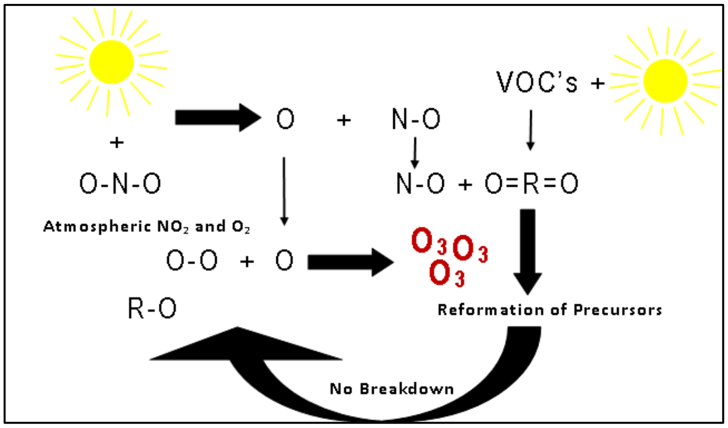


Unfortunately, ideal equilibrium in the Valley is rarely reached as the ozone life cycle becomes unbalanced in the presence of elevated VOC and NO_x emissions. Biogenic VOC emissions are especially high during the Valley's summer ozone season. The same photon energy that reacts with NO_2 in the balanced 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_2), 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):

Figure 4-2 Alternate Ozone Cycle

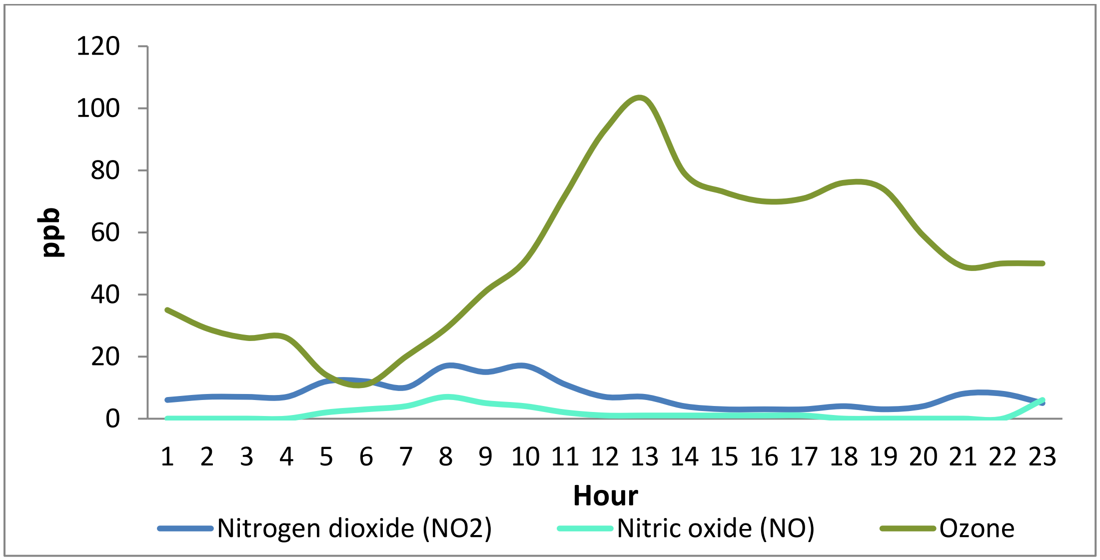
1. NO_2 + photon energy from the sun → NO + O
2. O + O_2 → O_3 (*ozone formed*)
3. RO_2 + NO → RO + NO_2 (*ozone does NOT break down*)



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_2, and ozone throughout the hours of a common summer day. The day begins with low ambient levels of NOx (NO and NO_2) and ozone. As the morning commute begins, motor vehicle traffic directly emits NOx pollutants and 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_2 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_2 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.

4.1.1 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 determination 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 *NOx-rich* 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 is NOx-limited; therefore, NOx reductions are the most effective way to reduce Valley ozone concentrations.

4.1.2 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,[1,2,3] of which the most frequently used is the *maximum incremental reactivity* (MIR) scale.[4,5] 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 the Valley to be NOx-limited; therefore, NOx reductions are the most effective strategy for reducing Valley ozone concentrations.

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[1] Bowman, F. M. & Seinfeld, J. H. (1994). Ozone Productivity of Atmospheric Organics. *Journal of Geophysical Research, 99*, 5309–5324.

[2] 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.

[3] Carter, W.P.L (1994). Development of Ozone Reactivity Scales for Volatile Organic Compounds. *Journal of the Air & Waste Management Association, 44*, 881–899.

[4] Ibid.

[5] 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.

4.1.3 SJV 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 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:[6]

> *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.*[7]

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.[8] 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

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[6] Clean Air Act, U.S.C. § 7509a.

[7] Ibid 5. 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.

[8] 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 http://www.nap.edu/catalog.php?record_id=12743#toc

now well-established in the scientific literature.[9] Driven by increasing fossil fuel combustion, tropospheric ozone concentrations entering the west coast of the U.S. have increased by about 10 parts per billion (ppb) from the mid-1980s to the mid-2000s.[10] 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%.[11] 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.[12]

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

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[9] 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.

[10] 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.

[11] 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.atmos-chem-phys.net/9/5131/2009/acp-9-5131-2009.pdf

[12] 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.

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 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	Type 1	Type 2	Type 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

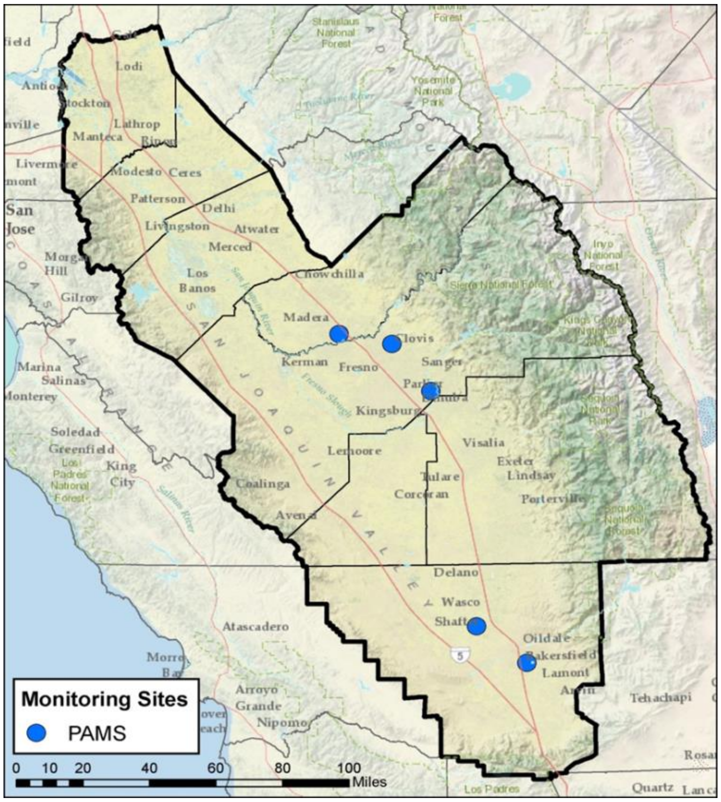

Table 4-2 PAMS VOC Target Species

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 trans-boundary ozone and PM2.5 monitoring station on Chews Ridge, east of Big Sur (see Figure 4-8). 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 trans-boundary 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 http://www.valleyair.org/topc.

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,[13] 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 trans-boundary ozone intrusion is necessary in order for the District to continue to plan for attainment.

4.3 MODELING

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

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[13] Zhang et al. (2011) Establishing Policy Relevant Background (PRB) Ozone Concentrations in the United States. Environmental Science & Technology, 45(22), 9484-97.