JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 8010–8022, doi:10.1002/jgrd.50559, 2013

Role of meteorological processes in ozone responses to emission controls in California's San Joaquin Valley

Ling Jin,[1] Aurore Loisy,[1] and Nancy J. Brown[1]

Received 17 September 2012; revised 16 May 2013; accepted 2 June 2013; published 25 July 2013.

[1] We conducted a first-order sensitivity analysis to investigate ozone responses to precursor emissions and source contributions (local versus upwind) for California's San Joaquin Valley (SJV) under four distinct meteorology conditions of summer 2000 using a three-dimensional photochemical transport model. Ozone-limiting reagents, nitrogen oxides (NO_x), or anthropogenic volatile organic compounds (VOCs) (AVOCs) and their transition regime were determined from ozone sensitivity coefficients and delineated spatially at high-ozone locations in the SJV. In general, AVOC-limited areas were located near urban centers, while NO_x-limited areas were located farther downwind. However, the spatial extent of AVOC-limited areas varied with meteorology. Meteorological dependence of predominant ozone-limiting precursors was found to vary significantly among different subregions within the SJV. Specifically, weaker dependences were identified for regions of the southern SJV located farther away from emission sources, where ozone chemistry was mostly limited by NO_x for the episodes considered. Stronger dependences were identified for the central and northern SJV, where ozone chemistry can be limited by NO_x or AVOC depending on meteorology. Source contributions to ozone sensitivities in the SJV were also investigated. Local sources were important for the eastern side of the central SJV, while upwind sources were also important (from ~40% to more than 50% of the total ozone sensitivities) for the western side of the valley, except for the most stagnant episode. Different contributing source regions were identified for the same VOC-limited areas in the northern SJV, and these depended on the flow characteristics. The predominant ozone-limiting reagent was found to exhibit less dependence on meteorology in the central and southern SJV as the baseline NO_x emissions were reduced, ultimately causing ozone formation to be limited by NO_x. In contrast, the VOC-limited areas in the northern SJV continued to be influenced by meteorology for two of the episodes.

Citation: Jin, L., A. Loisy, and N. J. Brown (2013), Role of meteorological processes in ozone responses to emission controls in California's San Joaquin Valley, *J. Geophys. Res. Atmos.*, *118*, 8010–8022, doi:10.1002/jgrd.50559.

1. Introduction

[2] Tropospheric ozone is a secondary pollutant formed by photochemical reactions involving nitrogen oxides (NO_x) and volatile organic compounds (VOCs). Due to its adverse health effect, ozone is designated as a criteria pollutant and regulated by the U.S. Environmental Protection Agency (EPA). Ambient levels of ozone depend not only on its precursor (NO_x and VOCs) emissions but also on meteorological conditions that contribute to air quality through various physical and chemical processes influencing the evolution of emissions and photochemical products [*Seaman*, 2000]. For example, wind circulation alters pollutant transport and accumulation, boundary layer height limits the degree of pollutant dilution, and solar radiation and temperature change chemical reaction rates and biogenic emissions [*Baertsch-Ritter et al.*, 2004; *Dawson et al.*, 2007; *Tao et al.*, 2007]. Important meteorological processes that lead to various types of spatial and/or temporal distributions of elevated ozone concentrations have been investigated in many regions with air pollution problems [e.g., *Sillman and Samson*, 1995; *Dayan and Levy*, 2002; *Edwards et al.*, 2004; *Kleeman*, 2008; *Bloomer et al.*, 2009; *Katragkou et al.*, 2010; *Jin et al.*, 2011]. Not only are ozone concentrations sensitive to meteorological changes but also ozone responses to emission reductions of its precursor species vary with meteorology (as discussed in *Lei et al.* [2008]). Such information is key to designing effective ozone control strategies for regions with diverse meteorological conditions but is a topic covered by fewer studies.

[3] Ozone production regimes are defined by ozone response to changes in emissions of NO_x and VOCs, which we refer to as the characteristics of the ozone limitation chemistry. Theoretically, meteorological parameters (mixing

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[1] Lawrence Berkeley National Laboratory, Berkeley, California, USA.

Corresponding author: N. J. Brown, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA. (njbrown@lbl.gov)

2169-897X/13/10.1002/jgrd.50559

height, temperature, humidity, wind speed, etc.) can be perturbed one at a time to simulate their individual effects on the characteristics of ozone limitation chemistry [e.g., *Baertsch-Ritter et al.*, 2004]. Studies like this greatly enriched our understanding of the dependence of ozone-precursor relationships on meteorology. Practically, there are limitations to considering only the individual effects of meteorological parameters. First, individual meteorological variables associated with different types of ozone episodes generally do not vary independently but are related to one another at the regional level to form "meteorological regimes" governed by synoptic and mesoscale phenomena [*Beaver and Palazoglu*, 2009; *Jin et al.*, 2011]. Moreover, compensating effects may exist on ozone limitation chemistry for different meteorological variables. For example, stagnant conditions, conducive to high ozone levels, are often associated with lower wind speed and higher temperature, while *Raertsch-Ritter et al.* [2004] found that NO_x-limited areas decrease with higher temperature and increase with lower wind speed. Finally, wind directions and flow patterns are important to regional pollutant transport, which affects the source-receptor relationships and ozone chemical regimes along the transport paths [*Fast et al.*, 2002]. However, it is difficult to perturb these variables systematically in air quality models for quantifying their effects on ozone sensitivities.

[4] Investigating the combined meteorological effects on ozone responses to emission controls in a specified region is important. From a regulatory perspective, the key issue is to understand the extent to which the meteorological conditions, commonly occurring (present or future) in the study region, alter the characteristics of the ozone limitation chemistry. *Palacios et al.* [2002] showed that ozone responses were influenced by different transport and dispersion patterns established in the Greater Madrid area. *Lei et al.* [2008] characterized ozone production and responses under three distinctive meteorological categories in Mexico City and found weak dependence of the VOC limitation of ozone production in the urban areas, while *Song et al.* [2010] found that the range of VOC- or NO_x-limited areas depended on meteorology in this area in a more recent campaign year. *Liao et al.* [2007] simulated ozone sensitivities to emissions over the continental U.S. under meteorological conditions of present and future climates and also found a weak dependence of ozone control options (NO_x versus VOC) on meteorological conditions.

[5] California's San Joaquin Valley (SJV) has suffered from some of the worst air in the country and is designated as an "extreme" nonattainment area for the federal 8 h ozone standard. While ozone levels in much of California have fallen steadily over the years, progress in the SJV has been slower with ambient ozone exceeding the 8 h standard more than 100 days a year [*Hall et al.*, 2008]. EPA [*Federal Register*, 2008] has since strengthened the standard to 75 ppb from the previous value of 84 ppb for 8 h ozone, which makes it even more challenging to bring SJV into compliance.

[6] The trough-like topography of the SJV favors pollutant accumulation. Diverse emission sources from both local and occasionally upwind regions, namely, the San Francisco Bay (SFB) area, the Sacramento Valley (SV), and some coastal air basins, further complicate source and receptor relationships and make the SJV ozone control a regional problem [*Pun et al.*, 2000]. A first-order sensitivity analysis conducted previously over a 5 day ozone episode [*Jin et al.*, 2008] delineated the spatial variations in the ozone control options (NO_x versus VOC) in the SJV and found that (1) NO_x control is, overall, more effective for attaining the 8 h ozone standard in the region and (2) ozone sensitivities, especially in the northern part of the valley, were influenced by emissions from upwind air basins, while local contributions dominated most of the SJV. Modeling studies have since been expanded to a full summer season [*Jin et al.*, 2010, 2011] with additional seasonal perspectives gained by identifying statistically determined meteorological regimes that give rise to different spatial distributions of high ozone levels. Whether or not the ozone control options and interbasin contributions derived previously [i.e., *Jin et al.*, 2008] from one ozone episode can be applied to other meteorological regimes has not been investigated. Furthermore, occurrence frequencies of air quality related meteorological conditions in this region are expected to change in future climate [*Zhao et al.*, 2011]. Consequently, understanding the meteorological dependence of ozone sensitivities to emission changes and the local versus upwind contribution is needed to achieve a more comprehensive and effective regional ozone control strategy designed for the SJV for both present and future climates.

[7] In this study, employing the Community Multiscale Air Quality (CMAQ) modeling system [*Byun and Schere*, 2006], we extend the first-order ozone sensitivity analysis to include all four ozone episodes representative of the meteorological conditions found in both observational and modeling studies in the central California region (in *Fujita et al.* [1999] and *Jin et al.* [2011], respectively). The objective of this study is to understand the extent to which meteorological regimes alter the characteristics of the ozone limitation chemistry and the importance of local versus upwind emission contributions to different parts of the SJV. For any given meteorological conditions, simulated ozone production regimes are affected by underlying emission inputs that are subject to uncertainties and temporal changes (e.g., through weekly cycle and/or future emission controls). In response to this, first-order ozone sensitivities are also evaluated for alternative baseline emissions to understand how the meteorological dependence of ozone sensitivities interacts with different emission scenarios. Section 2 introduces the study domain and base case simulations conducted in *Jin et al.* [2011] as well as the model inputs. The selection and characteristics of the four meteorologically representative ozone pollution episodes are described, followed by presentations of sensitivity analysis methods, definitions of ozone control options, and alternative baseline emission cases. Section 3 presents the spatial distributions of first-order ozone sensitivities, ozone control maps, local versus upwind contributions, and changes in the characteristics of ozone-limiting chemistry under alternative emission cases. A summary of conclusions is provided in section 4.

2. Data and Methods

2.1. Study Domain and Data

[8] CMAQ v4.5, with the same configuration used in *Jin et al.* [2010, 2011], is applied to simulate hourly ozone mixing ratios over the Central California Ozone Study domain

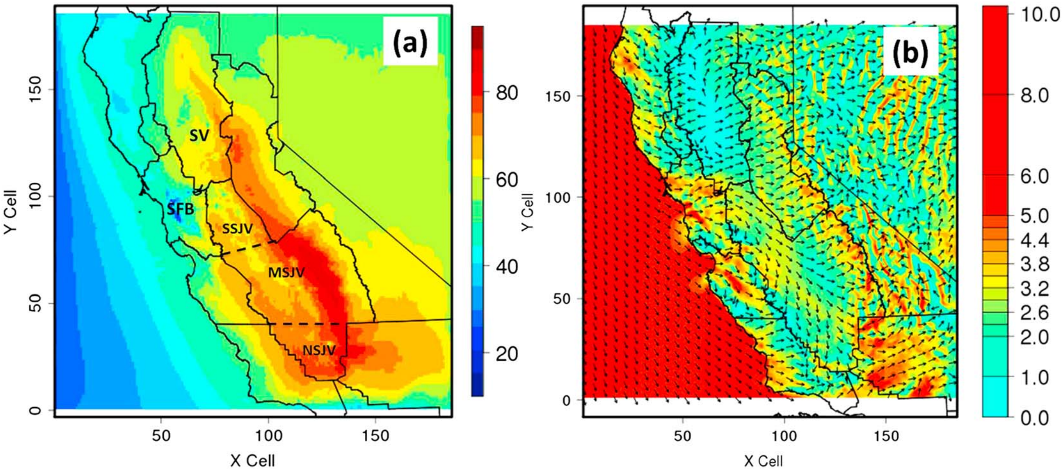

Figure 1. Summer average (a) 8 h ozone concentrations (ppb) and (b) wind fields for the interval [11 A.M., 6 P.M.] PDT. Major air basins are shown on the ozone map, and wind speed (m/s) is color coded.

(shown in Figure 1). The domain is gridded into 185 by 185 cells, with a horizontal grid spacing of 4 km. Vertically, the domain is divided into 27 layers from the surface to about 17 km. The Central Valley is surrounded by the Sierra Nevada and coastal mountains ranges. The San Francisco Bay (SFB) area and Sacramento Valley (SV) are the major upwind emission sources affecting air quality in the San Joaquin Valley (SJV). The SJV is further divided into northern (NSJV), central (MSJV), and southern (SSJV) parts as shown on the map. Hourly gridded emission inputs were obtained from the California Air Resources Board (CARB) with day-of-week differences in anthropogenic sources and day-specific biogenic emissions. Hourly meteorological fields were simulated with the PSU/NCAR mesoscale model (MM5). More detailed descriptions of the input data, model configuration, and performance evaluation are reported in *Jin et al.* [2010] for the summer of year 2000 (June to September).

[9] To isolate the meteorological effects, emission inputs in this study are modified as were done in *Jin et al.* [2011]: Anthropogenic emissions are not varied day to day and instead use a profile identical to typical Monday emissions, light- and/or temperature-sensitive biogenic emissions (mainly isoprene and terpenes) are allowed to vary with meteorology, and fire emissions are excluded. Summerlong CMAQ simulations with this emission setup have been conducted by *Jin et al.* [2011], and their model outputs are used as the study *base case*.

[10] Summer averaged 8 h ozone and surface wind fields are shown in Figure 1 for the [11 A.M., 6 P.M.] hour interval, when most daily 8 h ozone maxima occur (Figure S1 in the supporting information). Our analysis focuses on the SJV basin, where high ozone levels are concentrated and both CMAQ and MM5 perform better [*Jin et al.*, 2010] than other air basins. The average wind fields (Figure 1) reveal that the prevailing daytime summer flow is driven largely by mesoscale phenomena. Thermally induced pressure gradients between land and sea force the marine air to move through the SFB into the Central Valley, where orographic effects split the flow with the majority directed into the SJV. The down-valley flow exits at the southern end into the Mohave Desert. Within the SJV, thermal contrast between the Sierra Mountains and valley surface creates pressure gradient to drive upslope flow during the day. These flow patterns directly influence the transport of pollutants when they are photochemically active.

2.2. Ozone Episodes

[11] *Jin et al.* [2011] (hereafter referred to as "the cluster paper") applied cluster analysis to model simulation data for California's San Joaquin Valley (SJV) for the purpose of identifying meteorologically representative ozone pollution conditions for the summer of year 2000. Summer days were categorized according to their spatial distributions of ozone concentrations in the SJV, which were largely driven by meteorology. Ozone clusters in the SFB and SV were also identified for investigating the interbasin relationships between the SJV and its major upwind air basins (see Figure S2 for daily cluster memberships). Four SJV ozone clusters associated with moderate to high ozone levels were determined: three of them with elevated ozone concentrations relatively to the north, south, and west of the SJV and the fourth one with higher ozone levels throughout the valley. For convenience, these four conditions are referred to as "O_3-North," "O_3-South," "O_3-West," and "O_3-All." Despite the variability of ozone episodes within each cluster, the four episodes to be chosen in this study are intended to provide different "modes" of the joint distribution of individual meteorological variables that are representative of various ozone-forming conditions in the San Joaquin Valley. As shown in *Jin et al.* [2011], the O_3-North, O_3-South, and O_3-West conditions are statistically distinctive from each other by the flow-induced spatial variations in ozone concentrations, while O_3-All has statistically higher ozone associated with higher temperatures throughout the domain. Four ozone episodes representative of these conditions are identified: 23 to 25 June (O_3-North), 14 to 17 August (O_3-South), 17 to 20 September (O_3-West), and 29 July to 2 August (O_3-All), according to their cluster memberships, relationships to the SFB, and SJV ozone levels, as well as their occurrences in historical ozone observations, which will be described next.

[12] Ozone anomalies (i.e., episode average − seasonal average) and prominent circulation patterns are illustrated in Figure 2 for the four episodes. Synoptic conditions in these episodes give rise to the deviations of temperature, pressure,

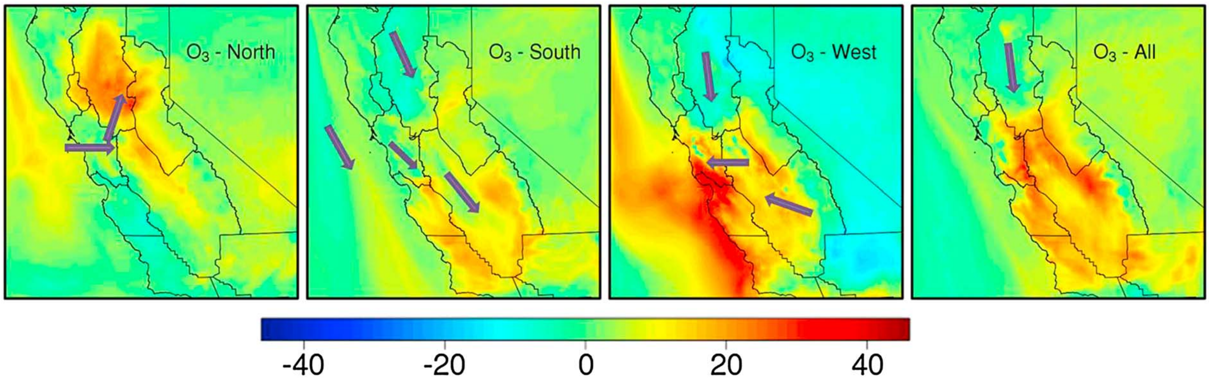

Figure 2. Eight hour ozone anomalies (ppb) for the four representative ozone episodes of the base case simulations with arrows illustrating the featured transport patterns.

and wind fields from their seasonal averages at the regional scale that result in different spatial patterns of elevated ozone anomaly levels.

[13] The *O_3-North* episode occurs under a pressure trough associated with relatively ventilated conditions. Higher temperatures are observed in the SV and the northern part of the domain (Figure S4). The sea surface pressure anomalies in this episode (Figure S5) indicate a pressure gradient (from south to north) that weakens northerly winds and strengthens southerly flow in the SV and creates a stronger westerly flow through the SFB. As a result, pollutant concentrations increase in the northern part of the SJV and in the SV basin.

[14] The *O_3-South* episode occurs under a “western U.S. high” anticyclone system located inland with higher temperatures in the eastern and southern parts of the domain (Figure S4). The sea surface pressure anomalies under this synoptic condition give rise to a strong northern westerly flow (Figure S5), enhancing the down-valley and upslope ventilation flows in the SJV. As a result, pollutant concentrations increase in the southeastern part of the valley and the SV and SFB are relatively clean.

[15] The *O_3-West* episode is under the influence of an “eastern Pacific high” system which heats up the ocean and coastal areas where higher temperature levels are observed (Figure S4). An enhanced surface pressure gradient from land to sea (Figure S5) leads to very stagnant conditions. With weakened onshore flows (from west to east), pollutant concentrations tend to increase on the western side of the SJV and in the SFB coastal regions.

[16] The above three episodes with their ozone concentration levels in the three air basins (SJV, SFB, and SV) have temperature and flow conditions that are also found to be representative of those observed frequently in historical years (see *Fujita et al.* [1999], with a summary in the supporting information).

[17] The *O_3-All* episode features a persistent western U.S. high system with light winds and much higher temperatures over the land than other episodes. The flow pattern resembles the summer mean because the wind anomalies (episode average − seasonal average) are generally small (Figure S6) with slightly enhanced southward flow in the SV. Elevated ozone levels are observed in much of the SJV, SFB, and SV metropolitan areas.

[18] Surface temperature, pressure, and wind fields as well as the 500 mbar geopotential heights representing synoptic conditions are averaged for the four episodes and provided in Figures S3–S7.

[19] Sensitivity simulations were previously conducted for the O_3-All episode for a smaller domain [*Jin et al*., 2008] to investigate ozone formation and transport. The study domain has since been expanded to include more areas upwind of the SJV. In this study, we extend our sensitivity analysis to include all four episodes. The four episodes are expanded to 5 days (Table 1) by including additional days at the beginning and using the first 2 days for model spin-ups. The meteorological parameters (temperature, wind, mixing layer height, humidity, etc.) and chemical simulation results presented in this study are 8 h averages over [11 A.M., 6 P.M.] (referred to as “afternoon” for simplicity) for the last 3 days of each simulated episode.

2.3. First-Order Ozone Sensitivity Coefficient

[20] The first-order seminormalized ozone sensitivity (defined below) to emitted NO_x or anthropogenic volatile organic compounds (AVOCs) from the whole domain or selected subregions (SFB, SJV, and SV) is approximated by a brute force perturbation of the respective emissions by +10% relative to their nominal values for the four ozone episodes. So here, $\partial p_i = 10\% \times P_i$ and $\epsilon = 10\%$ in equation (1):

$$S_i^{(1)} = P_i \frac{\partial C}{\partial p_i} = \frac{\partial C}{\partial \epsilon_i} \approx P_i \frac{C^{+10\%} - C}{10\% \times P_i} = \frac{C^{+10\%} - C}{10\%}, \qquad (1)$$

where P_i is the emission parameter (i.e., emissions from the whole domain or selected air basins), whose perturbation p_i

Table 1. Definition of Modeling Periods

Condition Categories	Ozone Episodes	Modeling Periods
O_3-North	June episode: 23 to 25 June (days 175–177)	21 to 25 June
O_3-South	August episode: 14 to 17 August (days 227–230)	13 to 17 August
O_3-West	September episode: 17 to 20 September (days 261–264)	16 to 20 September
O_3-All	July–August episode: 29 July to 2 August (days 211–215)	29 July to 2 August

is considered in a relative sense by defining a scaling variable ϵ_i, with its nominal value (unperturbed) being 1; C is the species concentration with the base case emissions; and $C^{+10\%}$ is the concentration simulated by perturbing the emissions by +10%. These first-order seminormalized sensitivity coefficients represent ozone concentration changes per unit change in emission parameter if the system is linear. It can be used to calculate pollutant responses to reductions in emissions by up to 25% in general [*Cohan et al.*, 2005] when the linearity holds. For example, $S_i^{(1)} = a$ (ppb) implies that a ±25% change in the emissions would cause (±0.25α) ppb change in the ozone concentration while all other parameters are held constant.

[21] Ozone sensitivities to domain-wide anthropogenic NO_x emissions $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}}\right)$ and to anthropogenic VOC (AVOC) emissions $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{AVOC}}}\right)$ are used to determine ozone-limiting reagents, while ozone sensitivities to emissions from individual air basins are used to evaluate local versus upwind contributions to the SJV ozone sensitivities.

2.4. Ozone Control Options

[22] Three ozone control options are defined, based on the relationship between the two sensitivity coefficients $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}} \text{ and } \frac{\partial[O_3]}{\partial\epsilon_{E_{AVOC}}}\right)$ following *Jin et al.* [2008]:

$$\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}} < 0 \quad \textit{VOC control},$$

$$\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}} > \frac{\partial[O_3]}{\partial\epsilon_{E_{AVOC}}} > 0 \quad \textit{NO}_x\ \textit{control},$$

$$0 < \frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}} < \frac{\partial[O_3]}{\partial\epsilon_{E_{AVOC}}} \quad \textit{transition}.$$

[23] The "VOC control" option is preferred when reducing AVOC reduces ozone concentration and reducing NO_x emissions would increase ozone concentrations (NO_x disbenefit). The "NO_x control" option is preferred when a percentage reduction in NO_x emissions results in larger decreases in ozone concentrations than the same percentage reduction in AVOC emissions. Between these two options, the third option is in a transition regime, where reducing NO_x emissions can reduce ozone concentrations but is not as effective as reducing AVOC by the same percentage.

2.5. Alternative Base Case Emissions

[24] The relationship between meteorological conditions and ozone sensitivities to precursor emissions can interact with the underlying nominal emission levels (base case) that are subject to uncertainties and temporal changes. CMAQ predictions of ambient AVOC and total reactive nitrogen for the whole summer period were found to have domain-wide normalized biases of 23% and 3%, respectively, when compared to observations. This most likely reflects the uncertainties in both modeled results and observations, but it does indicate uncertainties in emission inputs [*Jin et al.*, 2010]. This study employs identical anthropogenic daily emissions (Monday) to isolate meteorological effects. Weekend human activities are different from those on weekdays [e.g., *Tonse et al.*, 2008]. About 16% and 25% lower NO_x emissions, respectively, from area and mobile sources are inventoried on weekends than on weekdays for the modeling period [*Jin et al.*, 2010]. Emissions have also experienced longer-term changes since our modeling year of 2000. A recent study has shown a downward trend of NO_x emissions in recent years from the SJV mainly due to the economic downturn, with 20% lower NO_x emitted in 2010 than in 2000 [*McDonald et al.*, 2012].

[25] To understand whether the meteorological dependence of ozone control options may hold under different emission scenarios, ozone sensitivities are also calculated after altering the base case emissions by 20% (as defined below) in the four ozone episodes. Ozone control options are evaluated based on the sensitivities calculated under these alternative emission cases.

[26] The new alternative base cases (nominal values) are defined as follows:

[27] Case "mAVOC": AVOC emissions are reduced by 20%.

[28] Case "mNO_x": NO_x emissions are reduced by 20%.

[29] Case "mBoth": Both AVOC and NO_x emissions are reduced by 20%.

3. Results and Discussions

3.1. First-Order Ozone Sensitivities and Control Options

[30] To evaluate ozone control options for the SJV, first-order seminormalized ozone sensitivities to the domain-wide emissions of AVOC and NO_x are calculated. Ozone sensitivities to AVOC (Figure 3, second column) are positive throughout the domain, which indicates that reducing AVOC leads to lowered ozone levels. Greater ozone sensitivities to AVOC tend to be located in the areas where NO_x emissions are also large. Ozone sensitivities to NO_x change signs (Figure 3, first column). The negative sensitivities indicate a NO_x disbenefit. In general, the urban areas, namely, the Bay area, Sacramento, and urban areas in the SJV, such as Fresno and Bakersfield, all exhibit a NO_x disbenefit for the various meteorological conditions associated with the different episodes. The spatial extent of the NO_x disbenefit areas changes from episode to episode, especially for the northern part of the SJV.

[31] Ozone control options maps (Figure 3, third column) are evaluated for the cells where the afternoon 8 h average ozone concentrations are over 75 ppb (referred to as "high ozone" hereafter). This ozone level is the current national ambient air quality standard for ground-level ozone and is referred to as the 2008 standard. The white areas are those where the 8 h average ozone concentrations do not exceed the 2008 standard, and the colored areas indicate the extent of ozone exceedances. All episodes except the O_3-North episode exhibit extensive ozone exceedances especially for the O_3-All condition. The spatial trend in ozone control options is similar for the episodes: VOC control near urban and emission centers and NO_x control in rural areas. However, the extent of the NO_x disbenefit areas (i.e., VOC controlled, colored in red) varies across the meteorological conditions associated with the various episodes. Focusing on a single ozone episode (July–August, O_3-All), in a previous study, *Jin et al.* [2008] found that NO_x control was, overall, more beneficial for reducing 8 h ozone in the SJV. By considering different meteorological conditions, we can see that NO_x control is the dominant option for the O_3-South and O_3-All episodes,

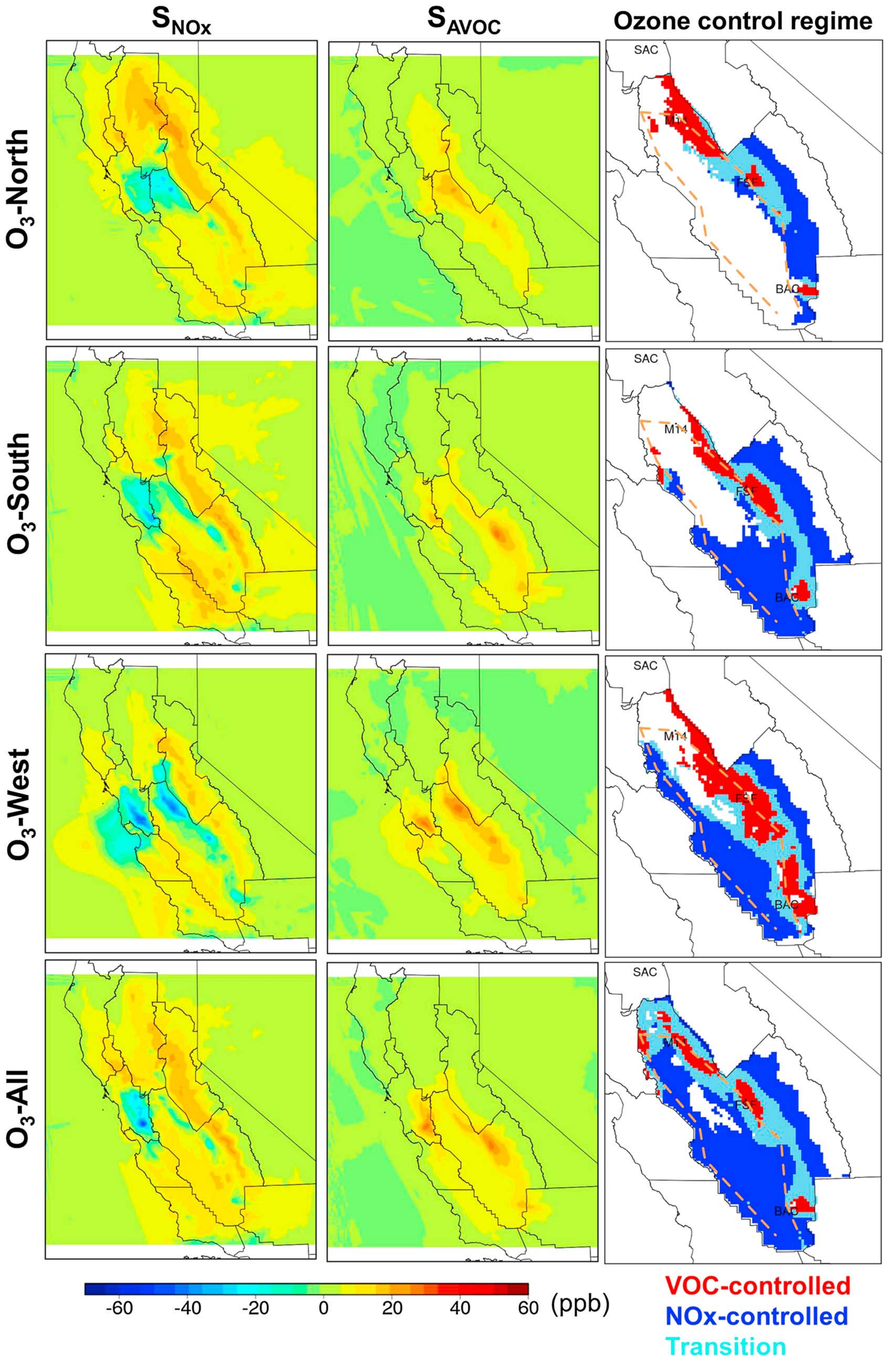

Figure 3. Afternoon 8 h ozone seminormalized sensitivities (ppb) to NO_x and AVOC and ozone control regimes in the SJV for each episode. Control options are color coded: VOC controlled (red); NO_x controlled (dark blue); transition regime (light blue). White in the SJV indicates areas where the 8 h average ozone does not exceed 75 ppb. Cities are labeled in the control option maps: Modesto (M14), Fresno (FSF), Bakersfield (BAC), and Sacramento (SAC). Dashed lines mark the eastern and western transects used in Figure 4.

Table 2. Effects of Meteorology-Related Parameters on Ozone Sensitivities to NO$_x$ and AVOC Identified in the Past Literature

Increasing Meteorological Related Variables	Effects on Ozone Sensitivities to NO$_x$ Versus AVOC
Temperature	Increases ozone sensitivity to AVOC and decreases sensitivity to NO$_x$ [*Jin et al*., 2010]; increases VOC-limited areas [*Baertsch-Ritter et al*., 2004].
Absolute humidity	Increases NO$_x$-limited areas and decreases VOC-limited areas [*Baertsch-Ritter et al*., 2004].
Temperature and humidity	Increases NO$_x$-limited areas and decreases VOC-limited areas [*Baertsch-Ritter et al*., 2004].
Temperature and biogenic emissions	Increases NO$_x$ limitation (*Jin et al*. [2008] and *Baertsch-Ritter et al*. [2004] both found small effects).
Wind speed	Depends on treatment of point sources in the model [*Baertsch-Ritter et al*., 2004].
Mixing height	Increases ozone sensitivity to NO$_x$ and shifts chemistry to NO$_x$ limitation [*Jin et al*., 2010]; increases NO$_x$-limited areas and decreases VOC-limited areas [*Baertsch-Ritter et al*., 2004].
Ventilation rate (= wind speed × mixing height)	Shifts ozone chemistry to NO$_x$ limitation [*Sillman*, 1995; *Biswas and Rao*, 2001].

when it accounts for 64% and 63%, respectively, of the high-ozone locations. Increased importance in AVOC control (colored in red) is identified in the O$_3$-North and O$_3$-West conditions, when NO$_x$-controlled high-ozone locations are reduced to 45% and 47%, respectively, in the SJV.

[32] Meteorological dependence of ozone control via NO$_x$ or AVOC limitation varies greatly by location (Figure S8). The dominant control options for the *southern SJV* show weak dependence on the meteorological conditions considered here, with NO$_x$ control benefiting the major portion (58% to 78%) of the area throughout all episodes while improvements from VOC control are limited to the urban centers. The control options in the *northern* and *central* SJV depend on meteorology. Ozone chemistry (of locations with high ozone) in the *northern SJV* is generally VOC limited (54~83% VOC controlled in three episodes), and the situation changes under the O3-All condition (20% areas are VOC controlled) with an increased percentage of NO$_x$-controlled grids as high ozone levels are extended to more rural areas. High ozone levels in the *central SJV* (*MSJV*) are generally limited by NO$_x$ (56~70% areas are NO$_x$ controlled in three episodes) except for the emission centers in the urban areas and along the highways. However, VOC control extends farther into the rural areas in the MSJV under the O$_3$-West conditions, while the percentage of NO$_x$-controlled grids is reduced (45% areas are NO$_x$ controlled). In this case, NO$_x$ control that works well for other episodes would result in an increase in ozone concentrations in some of the rural locations.

[33] Since anthropogenic emissions are held constant across the episodes, the aforementioned differences in ozone sensitivities and control options among episodes result from changes in meteorology. Effects of isolated meteorological variables on ozone sensitivities and NO$_x$ versus VOC limitation were investigated in past studies with findings summarized in Table 2.

[34] Higher rates of peroxyacetylnitrate (PAN) decomposition were found to be the most important reason for the enhanced ozone production under higher temperatures [*Baertsch-Ritter et al*., 2004]. Increased availability of NO$_2$ associated with decreased PAN formation shifts ozone chemistry toward VOC limitation with higher temperatures.

[35] Quantities such as absolute humidity and biogenic emissions that vary with temperature can also alter the ozone-limiting chemistry. Higher absolute humidity associated with higher temperature enhances the formation rate of OH radicals, which leads to faster removal of NO$_2$ by termination reactions as well as increased formation of peroxy radicals through VOC + OH oxidation. As a result, ozone chemistry is shifted toward NO$_x$ limitation under higher absolute humidity, which counteracts the temperature effects. Increased biogenic emissions that occur with higher temperature generally enhance NO$_x$ limitation. Biogenic emissions are similar for the O$_3$-North, O$_3$-South, and O$_3$-West episodes and are higher (~25% higher in isoprene and ~8% higher in terpene) in the O$_3$-All episode due to its higher temperature. However, for the O$_3$-All conditions, biogenic emissions were found to exert rather small effects on ozone sensitivities to NO$_x$ as they are largely not collocated with anthropogenic sources [*Jin et al*., 2008]. In addition, the study conducted by *Steiner et al*. [2008] under the O$_3$-All conditions found that the biogenic VOC emissions (isoprene and terpenes) were only a small fraction of the total VOC reactivities in the SJV region.

[36] Wind speed, mixing height, and ventilation rates affect the rate at which pollutants are diluted. Under more ventilated conditions, NO$_x$ concentrations are reduced and ozone chemistry is shifted toward NO$_x$ limitation, while under very stagnant conditions, concentrated NO$_x$ titrates ozone over larger areas, leading to an increase in the VOC-limited locations.

[37] As discussed previously, individual meteorological variables associated with different types of ozone episodes generally do not vary independently but are related to one another at the regional level. The ozone episodes studied here provide different modes of the joint distribution of individual meteorological variables that are representative of the ozone-forming conditions in the SJV. Table 3 summarizes the episodic averaged meteorological anomalies in different parts of the SJV as well as their summer averages including surface temperature and humidity, mixing height, and ventilation rate (mixing height multiplied by surface wind speed).

[38] All the episodes are warmer than the seasonal averages. The O$_3$-All episode exhibits the highest temperature and absolute humidity levels, while O$_3$-South exhibits the lowest. The atmospheric condition is the most stagnant in the O$_3$-West episode and the most ventilated in the O$_3$-North episode as indicated by mixing heights and ventilation rates.

[39] For *the central and southern SJV*, the differences in ozone control options observed in Figure 3 can largely be explained by the joint effects of these scalar meteorology quantities. For example, the VOC-limited area expands significantly under the most stagnant O$_3$-West condition, while it is more confined to urban centers under the most ventilated O$_3$-North condition. Higher humidity in the O$_3$-All episode produces much higher OH levels than those in the O$_3$-South episode (Figure S9) that shifts the overall ozone chemistry slightly in the central SJV toward NO$_x$ limitation (with slightly reduced VOC-controlled areas) than the O$_3$-South condition, despite the O$_3$-All higher temperatures.

[40] For *the northern SJV*, meteorological conditions described by the scalar quantities in Table 3 might suggest

Table 3. Summary of Afternoon Averaged Meteorological Variables for Different Parts of the SJV[a]

	Surface Temperature (K)			Surface Humidity (g/kg)			Mixing Height (m)			Ventilation Rate (m^2/s)		
	NSJV	MSJV	SSJV	NSJV	MSJV	SSJV	NSJV	MSJV	SSJV	NSJV	MSJV	SSJV
O_3-North	2.5	1.8	2.2	0.6	0.4	0.3	81	128	228	16	384	1196
O_3-South	1.1	2.1	1.8	0.0	0.1	0.1	−38	−78	−144	173	−97	−601
O_3-West	2.4	2.1	2.1	0.8	−0.2	0.4	−256	−173	−224	−1377	−877	−918
O_3-All	7.1	6.4	7	2.2	1.6	1.5	−5	−30	−56	−331	−105	−396
Summer average	310	300	310	9.1	8.4	8.2	580	607	813	1958	2126	2624

[a]Episodic anomalies (episodic average − summer average) for four episodes as well as the summer averages are presented.

to an opposite ozone control option from that indicated in Figure 3. VOC limitation dominates the O_3-North episode while the scalar quantities presented here, namely, lower temperature, moderate humidity, and more ventilation, all provide favorable conditions for NO_x limitation. Besides these scalar quantities, wind directions or flow patterns provide additional constraints on the ozone-limiting chemistry in this region.

3.2. Local Versus Upwind Contributions

[41] The transport patterns (wind flows) affect the source-receptor relationships and ozone chemical regimes along the transport paths, which differ from episode to episode. The interbasin transport effect is especially important for the SJV ozone response to NO_x emissions due to the nonlinearity characteristics of the chemistry (i.e., $\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}}$ changes signs). NO_x emissions from large upwind sources (e.g., in an urban plume) first titrate ozone, resulting in negative ozone sensitivities to NO_x. As NO_x emissions are transported farther downwind, they contribute to ozone formation by increasing the supply of odd oxygen ($NO_2 + O_3$), resulting in positive ozone sensitivities to NO_x [*Jin et al.*, 2008]. To illustrate the local and upwind contributions to the SJV ozone responses to NO_x emissions, the total sensitivity $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}}\right)$ is decomposed into contributions from the local $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{SJVNO_x}}}\right)$ and upwind air basins $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{SFBNO_x}}} \text{ and } \frac{\partial[O_3]}{\partial\epsilon_{E_{SVNO_x}}}\right)$. The episodic averages are plotted (Figure 4) at grid cells along two transects (illustrated in Figure 3) to illustrate their spatial evolution along the eastern and western sides of the SJV, where high ozone levels occur. Both transects start from the same location at the border between the SFB and SJV in the northern SJV and move downwind toward the southern SJV. The western side of the SJV is largely limited by NO_x emissions except the northern part, which is closer to the emissions from the SFB and SV. The eastern transect runs along Interstate 5 and urban centers where NO_x disbenefits occur $\left(\frac{\partial[O_3]}{\partial\epsilon_{E_{NO_x}}} < 0\right)$. The sum of sensitivities from the three air basins (SJV, SFB, and SV) generally does not equal the total sensitivity (black dotted line) because emissions from the other air basins also play a role.

[42] The SFB NO_x emissions generally reduce ozone levels through titration in the northern SJV and contribute positively to ozone levels farther downwind, while the SV NO_x emissions generally exhibit positive contributions throughout the SJV because the transects start farther away from it. $\frac{\partial[O_3]}{\partial\epsilon_{E_{SFBNO_x}}}$ and $\frac{\partial[O_3]}{\partial\epsilon_{E_{SVNO_x}}}$ provide direct means to quantify the importance of the effects of transported pollutant on the SJV ozone sensitivities with their magnitude and spatial extent depending on the flow characteristics of the episodes.

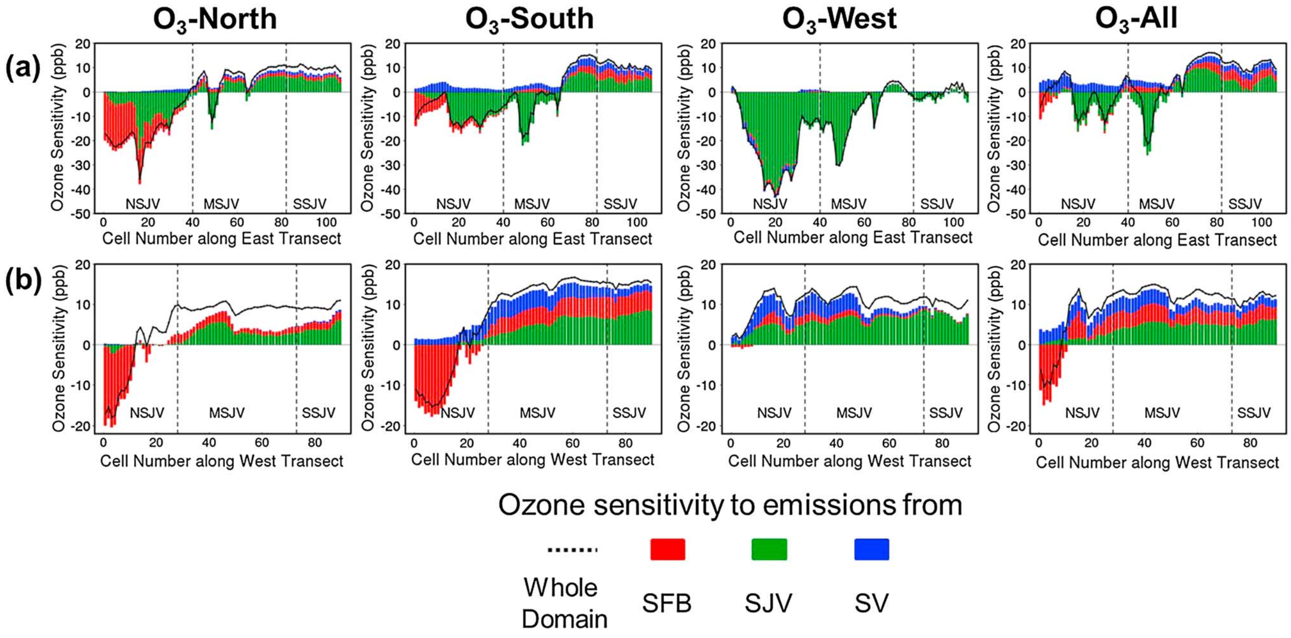

Figure 4. Afternoon 8 h ozone sensitivities (ppb) to NO_x and decomposition of contribution from subregions (SJV, SFB, and SV) in four episodes along the (a) eastern and (b) western transects.

[43] Under O_3-North conditions, enhanced eastward transport leads the SFB emissions to penetrate farther into the northern SJV along the eastern transect. As a result, SFB emissions contribute to extensive NO_x disbenefit areas as we have seen in Figure 3, a phenomenon that was not explained by the scalar meteorological parameters considered previously. The weakened southward flow in this episode reduces the impact of SFB emissions farther downwind, and the SV emissions show minimum effects on the SJV ozone. Large gaps along the western transect between the total sensitivity (black dotted line) and the sum of subregional sensitivities considered here indicate important contributions from other coastal emissions in this episode due to the strengthened westerly flows.

[44] The enhanced southward transport under O_3-South conditions causes a wider spread of NO_x disbenefit areas of SFB emissions in the northern SJV *along the western transect* than other episodes and increases the positive contributions of both the SFB and SV farther south which account for more than 50% of the total sensitivities. The NO_x disbenefit areas along the *eastern transect* are also slightly enhanced by the SFB emissions in the northern SJV while positive contributions of both SFB and SV spread farther south.

[45] Stagnant conditions during the O_3-West episode feature the weakest eastward transport as well as slower southward transport within the SJV, which greatly reduces the influence of SFB emissions on the SJV ozone. Local (SJV) emissions dominate ozone sensitivities along the eastern transect with an extensive spread of the NO_x disbenefit areas. Increased contributions of the SV emissions are only observed along the western transect but are limited to the northern half of the SJV.

[46] The regional flow pattern in the O_3-All episode resembles the O_3-South episode but with a weaker southward flow than the latter in the SJV. As a result, the NO_x disbenefit areas caused by SFB emissions are reduced in the northern SJV and the sensitivities are smaller in this episode than in O_3-South.

[47] In general, along the *eastern transect*, only the central SJV exhibits weak dependence on meteorology, where local contributions always dominate and determine the signs of the total sensitivities, while the northern and southern SJV both depend on the meteorology where interbasin contributions play important roles except for the O_3-West condition. Along the *western transect*, upwind sources exert greater influences on the total sensitivities especially in the northern SJV. Decreases in NO_x emissions of both local and upwind sources can benefit the ozone control in the NO_x-limited regions on the western side of the valley. Important upwind source regions also change with meteorology. The SFB and SV are largely the major upwind contributors. However, under O_3-North conditions, the SV contribution diminishes and the increased SFB contribution is limited to the northern SJV, while coastal contributions increase greatly along the western transect throughout the SJV.

[48] Control of AVOC emissions is important for the northern SJV as well as for the urban areas in the central and southern SJV. VOCs have a longer lifetime than NO_x [*Finlayson-Pitts and Pitts*, 1997] in the air, so they are more likely to be transported farther downwind and can capture better how wind fields influence the transport of pollutants. As ozone sensitivities to AVOC are always positive (Figure 3), the importance of local emissions versus interbasin transport can be conveniently presented with the metric "contribution of SJV AVOC emissions" defined below:

$$\text{Contribution}_{\text{SJV,AVOC}}\ (\%) = \frac{S_{\text{SJV,AVOC}}}{S_{\text{AVOC}}} \times 100, \qquad (2)$$

where $S_{\text{SJV,AVOC}}$ is the sensitivity to SJV AVOC emissions and S_{AVOC} is the ozone sensitivity to domain-wide AVOC emissions. A "contribution map" is shown in Figure 5: Contributions greater than 50% indicate a major local influence, while contributions less than 50% indicate a greater contribution from upwind air basins, i.e., the sum of all upwind air basins except the SJV. In this manner, we can develop the notion of a "contribution pattern," i.e., how local and upwind contributions spatially evolve within an episode, and evaluate the variability of this pattern with meteorology.

[49] The contribution maps generally present a contrast between west and east with the upwind influences dominating the western side of the SJV while local influences dominate the eastern side where VOC limitation usually occurs. Distinctive contrast is seen for the O_3-North and O_3-West conditions. In the O_3-North episode, the local contributions (%) are the smallest throughout the SJV among all the episodes, and the upwind contributions dominate the entire northern SJV including those VOC-limited locations where local sources exert greater influences in other episodes. Effective ozone control here would require reduction of both local and upwind AVOC emissions. In the O_3-West episode, however, the local contributions increase greatly and expand farther west, covering part of the northern SJV and the entire southern SJV. The ozone control in the VOC-limited areas here can be well achieved by reducing local AVOC emissions. Increased importance of VOC controls was previously identified for these two episodes (Figure 3), and the results presented here have highlighted the differences in their targeted source regions governed by the distinctive flow characteristics.

[50] The flow characteristics that *Zhao et al.* [2011] simulated under future climate showed overall decreased ventilation rates in the SJV and identified a wind anomaly from the southwest (i.e., southwesterly winds) that enhances the sea breezes as the result of higher temperature rise over the land than ocean. The enhanced southwesterlies can reduce the contributions from the SV to the SJV while increasing the contributions from the SFB and coastal areas to the northern and western parts of the SJV, like the behavior seen under the O_3-North flow pattern. The local contributions within the eastern side of the valley would be strengthened with the increasing overall stagnation.

3.3. Alternative Base Case Emissions

[51] The spatial distribution of both high ozone levels and their sensitivities to emission reductions under a given set of meteorology is also a function of the underlying emissions, which are subject to uncertainties and changes. First-order sensitivities to domain-wide emissions are calculated under alternative baseline emissions, where emitted AVOC, NO_x, or both are reduced by 20% (mAVOC, mNO_x, and mBoth, respectively). The derived control options at high-ozone locations under these alternative emission cases are compared to the ones under the original base case (hereafter called "OrigBase") to investigate the influences of baseline emissions on the meteorological dependence of choices of ozone control in the SJV.

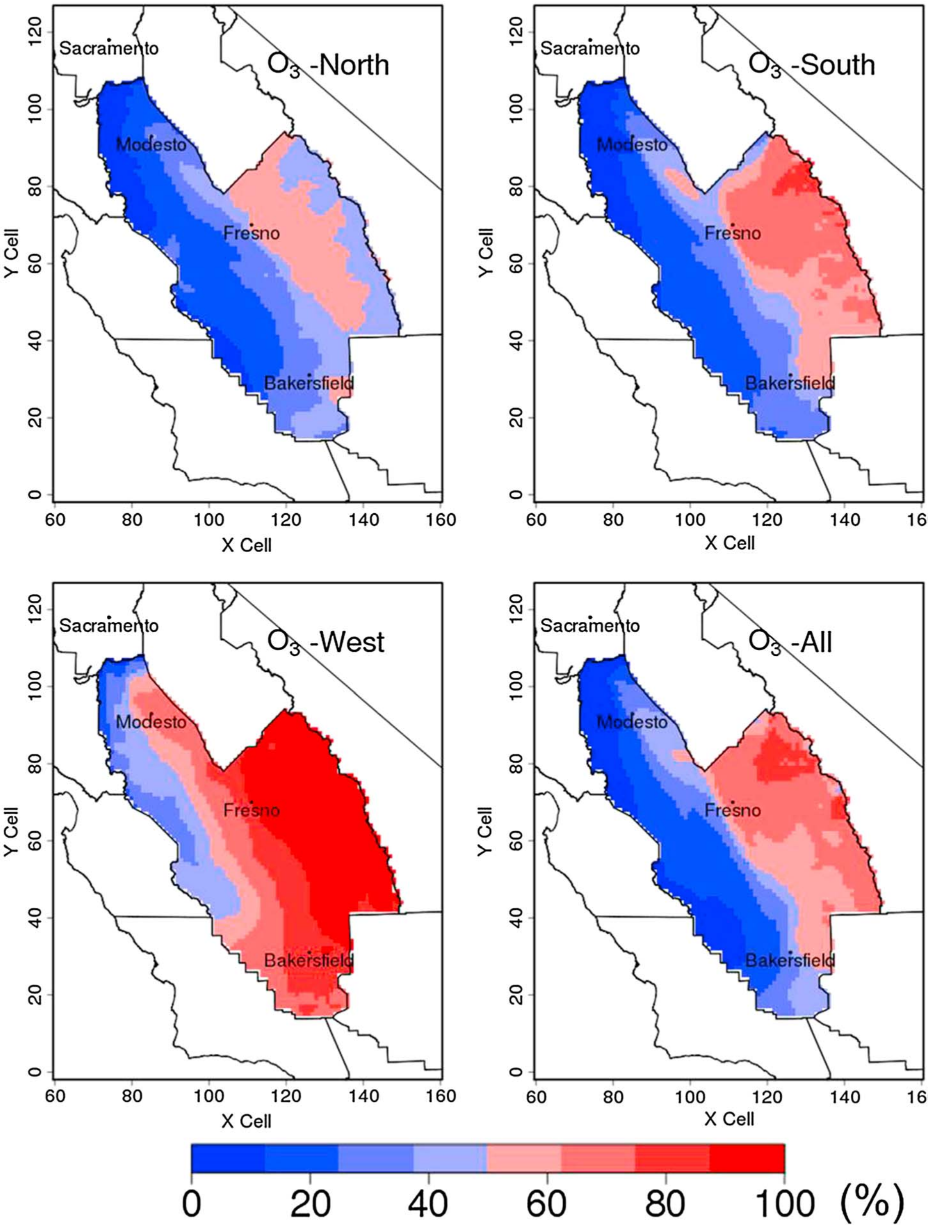

Figure 5. Contribution maps associated with each episode that indicate the relative importance of local versus upwind contributions to ozone sensitivity to AVOC. Light blue to dark blue colors indicate that the larger contributions come from upwind air basins (i.e., <50% from local sources). Pink to red colors indicate that the larger contributions to the sensitivity come from the local air basin (i.e., >50% from local).

[52] For our studied periods and domain, reducing AVOC emissions (i.e., mAVOC) has a smaller impact on the ozone sensitivities than reducing NO_x or reducing both (i.e., mNO_x or mBoth), which can be seen in the difference maps shown in Figure S10. In particular, $\frac{\partial[O_3]}{\partial \epsilon_{E_{NO_x}}}$ increases greatly as baseline NO_x is reduced in the mNO_x and mBoth cases. Throughout all the alternative baseline emission cases, the percentage of VOC-controlled areas in the SJV under the O_3-North and O_3-West conditions is greater than that under the O_3-South and O_3-All conditions, while the opposite is true for the NO_x control options (Figure S11), which is similar to the behavior observed in the OrigBase case. In an absolute sense, a reduction in AVOC emissions exerts small effects on control options as we can see that mAVOC is similar to OrigBase and mNO_x is similar to mBoth (Figures S10 and S11). On the other hand, reductions of NO_x (in mNO_x or mBoth) simultaneously increase NO_x-limited areas and decrease VOC-limited areas, which leads to the majority of the high-ozone locations (55%~80%) in the SJV requiring NO_x control for all the meteorological conditions (Figure S11).

[53] Spatially (Figure S12), the resulting changes in control options are limited to regions close to large emission sources (Fresno, Bakersfield, or the northern SJV). Similar distributions of control options are seen between the mAVOC and OrigBase cases. On the other hand, NO_x control and transition areas expand as VOC-controlled areas reduce greatly under the mNO_x or mBoth cases. This is

Table 4. Percentage of VOC-Controlled High-Ozone Grid Cells in the Three Subregions of SJV Under Different Baseline Emission Cases and Meteorological Conditions

	O_3-North	O_3-South	O_3-West	O_3-All
		NSJV		
OrigBase	83%	60%	54%	20%
mAVOC	89%	58%	52%	28%
mNO_x	57%	15%	44%	2%
mBoth	60%	17%	51%	6%
		MSJV		
OrigBase	5%	11%	27%	5%
mAVOC	9%	16%	35%	9%
mNO_x	1%	2%	5%	1%
mBoth	2%	4%	9%	2%
		SSJV		
OrigBase	12%	5%	20%	5%
mAVOC	13%	7%	22%	7%
mNO_x	2%	2%	8%	1%
mBoth	10%	2%	10%	1%

especially true in the central and southern SJV where VOC limitation is now confined to the urban locations across all episodes, accounting for no more than 10% of the high-ozone locations (Table 4). Consequently, the control options in the central and southern SJV both exhibit weak dependence on meteorology after the baseline NO_x emissions are reduced. These modeling results suggest that the chemistry has moved toward NO_x limitation and NO_x control in the central and southern SJV has become more effective in recent years as the result of reduced NO_x emissions from the level of year 2000. Such behavior is also observed in the ambient measurements [*Pusede and Cohen*, 2012].

[54] The control options in the northern SJV, however, still vary greatly with meteorology for all baseline emission cases. With reduced NO_x emissions (mNO_x or mBoth), VOC control remains important in this region under the O_3-North and O_3-West conditions (Table 4). The northern SJV is closest to large emission source regions (the SFB and SV) upwind of the SJV. When designing an ozone control strategy for this subregion, it would be important to consider the meteorological influences, especially those associated with flow characteristics, on the limiting precursor emissions and targeted source regions for emission scenarios in both year 2000 and more recent years.

3.4. Discussions

3.4.1. Comparison to Past Studies

[55] Extensive studies reported in the literature have investigated ozone formation in central California [e.g., *Pun et al.*, 2000; *Liang et al.*, 2006; *Steiner et al.*, 2006; *Tonse et al.*, 2008; *Jin et al.*, 2008; *Beaver and Palazoglu*, 2009; *Zhao et al.*, 2011; *Pusede and Cohen*, 2012]. While some of these investigated the role of meteorology [e.g., *Beaver and Palazoglu*, 2009; *Zhao et al.*, 2011], they focused on the influence of meteorology on ozone concentrations rather than on ozone sensitivities to precursor emissions and source-receptor relationships. The latter is the focus of our study.

[56] In practice, several representative episodes were selected for developing ozone control strategies for the San Joaquin Valley State Implementation Plan (SIP) (CARB 2007) submitted to the U.S. Environmental Protection Agency by the California Air Resources Board (CARB). The CARB submittal (CARB 2007) relied on three representative episodes: 7–13 July 1999, 29 July to 2 August 2000, and 17–21 September 2000, and modeling was conducted for the first two episodes. Our study focused on summer 2000, and thus, the episode in 1999 was not included. The other two CARB episodes were also included in our work (O_3-All and O_3-West). Note that ozone concentrations in excess of 75 ppb in these two CARB episodes were more extensive than in the other two episodes that CARB did not include (Figure 3, third column). Hence, the CARB episodes may represent the worst-case scenarios for ozone pollution.

[57] Selection of the four episodes for this study was based on the ozone spatial patterns in addition to ozone levels modeled for summer 2000 [*Jin et al.*, 2011] and observed historically [*Fujita et al.*, 1999]. As a result, despite their lower ozone levels than the "worst cases," O_3-South and O_3-North were also selected due to their distinctive flow patterns. Nevertheless, ozone levels exceeding 75 ppb were observed in a number of places during these two (non-CARB) episodes. The 8 h standard has been reduced from 84 ppb to 75 ppb a year after the submittal of CARB SIP (CARB 2007) and will continue to be reduced further. It will become increasingly important to consider these two (non-CARB) episodes because they also contribute to the nonattainment of the current and future ozone standards.

[58] For the O_3-All episode, our findings are similar to the CARB SIP submittal. NO_x is found to be the predominant limiting reagent. However, by including more types of episodes, our work indicates meteorology-induced variabilities in the ozone limitation chemistry as well as in the importance of source contributions. VOC control can be important especially for the northern part of the SJV during two episodes (O_3-North and O_3-West). The importance of contributing source locations to the SJV ozone is found to be greatly affected by flow patterns. For example, the upwind contribution is enhanced during the more ventilated O_3-North episode in the northern SJV, while local source contribution dominates ozone formation during the more stagnant O_3-West episode.

3.4.2. Uncertainties

[59] Model-simulated ozone sensitivities to precursor emissions can be influenced by the quality of emission inputs. We have addressed the effects of uncertainties and variations in emissions on the ozone limitation chemistry by computing ozone sensitivities under alternative emission cases and compared them to the original case. Changes in AVOC emissions are found to exert small effects on ozone sensitivities and control options. Changes in NO_x emissions have greater effects; ozone chemistry was shifted toward NO_x limitation with decreasing NO_x. With 20% reduction in NO_x, NO_x control became, overall, beneficial for the central and southern parts of the SJV throughout all four episodes.

[60] Analysis in this study for control options has been focused on "high-ozone" locations. As ozone sensitivity to NO_x changes sign, it is possible that NO_x control may cause other areas to become noncompliant while cleaning up some of the already noncompliant areas and thus affect the efficacy of emission controls. This concern can be addressed by examining changes in the number of grid cells exceeding the ozone standard under alternative emission cases (with reduced precursor emissions) relative to those having the original base case emissions. The number of grid cells exceeding the 75 ppb ozone standard is decreased for all

alternative emission cases relative to the original base case (Table S1). The effectiveness of VOC versus NO_x reductions varies with episode in terms of reducing the spatial extent of ozone exceedances and is consistent with the control options described in section 3.1. The O_3-All and O_3-South episodes benefit more from NO_x reductions, while the O_3-North and O_3-West episodes benefit more from AVOC reductions.

[61] Some uncertainties are not addressed in this work which could also influence the model-simulated ozone sensitivities.

[62] 1. Simulated ozone sensitivities can be influenced by the choice of chemical mechanism used in the model. A recent study indicated greater ozone sensitivities to NO_x simulated by the newly released Statewide Air Pollution Research Center '07 SAPRC07 mechanism [*Shearer et al*., 2012] than by the Statewide Air Pollution Research Center '99 SAPRC99 mechanism that is used by this study. *Cai et al.* [2011] also indicated that the NO_x disbenefit areas are spatially expanded using the condensed version of SAPRC07. Using observable indicators [*Liang et al*., 2006] and ozone production efficiencies calculated by ambient concentration measurements may provide another independent measure of ozone sensitivities to precursors.

[63] 2. Forest fire emissions were found to be important ozone precursors and can interact with urban emissions [*Pfister et al*., 2008; *Bein et al*., 2008; *Jaffe and Wigder*, 2012; *Strada et al*., 2012; *Singh et al*., 2012]. Forest fire emissions are not included in this study and need to be investigated in future research.

[64] 3. The choice of model year can also influence the application of our results to other years. Summer 2000 (June to September) was found to be statistically cooler than its 30 year climatology [*Fujita et al*., 1999]. Extending a similar modeling study to a different summer will be an additional important step for verifying the effects of temperature on model-simulated ozone sensitivities.

4. Conclusions

[65] We have investigated the meteorological dependence of ozone chemical limitation characteristics and local versus upwind contributions in the SJV by applying a three-dimensional photochemical model to simulate four ozone episodes, i.e., O_3-North, O_3-South, O_3-West, and O_3-All, that were found to be representative of the regional ozone pollution meteorology. Spatial distributions of ozone control options via NO_x or AVOC and the transition regime have been delineated at high-ozone locations (i.e., with afternoon 8 h average ozone greater than 75 ppb) according to their first-order ozone sensitivity coefficients. Despite similar spatial trends with VOC-controlled areas that are found near emission centers and NO_x-controlled areas located farther downwind, the spatial extent of the NO_x disbenefit areas changes with meteorology, especially for the northern SJV. In contrast to previous findings obtained by studying a single ozone episode (O_3-All) which revealed that NO_x control was, overall, more beneficial for reducing 8 h ozone in the SJV [*Jin et al*., 2008], our current study results have suggested an increased importance of VOC control for the O_3-North and O_3-West conditions relative to the O_3-All and O_3-South conditions.

[66] The meteorological dependence of ozone control via NO_x or AVOC varies significantly by location. Specifically, weaker dependences have been identified for the southern SJV and stronger dependences for the northern and central SJV. The effects of the scalar meteorological quantities considered here, namely, temperature, humidity, mixing height, and ventilation rate, can explain the ozone limitation chemistry characterized for the four episodes in the central and southern SJV. The northern SJV, being closest to large emission source regions (SFB and SV) upwind of the SJV, is subject to additional constraints by wind direction and flow characteristics that influence the choices of its control options. As has been revealed in the transect analyses, the extensive NO_x disbenefit (or VOC control) areas identified under O_3-North in the northern SJV are influenced by the transport of SFB pollutants.

[67] The importance of contributing source regions to the ozone formation in the SJV is also dependent on meteorology and is different from location to location along the flow paths. In general, the local contributions are more important for the eastern side of the central SJV, while upwind sources are also important (from ~40% to more than 50% of ozone sensitivities) for the western side of the valley, except for the most stagnant O_3-West episode, when the SJV ozone is mostly sensitive to local sources at high-ozone locations. The VOC control was found to be important for the northern SJV for both the O_3-West and O_3-North conditions, and the results here have highlighted the differences in their VOC source regions, local SJV and upwind SFB, respectively, which are governed by the flow differences.

[68] The meteorological dependence of ozone control options identified in this study is also a function of the underlying emissions that influence the atmospheric composition and chemistry. Changes in AVOC emissions have been found to exert much smaller influence than changes in NO_x emissions on the determination of ozone control options. With reduced baseline NO_x emissions, the spatial extent of NO_x disbenefit areas (VOC control) is reduced greatly in the central and southern SJV. This leads to a weaker dependence of the ozone limitation chemistry characteristics on meteorology in these two subregions, and NO_x control is always the dominant option. The northern SJV, which is closer to the large upwind source regions (SFB and SV) than the rest of the valley, remains influenced by meteorology with VOC control dominant under the O_3-North and O_3-West conditions. When designing an ozone control strategy for this subregion, it would be important to consider the meteorological influences, especially those associated with flow characteristics, on the limiting precursor emissions and targeted source regions for various emission scenarios.

[69] **Acknowledgments.** The study summarized in this paper was performed with support from the California Energy Commission's PIER Environmental Program. It does not necessarily represent the views of the Energy Commission, its employees, or the state of California. We thank Marla Mueller in the California Energy Commission for managing the project. We also thank Robert A. Harley for the valuable technical advice and the three anonymous reviewers' help with improving the clarity of the manuscript.

References

Baertsch-Ritter, N., J. Keller, J. Dommen, and A. S. H. Prevot (2004), Effects of various meteorological conditions and spatial emission resolutions on the ozone concentration and ROG/NOx limitation in the Milan area (I), *Atmos. Chem. Phys.*, *4*, 423–438.

Beaver, S., and A. Palazoglu (2009), Influence of synoptic and mesoscale meteorology on ozone pollution potential for San Joaquin Valley of California, *Atmos. Environ.*, *43*(10), 1779–1788.

Bein, K. J., Y. J. Zhao, M. V. Johnston, and A. S. Wexler (2008), Interactions between boreal wildfire and urban emissions, *J. Geophys. Res.*, *113*, D07304, doi:10.1029/2007JD008910.

Biswas, J., and S. T. Rao (2001), Uncertainties in episodic ozone modeling stemming from uncertainties in the meteorological fields, *J. Appl. Meteorol.*, *40*(2), 117–136.

Bloomer, B. J., J. W. Stehr, C. A. Piety, R. J. Salawitch, and R. R. Dickerson (2009), Observed relationships of ozone air pollution with temperature and emissions, *Geophys. Res. Lett.*, *36*, L09803, doi:10.1029/2009GL037308.

Byun, D. W., and K. L. Schere (2006), Review of the governing equations, computational algorithms, and other components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system, *Appl. Mech. Rev.*, *59*(2), 51–77.

Cai, C. X., J. T. Kelly, J. C. Avise, A. P. Kaduwela, and W. R. Stockwell (2011), Photochemical modeling in California with two chemical mechanisms: Model intercomparison and response to emission reductions, *J. Air Waste Manage. Assoc.*, *61*(5), 559–572, doi:10.3155/1047-3289.61.5.559.

Cohan, D. S., A. Hakami, Y. Hu, and A. G. Russell (2005), Nonlinear response of ozone to emissions: Source apportionment and sensitivity analysis, *Environ. Sci. Technol.*, *39*(17), 6739–6748.

Dawson, J. P., P. J. Adams, and S. N. Pandis (2007), Sensitivity of ozone to summertime climate in the eastern USA: A modeling case study, *Atmos. Environ.*, *41*(7), 1494.

Dayan, U., and I. Levy (2002), Relationship between synoptic-scale atmospheric circulation and ozone concentrations over Israel, *J. Geophys. Res.*, *107*(D24), 4813, doi:10.1029/2002JD002147.

Edwards, D. P., et al. (2004), Observations of carbon monoxide and aerosols from the Terra satellite: Northern Hemisphere variability, *J. Geophys. Res.*, *109*, D24202, doi:10.1029/2004JD004727.

Fast, J. D., R. A. Zaveri, X. Bian, E. G. Chapman, and R. C. Easter (2002), Effect of regional-scale transport on oxidants in the vicinity of Philadelphia during the 1999 NE-OPS field campaign, *J. Geophys. Res.*, *107*(D16), 4307, doi:10.1029/2001JD000980.

Federal Register (2008), Rules and Regulations, Vol. 73, No. 60.

Finlayson-Pitts, B. J., and J. N. Pitts (1997), Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons and particles, *Science*, *276*, 1045–1052.

Fujita, E., R. Keislar, W. Stockwell, H. Moosuller, D. DuBois, D. Koracin, and B. Zielinska (1999), *Central California Ozone Study, vol. 1*, *Field Study Plan*, California Air Resources Board, Sacramento.

Hall, J. V., V. Brajer, and F. W. Lurmann (2008), *The Benefits of Meeting Federal Clean Air Standards in the South Coast and San Joaquin Valley Air Basins*, Sonoma Technol., Petaluma, Calif.

Jaffe, D. A., and N. L. Wigder (2012), Ozone production from wildfires: A critical review, *Atmos. Environ.*, *51*, 1–10, doi:10.1016/J.Atmosenv.2011.11.063.

Jin, L., S. Tonse, D. S. Cohan, X. Mao, R. A. Harley, and N. J. Brown (2008), Sensitivity analysis of ozone formation and transport for a central California air pollution episode, *Environ. Sci. Technol.*, *42*(10), 3683–3689.

Jin, L., N. J. Brown, R. A. Harley, J. W. Bao, S. A. Michelson, and J. M. Wilczak (2010), Seasonal versus episodic performance evaluation for an Eulerian photochemical air quality model, *J. Geophys. Res.*, *115*, D09302, doi:10.1029/2009JD012680.

Jin, L., R. A. Harley, and N. J. Brown (2011), Ozone pollution regimes modeled for a summer season in California's San Joaquin Valley: A cluster analysis, *Atmos. Environ. 45*(27), 4707–4718.

Katragkou, E., P. Zanis, D. M. Tegoulias, I. Kioutsioukis, B. C. Krüger, P. Huszar, T. Halenka, and S. Rauscher (2010), Decadal regional air quality simulations over Europe in present climate: Near surface ozone sensitivity to external meteorological forcing, *Atmos. Chem. Phys.*, *10*(23), 11,805–11,821.

Kleeman, M. (2008), A preliminary assessment of the sensitivity of air quality in California to global change, *Clim. Change*, *87*(0), 273–292.

Lei, W., M. Zavala, B. de Foy, R. Volkamer, and L. T. Molina (2008), Characterizing ozone production and response under different meteorological conditions in Mexico City, *Atmos. Chem. Phys.*, *8*(24), 7571–7581.

Liang, J., B. Jackson, and A. Kaduwela (2006), Evaluation of the ability of indicator species ratios to determine the sensitivity of ozone to reductions in emissions of volatile organic compounds and oxides of nitrogen in northern California, *Atmos. Environ.*, *40*(27), 5156–5166, doi:10.1016/J.Atmosenv.2006.03.060.

Liao, K.-J., E. Tagaris, K. Manomaiphiboon, S. L. Napelenok, J. H. Woo, S. He, P. Amar, and A. G. Russell (2007), Sensitivities of ozone and fine particulate matter formation to emissions under the impact of potential future climate change, *Environ. Sci. Technol.*, *41*(24), 8355–8361.

McDonald, B. C., T. R. Dallmann, E. W. Martin, and R. A. Harley (2012), Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales, *J. Geophys. Res.*, *117*, D00V18, doi:10.1029/2012JD018304.

Palacios, M., F. Kirchner, A. Martilli, A. Martilli, F. Martın, and M. E. Rodrıguez (2002), Summer ozone episodes in the Greater Madrid area. Analyzing the ozone response to abatement strategies by modelling, *Atmos. Environ.*, *36*(34), 5323–5333.

Pfister, G. G., C. Wiedinmyer, and L. K. Emmons (2008), Impacts of the fall 2007 California wildfires on surface ozone: Integrating local observations with global model simulations, *Geophys. Res. Lett.*, *35*, L19814, doi:10.1029/2008GL034747.

Pun, B. K., J. F. Louis, P. Pai, C. Seigneur, S. Altshuler, and G. Franco (2000), Ozone formation in California's San Joaquin Valley: A critical assessment of modeling and data needs, *J. Air Waste Manage. Assoc.*, *50*(6), 961–971.

Pusede, S. E., and R. C. Cohen (2012), On the observed response of ozone to NOx and VOC reactivity reductions in San Joaquin Valley California 1995–present, *Atmos. Chem. Phys. Discuss.*, *12*(4), 9771–9811.

Seaman, N. L. (2000), Meteorological modeling for air quality assessments, *Atmos. Environ. 34*, 2231–2259.

Shearer, S. M., R. A. Harley, L. Jin, and N. J. Brown (2012), Comparison of SAPRC99 and SAPRC07 mechanisms in photochemical modeling for central California, *Atmos. Environ.*, *46*(0), 205–216, doi:10.1016/j.atmosenv.2011.09.079.

Sillman, S. (1995), The use of NOy, H2O2, and HNO3 as indicators for ozone-NOx-hydrocarbon sensitivity in urban locations, *J. Geophys. Res.*, *100*(D7), 14,175–14,188.

Sillman, S., and P. J. Samson (1995), Impact of temperature on oxidant photochemistry in urban, polluted rural and remote environments, *J. Geophys. Res.*, *100*(D6), 11,497–11,508.

Singh, H. B., C. Cai, A. Kaduwela, A. Weinheimer, and A. Wisthaler (2012), Interactions of fire emissions and urban pollution over California: Ozone formation and air quality simulations, *Atmos. Environ.*, *56*, 45–51, doi:10.1016/J.Atmosenv.2012.03.046.

Song, J., W. Lei, N. Bei, M. Zavala, B. de Foy, R. Volkamer, B. Cardenas, J. Zheng, R. Zhang, and L. T. Molina (2010), Ozone response to emission changes: A modeling study during the MCMA-2006/MILAGRO campaign, *Atmos. Chem. Phys.*, *10*(8), 3827–3846.

State of California Air Resources Board (2007), Analysis of the San Joaquin Valley 2007 Ozone Plan, final draft staff report, California Air Resources Board, Sacramento.

Steiner, A. L., R. C. Cohen, R. A. Harley, S. Tonse, D. B. Millet, G. W. Schade, and A. H. Goldstein (2008), VOC reactivity in central California: Comparing an air quality model to ground-based measurements, *Atmos. Chem. Phys.*, *8*(2), 351–368.

Steiner, A. L., S. Tonse, R. C. Cohen, A. H. Goldstein, and R. A. Harley (2006), Influence of future climate and emissions on regional air quality in California, *J. Geophys. Res.*, *111*, D18303, doi:10.1029/12005JD006935.

Strada, S., C. Mari, J. B. Filippi, F. Bosseur (2012), Wildfire and the atmosphere: Modelling the chemical and dynamic interactions at the regional scale, *Atmos. Environ.*, *51*, 234–249, doi:10.1016/J.Atmosenv.2012.01.023.

Tao, Z., A. Williams, H.-C. Huang, M. Caughey, and X.-Z. Liang (2007), Sensitivity of U.S. surface ozone to future emissions and climate changes, *Geophys. Res. Lett.*, *34*, L08811, doi:10.1029/2007GL029455.

Tonse, S. R., N. J. Brown, R. A. Harley, and L. Jin (2008), A process-analysis based study of the ozone weekend effect, *Atmos. Environ.*, *42*(33), 7728–7736.

Zhao, Z., S.-H. Chen, M. J. Kleeman, M. Tyree, and D. Cayan (2011), The impact of climate change on air quality-related meteorological conditions in California. Part I: Present time simulation analysis, *J. Clim.*, *24*(13), 3344–3361.