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## 1. Introduction

This document evaluates the need for additional VOC controls to achieve more stringent annual PM<sub>2.5</sub> and 8-hour ozone standards in the SoCAB. It assesses the role of VOCs in forming ozone and PM<sub>2.5</sub> to inform policymakers of the most efficient and effective strategies to attain the federal standards that are the subject of the upcoming 2016 AQMP.

The science behind the formation of ozone and particulate matter from VOCs is also summarized. A state-of-the-science numerical modeling system (WRF-CMAQ) is used to estimate the maximum allowable NO<sub>x</sub> and VOC emissions that will lead to regional ozone and PM<sub>2.5</sub> concentrations that meet the federal standards. Given the results of this modeling, the implications of various NO<sub>x</sub> and VOC control strategies are analyzed.

## 2. What are VOCs?

VOCs are chemicals containing carbon that readily evaporate. VOCs are widely used in modern society in fuels, solvents, coatings, cleaning supplies, building products, and many other materials. In addition to evaporation, some VOCs are emitted as a product of combustion processes, such as wood burning or internal combustion engines. Thus, VOCs are emitted from mobile sources such as cars and trucks, and stationary sources such as refineries, chemical plants, and households. Since VOCs evaporate readily, in the absence of appropriate control measures, these compounds will ultimately end up in the atmosphere. Subsequent chemical reactions of VOCs in the atmosphere can form surface level ozone pollution and particulate matter.

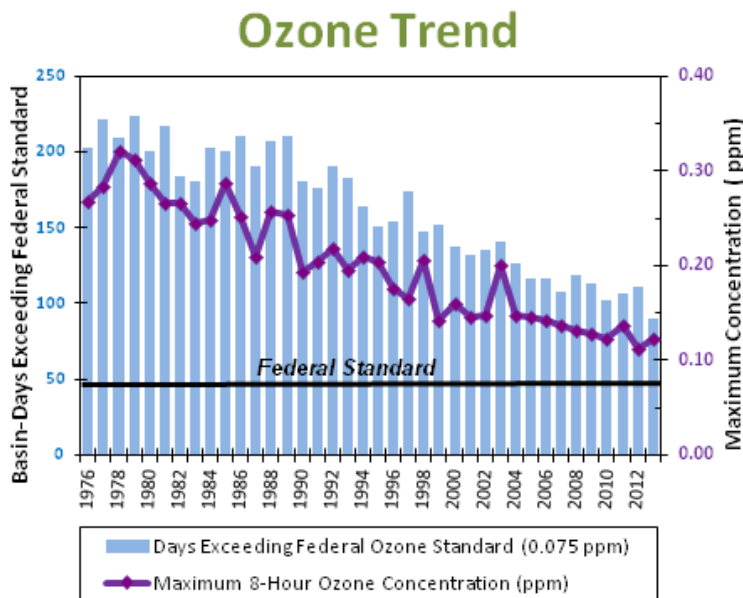
Atmospheric scientists classify VOCs into several subcategories. The rate that each specific VOC forms ozone is a function of its unique chemical reactivity, its atmospheric concentration, and the atmospheric concentrations of other chemicals needed for these complex chemical reactions. VOCs that form ozone at extremely slow rates are considered non-reactive and are often classified as “exempt” from current VOC rules and regulations. However, toxicity or other potential adverse environmental impacts from these VOCs should also be considered. The ability for a specific VOC to form particulate matter is dependent on how fast it reacts with other atmospheric compounds and the physical properties of the resulting products.

We can also classify VOCs and their chemical reaction products into three sub-categories dependent on how readily they evaporate. VOCs with high volatility evaporate quickly, but are less likely to contribute to particulate matter, because these compounds generally remain as gases once they evaporate. On the other hand, compounds with lower volatilities evaporate at a slower rate, but are more likely to contribute to particulate matter as they or their reaction products may condense (transition from gas to liquid or solid form) once they are in the atmosphere. Compounds that have a significant fraction of their mass in both the gas and particle-phase in the atmosphere are referred to Semi-Volatile Organic Compounds (SVOCs). Compounds that have most of their mass in the gas-phase, but can transition to the particle phase under certain atmospheric conditions are termed Intermediate Volatility Organic Compounds (IVOCs). While a direct comparison is difficult, low vapor pressure volatile organic compounds (LVP-VOCs), defined under the California Air Resources Board consumer products regulations, fall into the IVOC and SVOC categories. In addition, atmospheric reactions can produce products with drastically different volatilities than the parent compounds.

### 3. The role of VOCs in ozone formation

#### *Ozone concentrations in the South Coast Air Basin*

Ground-level ozone pollution is a powerful oxidant with significant adverse effects on human health. While ozone concentrations within the SoCAB have declined significantly over the past few decades, the SoCAB does not meet federal or state ozone standards. In addition, the recently proposed federal limit of 65-70 ppb will make future attainment even more challenging [1]. In recent years, the significant downward trend in Basin-wide ozone concentrations has begun to level off. Figure 1 details the yearly trend in ozone concentrations and the trend in the number of days that exceed the current federal standard.



**Figure 1: Basin-wide maximum 8-hour ozone concentration and Basin-days exceeding the federal standard.**

Certain air quality monitoring stations located in the Inland Empire and the San Bernardino Mountains exceed the federal ozone standard over 60 days per year (Figure 2). Higher local ozone concentrations in these regions can be attributed to the significant upwind NOx and VOC precursor emissions transported by the daily sea-breeze in the summer, local emissions, and the timing of the daily emissions and peak sunlight intensity.

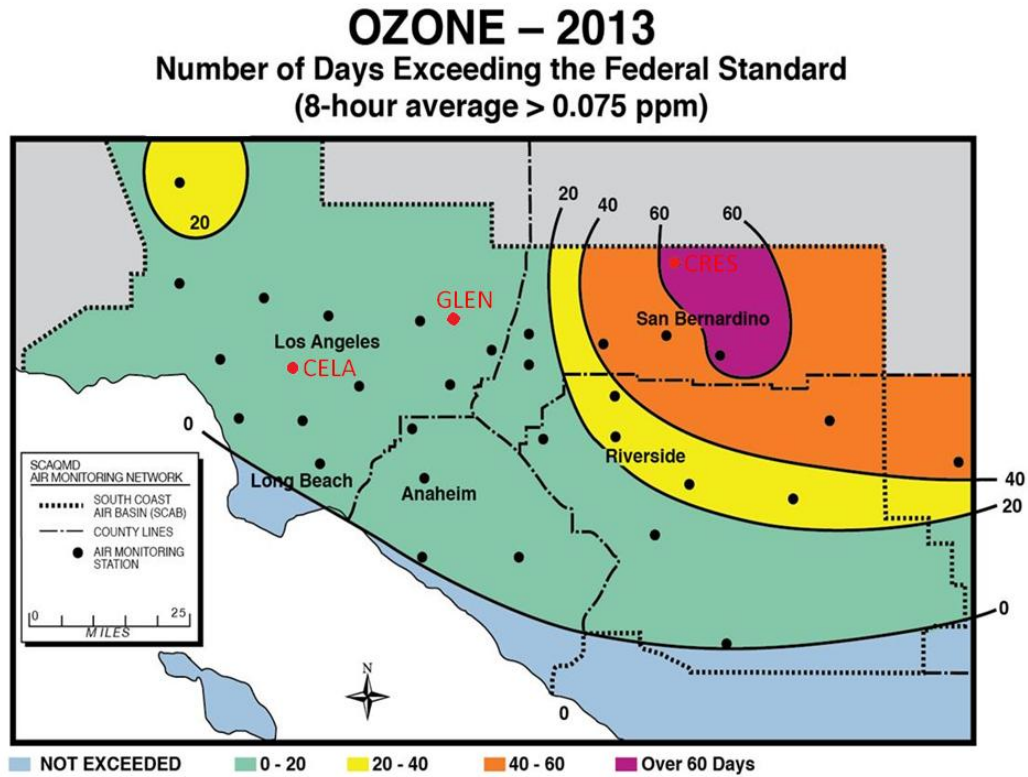


Figure 2: Spatial distribution of ozone exceedances in the SoCAB. Central Los Angeles (CELA), Glendora (GLEN), and Crestline (CRES) are highlighted.

### How do VOCs form ozone?

Ozone (O<sub>3</sub>) is not emitted directly into the atmosphere; it is formed in the atmosphere by reaction of VOCs with oxides of nitrogen (NO<sub>x</sub>) in the presence of sunlight. NO<sub>x</sub> is generated from combustion processes and is emitted in large quantities within the South Coast Air Basin (SoCAB). The chemical reactions that form ozone are highly complex and depend not only on NO<sub>x</sub> and VOC levels, but also on the ratio of VOC to NO<sub>x</sub> concentrations. NO<sub>x</sub> emissions can even reduce ozone concentrations in the immediate vicinity of an emission source, but will contribute to ozone formation downwind.

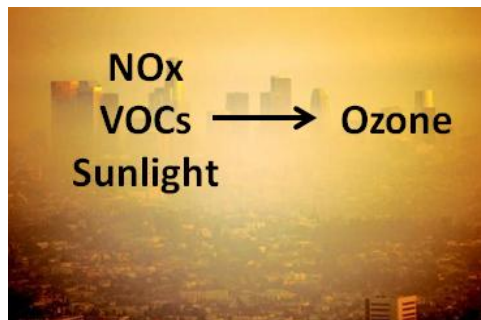


Figure 3: Recipe for ozone production

A decrease in ambient VOC concentrations generally leads to a decrease in ozone. However, because of the complex chemistry involved, a decrease in NO<sub>x</sub> concentrations may lead to a

decrease or an increase in ambient ozone depending on the local VOC concentration. This complex dependence on NO<sub>x</sub> and VOC concentrations leads to interesting policy implications, which can be explored using comprehensive air quality models.

#### 4. How do VOCs form particulate matter?

The South Coast Air Basin does not currently meet federal and state standards for PM<sub>2.5</sub>, particles with diameters less than 2.5 μm (Figure 4). These particles consist of a myriad of different chemical compounds in both solid and liquid form. While some PM<sub>2.5</sub> is emitted directly from sources, the majority of ambient PM<sub>2.5</sub> is formed from chemical reactions and processes in the atmosphere. These small particles are particularly dangerous due to their ability to penetrate deep into the lungs. Many studies have linked inhalation of PM to serious adverse respiratory and cardiovascular affects. In order to develop an effective control strategy, one must consider the composition and by extension, the sources of PM<sub>2.5</sub> in the Basin. In the Basin, approximately 30-50% of the PM<sub>2.5</sub> mass is composed of organic compounds. The remaining fraction consists of elemental carbon, metals, dust, inorganic sulfate, inorganic nitrate, ammonium, and chloride. The organic fraction, known as organic aerosol (OA), is composed of a complex mixture of organic chemicals that may continue to evolve as it ages in the atmosphere.

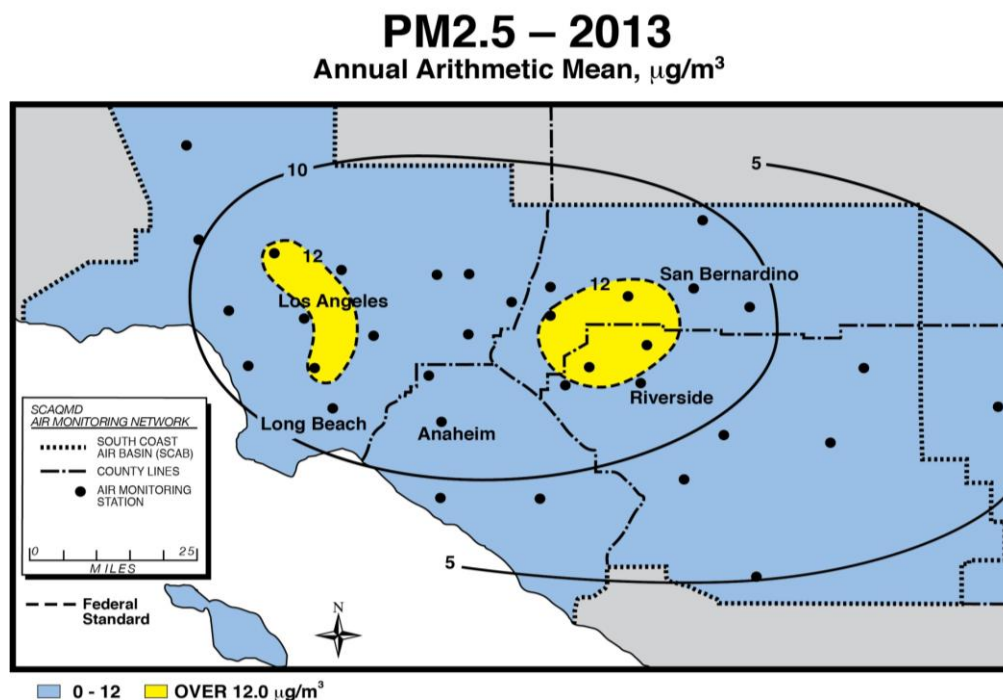


Figure 4: Spatial distribution of PM<sub>2.5</sub> concentrations in the SoCAB

Different chemical reactions are responsible for the formation of ozone and OA from gaseous organic compounds. Since both ozone and PM<sub>2.5</sub> formation are largely dominated by atmospheric reactions, we must consider the potential for a gaseous organic compound to contribute to both ozone and PM<sub>2.5</sub> levels. Organic compounds with large ozone formation potentials may or may not contribute significantly to PM<sub>2.5</sub> mass. Similarly, many gaseous

organic compounds classified as VOCs, IVOCs, or SVOCs that contribute to OA may or may not play a role in the formation of ozone [5].

## **5. Ozone Control Modeling Analysis**

The Community Multiscale Air Quality (CMAQ) model has been used to investigate the resulting O<sub>3</sub> concentrations with various levels of VOC and NO<sub>x</sub> emissions under different control strategies. The CMAQ model, which is the U.S. EPA recommended regulatory model, is considered the preeminent, state-of-the-science air quality model for analyzing air quality improvement strategies. Since ozone concentrations are a complex function of both NO<sub>x</sub> and VOCs concentrations, we use a three-dimensional plot to visualize this dependency. The Empirical Kinetics Modeling Approach (EKMA) ozone “isopleths” diagrams illustrate the outcomes of this complicated chemistry.

The ozone isopleth diagram in Figure 5 illustrates how 8-hr ozone concentrations in Crestline (the monitoring station currently with the most ozone exceedances in the Basin) respond to decreases in total Basin-wide anthropogenic VOC and NO<sub>x</sub> emissions beyond the existing adopted rules and regulations. The corresponding ozone isopleths diagram for Central Los Angeles is presented in Figure 6. Estimated VOC and NO<sub>x</sub> emissions following the continued implementation of adopted rules and regulations in the 2023 timeframe are defined by the upper-right corner of the plot. The federal ozone standard is met within the yellow and green regions of the diagram (corresponding to Air Quality Index levels and colors). Three paths are illustrated on both isopleths diagrams to highlight the potential effects of different control strategies and to aid in policy discussions. Path C illustrates the impact of a control scenario that attains the ozone standards with only additional NO<sub>x</sub> reductions beyond what is required in current rules. In this scenario, additional VOC reductions beyond current requirements are not applied. A control scenario focusing solely on additional VOC control is shown with Path A. A hypothetical control scenario where additional (beyond scheduled reductions) NO<sub>x</sub> and VOC reductions occur at the same rate is illustrated with Path B. This is provided as an example of the results of a control strategy emphasizing VOC and NO<sub>x</sub> reductions equally.



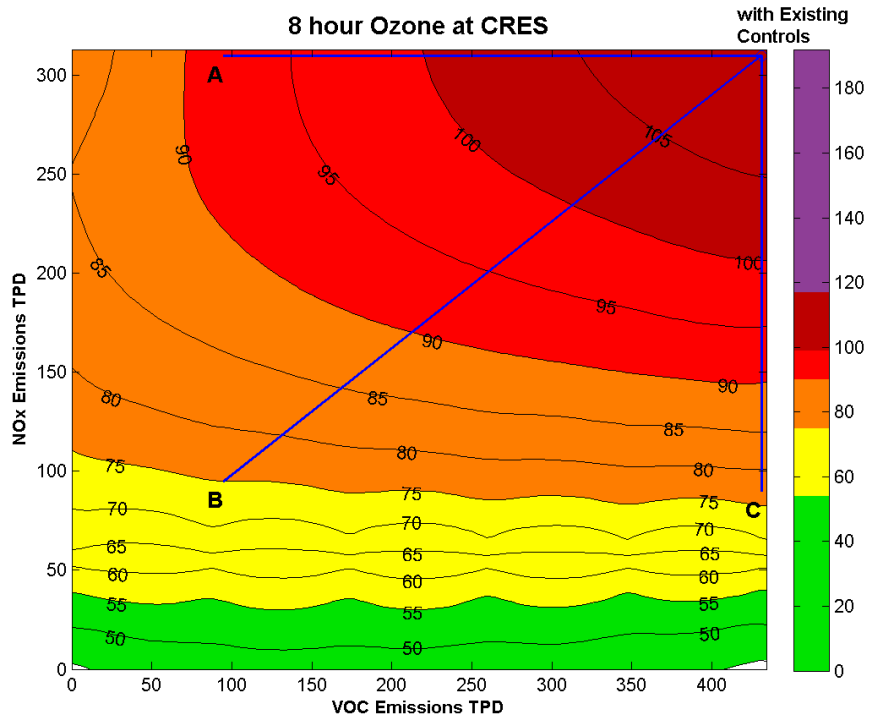


Figure 5: EKMA ozone isopleths diagram showing 8-hr ozone isopleth at Crestline. The color shading corresponds to the air quality index (AQI) color code. This analysis is based on the emissions inventory used for the 2012 AQMP using CMAQ version 4.7.

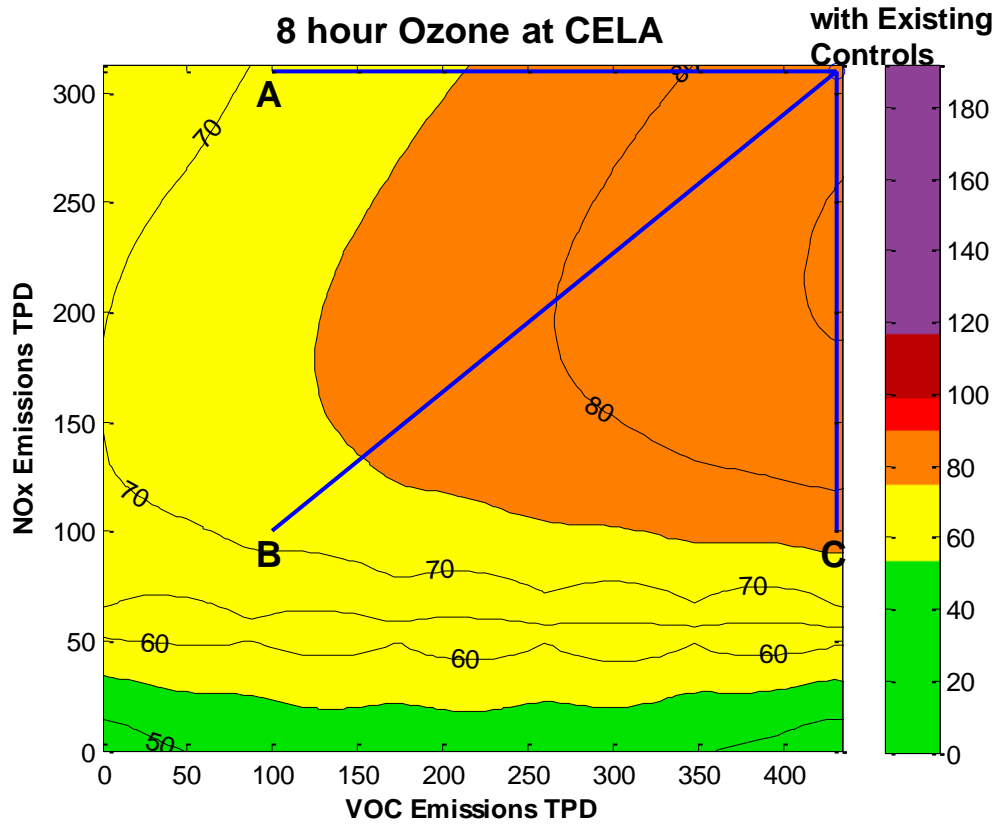


Figure 6: EKMA ozone isopleths diagram showing 8-hr ozone isopleth at Central Los Angeles. The color shading corresponds to the air quality index (AQI) color code. This analysis is based on the emissions inventory used for the 2012 AQMP using CMAQ version 4.7.

It is necessary to understand how ozone concentrations evolve during each of these three control paths at the Crestline and Central L.A. monitoring locations (Figure 7).

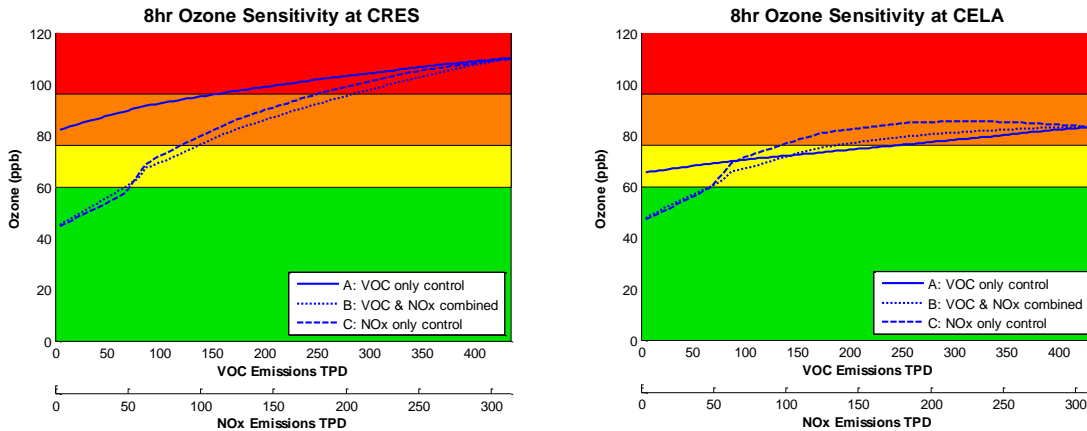


Figure 7: Ozone concentrations at Crestline and Central Los Angeles predicted to occur as a result of the specific control strategies (path A, B, and C) marked in Figure 5 and 7.

While the VOC heavy control strategy (Path A from right to left) reaches attainment in CELA with the minimum amount of emissions reductions, this strategy will not lead to attainment in CRES, and thus the Basin, even with zero anthropogenic VOC emissions. Therefore, additional NO<sub>x</sub> reductions are required to achieve the ozone standards for both sites.

Not only is the achievable endpoint different in each of the scenarios, the ozone concentrations predicted to occur along the path to attainment are also quite different. Moving from right to left in these figures along Path C, the NO<sub>x</sub> heavy control strategy suggests that approximately an additional 200 TPD of NO<sub>x</sub> reductions beyond current regulations is required to attain the federal ozone standard. If NO<sub>x</sub> is reduced without additional VOC reductions beyond what is projected from current rules, as illustrated in Figure 8 there could be up to a 2 ppb increase in ozone in certain parts of the western Basin surrounding central LA along the path to attainment. Figure 9 shows the area that would be above the 1997 ozone standard of 80 ppb and how much the potential ozone exposure increase would be. The population potentially subject to this effect is estimated to be a few million. It should be noted that this increased ozone phenomenon attributable to a pure NO<sub>x</sub> reduction strategy is temporary and exists only along the path to attain the 80 ppb standard, but does not occur with additional NO<sub>x</sub> reductions designed to attain the more stringent 75 ppb or the future proposed standard (65 to 70 ppb).

### Additional Reductions Beyond Existing Controls

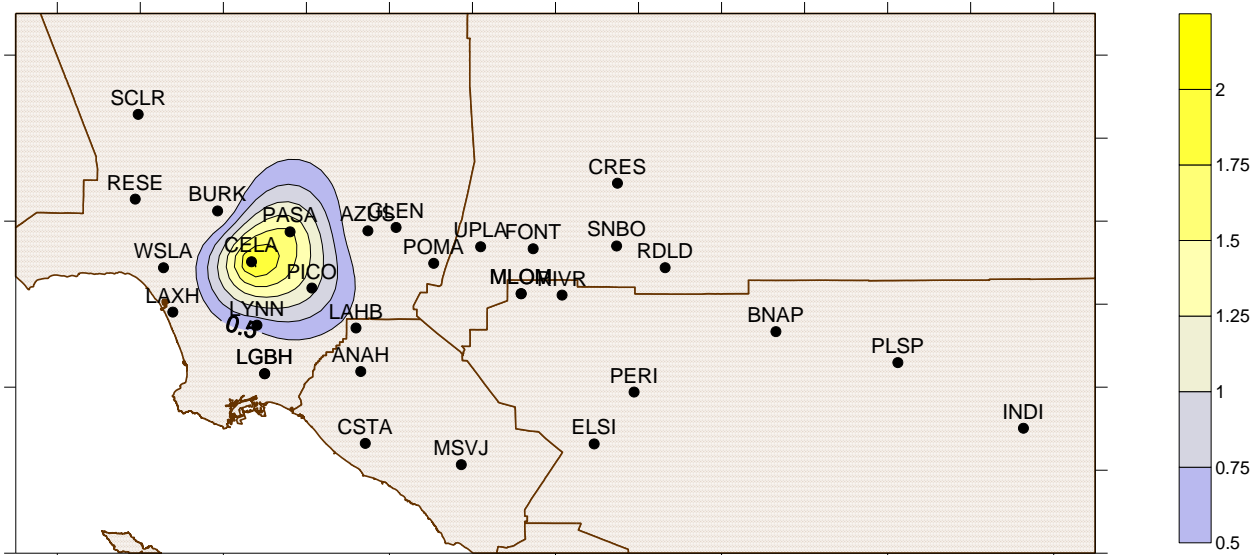


Figure 8: Maximum increase in ozone along the path to attainment with a pure NO<sub>x</sub> control strategy

## 6. Consideration of “Path to Clean Air” Scenarios

There are different paths to achieve ozone and PM<sub>2.5</sub> standards based on various levels of control among the precursor pollutants. The total magnitude of reductions required, technology readiness, cost-effectiveness, economic impacts, attainment deadlines, and the interaction with other attainment deadlines for other pollutants are all critical considerations in developing an overall multi-pollutant control strategy. Complex atmospheric chemistry and the non-uniform spatial distribution of both sources and the resulting ambient concentrations requires a comprehensive analysis that ensures not only that ozone and PM<sub>2.5</sub> concentrations meet standards in all areas, but that unintended exposure increases in specific areas are avoided if at all possible. Furthermore, concurrent reductions of other pollutants such as air toxics and greenhouse gases should also be considered in optimizing a path to meeting multiple standards, objectives, and deadlines.

### *NOx-Only Control Strategy (Path C)*

As demonstrated above, a NOx-only approach without new VOC controls provides a potential path to ozone attainment for both stations that minimizes the overall tons of emissions reductions needed and has commensurate benefits for PM<sub>2.5</sub>. Many of the currently available technologies needed for NOx reductions have air toxics and greenhouse gas co-benefits and vice-versa. Reducing NOx emissions will also mitigate adverse health effects associated with inhalation of locally elevated concentrations of NO<sub>2</sub>, another criteria pollutant. However, this NOx-only (path C) approach leads to increased ozone concentrations and exposure in the more densely populated areas of the western Basin in the short-term. Consequently, a certain portion of the Basin's population would experience worse ozone air quality at levels above federal standards in the interim years under a NOx only approach. This approach requires an additional NOx reduction beyond adopted regulations of approximately 65-75% to attain the federal ozone standards. While a reduction of this magnitude is challenging and will require significant investments, zero- and near zero- NOx emission reduction technologies are currently available and in limited use and can potentially be widely deployed in the next 10 to 20 years.

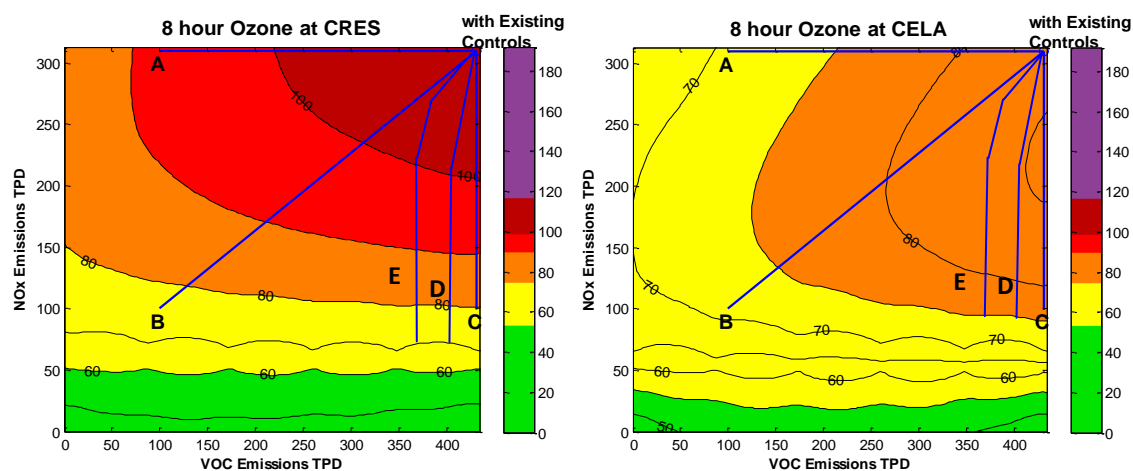
### *VOC-Only Control Strategy (Path A)*

A VOC heavy control strategy without additional NOx controls, illustrated by path A in Figure 6, will not lead to attainment of the ozone standards for the eastern Basin, even in the absence of any man-made VOC emissions. This control strategy avoids a short-term increase in ozone inherent in the NOx-only strategy, however, it will not be possible to achieve the ozone standards by reducing VOCs alone. Furthermore, zero- and near zero-VOC technologies for many of the major VOC emitting categories (e.g. consumer products) may take many years for reformulation and market penetration, and are thus less mature than current low NOx technologies.

### *Combined NOx and VOC Control Strategies*

A VOC and NOx combined strategy would require greater combined tons of reductions with greater associated compliance costs than a single pollutant approach. However, a combined strategy will aid in mitigating short-term increases in ozone in certain areas while potentially providing additional benefits for PM<sub>2.5</sub>, toxics, and greenhouse gases. Note that Path B in the above figures is provided only as an example, and a combined control strategy could lie anywhere between path A and path C that still reaches ozone attainment.

For example, Figure 10 adds two additional emissions reduction scenarios to the Central L.A ozone isopleths in Figure 7. Path D provides just enough additional VOC control (30 - 40 tons per day) to avoid any increases in ozone exposure above the 2023 attainment target of 84.5 ppb (this standard has been revoked, but the 2023 target remains with U.S. EPA's anti-backsliding provisions). Another policy option is Path E, which includes enough early VOC reductions to avoid any increases in ozone exposure in the western Basin. This would require approximately 100 tons per day of additional VOC controls, and for those controls to be timed to occur before the bulk of the NOx controls. In any case, the choice of the optimal path should consider multiple policy goals, including public health, cost-effectiveness, and economic impacts.



**Figure 10: Additional emissions reduction options (Paths D and E) mitigating ozone increases in the western Basin (CELA)**

*Recommendations- NOx-Heavy Controls with Strategic and Tiered VOC Reductions*

Given the availability of technology, climate and  $PM_{2.5}$  objectives, a desire to minimize control costs, and the lack of a viable path to attainment with VOC reductions only, a NOx heavy approach with modest VOC controls as shown in Path D is preferred. It is the same path that was taken by both the 2007 and 2012 AQMPs that focuses primarily on NOx reductions, but is augmented with modest VOC reductions to mitigate the higher ozone exposures along the path to attainment. According to this analysis, approximately 200 tons per day of NOx would be needed by 2023, and mitigating the interim ozone increases would require about 30 to 40 tons per day, or less than 10 percent of total anthropogenic VOC emissions beyond the existing adopted rules and regulations. Once the 84.5 ppb level is reached, these or additional VOC reductions would not be needed to avoid increases in ozone exposure. It should be noted that Path D would also result in concurrent  $PM_{2.5}$  reductions throughout the entire air basin which are needed to address the current  $PM_{2.5}$  annual standard of 12  $\mu\text{g}/\text{m}^3$ .

These additional VOC reductions will help to mitigate the increase in ozone in the western Basin inherent in this NOx heavy control strategy. Therefore, a control strategy that continues to focus on NOx reductions, with additional strategic and cost-effective VOC reductions, is the most desirable way to minimize the general public's exposure to unhealthy ozone pollution not only in the target attainment year, but also during the course of the control effort. The next section discusses a prioritized strategy to achieve cost-effective VOC reductions that maximize co-benefits and emphasize non-regulatory approaches.

Note that this analysis is based on the results of analyses conducted for the 2012 AQMP. This analysis will be repeated for the 2016 AQMP with an updated emissions inventory and new attainment demonstration modeling methods from the US Environmental Protection Agency, following the same approach and rationale outlined above. The general findings of the control pathways outlined above is not expected to change, but the amount of reductions needed will be refined to reflect the latest planning assumptions and methodologies.

## 7. Tiered Approach to VOC Reductions

Based on the above analysis of the overall path to attainment and the role VOCs play in the ozone control program, a strategy that continues to focus on significant NO<sub>x</sub> reductions but includes meaningful VOC reductions where appropriate is recommended. In order of priority, the following potential strategy considerations are designed to achieve VOC reductions in a cost-effective and targeted fashion considering the co-benefits from and to other air quality objectives:

1. *Maximize co-benefits from NO<sub>x</sub>, GHG or air toxic controls that produce concurrent VOC reductions*

Certain zero- or near-zero NO<sub>x</sub> technologies would also lead to VOC reductions. Given the continued NO<sub>x</sub> heavy strategy, policies should promote technologies with these additional VOC co-benefits. For example, electric and hydrogen fuel cell vehicles, efficiency measures, or VMT reductions produce both NO<sub>x</sub> and VOC reductions; many of these strategies also avoid evaporative losses associated with traditional fuels like gasoline. Similarly, control technologies for GHG or air toxics may also produce concurrent VOC reductions. The 2016 AQMP will aim to better integrate and quantify these VOC reductions into the attainment plan.

2. *Promote pollution prevention at the source with associated cost savings*

Reducing waste at the source is an efficient and effective way to reduce emissions. This strategy could involve the implementation of more robust leak detection and repair (LDAR) programs, including Smart LDAR using advanced infrared or optical technologies. This approach can lead to cost savings as less product is lost through fugitive emissions. In other cases, this approach could reduce the use of VOC containing products and/or the reliance on after-treatment control technology. This also can lead to cost savings. Examples of this are incentives and programs promoting the use of higher transfer efficiency spray painting equipment.

3. *Incentivize super-compliant-zero- and near-zero VOC materials, especially during peak ozone season*

Super-compliant zero and near-zero VOC materials eliminate or drastically reduce emissions during the use of these products. There are several product categories where these materials perform as well as traditional products and are widely available in the market. Incentives to promote the use of super-compliant products containing no or little VOC during ozone season could reduce ozone concentrations when exceedances are typically experienced.

4. *Maximize reductions from existing regulations via enhanced enforcement actions, removal of potential regulatory loopholes, and expanded reporting programs.*

Enhanced enforcement and the tightening of regulatory exemptions that may be used as loopholes in lieu of compliant technologies can lead to reduced emissions. Additionally, recent sales and emissions reporting programs have led to increased understanding of the VOC inventory, incentivized clean technology through fee structures, and better focused

future enforcement and regulatory actions. These enhancements not only ensure that the reductions assumed in the AQMP are actually occurring, but also allow the plan to capture market trends and compliance margins that go beyond the regulatory requirements.

5. *Prioritize emission reductions of the VOC species that are most reactive for ozone and/or PM<sub>2.5</sub> formation and that produce concurrent air toxic or GHG benefits*

The California Air Resources Board has an active reactivity program to investigate the scientific and policy implications of reactivity-based regulations. Reducing emissions of the most reactive species, considering ozone and PM<sub>2.5</sub> formation along with enforceability, toxicity, and climate impacts, may be an efficient method to reduce ambient ozone and PM<sub>2.5</sub> concentrations, achieve multiple environmental and health benefits, while minimizing market disruptions.

6. *Avoid toxicity trade-offs from exempt VOC replacements*

In recent years more and more manufacturers are formulating their compliant products using exempt VOCs, which are VOCs that do not contribute significantly to ozone formation. However, sometimes these compounds may have or be suspected of having health impacts. Their associated potential toxic risks, in comparison with existing products, are a complex issue in terms of how they are being used by workers or the general public and associated work practices to reduce exposure. In some cases, health impacts may involve different health end points (acute vs. chronic or cancer risks) than existing formulations. SCAQMD staff held a one-day technical symposium on this very issue to solicit inputs from experts in the field with no clear conclusions. Emerging from this and other discussions, is a policy debate as to whether we should treat new chemicals as “innocent until proven guilty” (i.e., not toxic until a risk factor is formally assigned by a health agency). In light of the amount of VOC reductions needed for attainment and other available VOC control opportunities, a precautionary approach is recommended that avoids regulatory VOC reductions that could potentially increase the use of more chemicals that are known or suspected to be toxic until it can be demonstrated that they would not create more toxic risks for workers or the public than the compounds they are replacing.

7. *Further evaluation of the practicality and effectiveness for time and place controls*

Most ozone exceedances occur during the months of May through September (the “ozone season”) when higher ambient temperatures and stronger solar intensities accelerate ozone formation rates. In addition, during the ozone season, higher temperatures increase the volatility of organic compounds, leading to accelerated evaporation and larger emissions of precursor compounds. In contrast, PM<sub>2.5</sub> concentrations are typically highest during the winter months when stagnant weather and temperature inversions trap emissions close to the ground. The implications of controlling ozone and PM<sub>2.5</sub> sources differently based on location and season can be evaluated further through modeling exercises.

## 8. Conduct further studies related to VOCs

Over the years, knowledge of the VOC emissions inventory, speciation profiles, and reactivity has improved significantly. Several topics should be further investigated to build a stronger scientific-basis for future VOC control programs. These include optical remote sensing technologies that allow for the detection of emissions in locations where traditional monitoring techniques are not practical. Such fence-line systems could enhance the accuracy of emissions inventories, provide an alarm system in the case of process disruptions, and offer opportunities for real-time feedback for process and emissions control to the facility operator. Furthermore, ongoing and future studies of emissions, evaporation rates, ambient concentrations, ozone formation, and PM<sub>2.5</sub> formation from SVOCs, IVOCs, and LVP-VOCs will help determine if controlling these compounds could assist the attainment strategies for ozone and PM<sub>2.5</sub>.

## 8. Conclusions

While air quality has improved considerably in the SoCAB over the past few decades, further emission reductions must be made to attain the federal standards for ozone and PM<sub>2.5</sub>. The analysis herein indicates that a NO<sub>x</sub>-heavy strategy accompanied by modest VOC reductions will help to avoid temporary increases in ozone concentrations in the western side of the Basin. This finding reaffirms the previous NO<sub>x</sub>-heavy SIP strategies to meet both PM<sub>2.5</sub> and ozone standards, but recognizes that VOC reductions can be given a lower priority. To this end, a strategic VOC control program is recommended for the 2016 AQMP to first maximize co-benefits of NO<sub>x</sub>, GHG, and air toxic controls, followed by controls that could create a win-win, “business case” for the affected entities, incentives for super-compliant products, while ensuring and capturing benefits from implementation of existing rules. When additional VOC controls are still needed, it is recommended to prioritize controls that will produce co-benefits for air toxics, GHGs, with a focus on VOC species that are most reactive in ozone and/or PM<sub>2.5</sub> formation.

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