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# The ozone-climate penalty: past, present, and future

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## Abstract

Climate change is expected to increase global mean temperatures leading to higher tropospheric ozone  $(O_3)$  concentrations in already polluted regions, potentially eroding the benefits of expensive emission controls. The magnitude of the "O<sub>3</sub>-climate penalty" has generally decreased over the past three decades which makes future predictions for climate impacts on air quality uncertain. Researchers attribute historical reductions in the O<sub>3</sub>-climate penalty to reductions in NO<sub>x</sub> emissions, but have so far not extended this theory into a quantitative prediction for future effects. Here we show that a three-dimensional air quality model can be used to map the behavior of the O<sub>3</sub>-climate penalty under varying NO<sub>x</sub> and VOC emissions in both NO<sub>x</sub>-limited and NO<sub>x</sub>saturated conditions in Central and Southern California, respectively. Simulations suggest that the planned emissions control program for O<sub>3</sub> precursors will not diminish the O<sub>3</sub>-climate penalty to zero as some observational studies might imply. The results further demonstrate that in a  $NO_r$ limited air basin, NO<sub>x</sub> control strategies alone are sufficient to both decrease the O<sub>3</sub>-climate penalty and mitigate O<sub>3</sub> pollution, while in a NO<sub>x</sub>-saturated air basin, a modified emissions control plan that carefully chooses reductions in both  $NO_r$  and VOC emissions may be necessary to eliminate the O<sub>3</sub>-climate penalty while simultaneously reducing base case O<sub>3</sub> concentrations to desired levels. Additional modeling is needed to determine the behavior of the O<sub>3</sub>-climate penalty as NO<sub>x</sub> and VOC emissions evolve in other regions.

## Introduction

Surface ozone  $(O_3)$  is a secondary pollutant produced by the photochemical oxidation of CO and/or volatile organic compounds (VOCs) by hydroxyl radical (\*HO) in the presence of oxides of nitrogen (NO<sub>x</sub>  $\equiv$  NO<sub>2</sub> + NO). Model perturbation studies have identified temperature as the most important weather variable affecting surface O<sub>3</sub> concentrations in polluted regions (1–5). These findings have been validated against observations on multiple time scales that have shown strong correlations between temperature and O3 concentrations

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Supporting Information Available

Supplemental figures showing the location of the ozone receptors used in this study and model results for each air basin showing the spatial distribution of the ozone-climate penalty are available online.

This material is available free of charge via the Internet at http://pubs.acs.org/.

in excess of about 60 ppb (6–8). California is home to seven of the top ten most heavily  $O_3$  polluted metropolitan areas in the United States <sup>1</sup>, despite the dramatic reductions of  $NO_x$  and VOC precursor emissions over the past three decades (3–6, 9–11). A warming climate is expected to exacerbate surface  $O_3$  in California's two major air basins: the South Coast Air Basin (SoCAB) and the San Joaquin Valley (SJV). Median surface temperatures during the  $O_3$  season over Western North America, including the SoCAB and SJV, are projected to warm between +1 to +5 K by the end of the 21<sup>st</sup> century (12). These temperature increases may counter the benefits from pollution control strategies used in an effort to meet established air quality standards, resulting in a "climate penalty" (13, 14).

In this study, the sensitivity of  $O_3$  to temperature and  $NO_x$  and VOC emissions is calculated in both  $NO_x$ -saturated and  $NO_x$ -limited conditions with a reactive chemical transport model during two historical severe weekday pollution episodes in California: the SoCAB during September 7–9, 1993 ( $NO_x$ -saturated) (15, 16) and the SJV during July 25–27, 2005 ( $NO_x$ limited). Historical episodes are used for the base case analysis to enable the study of  $O_3$ temperature relationships over a period spanning the past two decades to future conditions over which  $NO_x$  and VOC emissions have evolved. The results in this study are presented as an  $O_3$  isopleth diagram that simultaneously describes the maximum concentration (ppb) and sensitivity to temperature (ppb K<sup>-1</sup>) of surface  $O_3$  under specified  $NO_x$  and VOC emissions (17). This map of  $O_3$ -temperature relationships is compared to historical trends for validation and then projected forward to predict climate impacts on future  $O_3$  pollution.

## The O<sub>3</sub>-climate penalty

Varying definitions of the O<sub>3</sub>-climate penalty have been presented in the literature. Wu et al. consider the climate penalty to represent either the additional decreases in NO<sub>x</sub> emissions to counter any climate driven increase in O<sub>3</sub> (assuming NO<sub>x</sub> is the limiting precursor) or the reduced benefits of emissions controls due to the increase in O<sub>3</sub> due to a warmer climate (14). Bloomer et al. calculate the "ozone-climate penalty factor", the slope of the best fit line between long-term observational measurements of O<sub>3</sub> and temperature (18). Other studies utilizing air quality models quantified the change in O<sub>3</sub> due to a prescribed temperature perturbation, but did not refer to this sensitivity as a "climate penalty" (3, 4, 6). Here, we employ the temperature perturbation approach and refer to the direct increase in O<sub>3</sub> concentrations due to increasing temperatures (ppb K<sup>-1</sup>) as the "O<sub>3</sub>-climate penalty" or "climate penalty". Previous work has shown the past and present climate penalty to be highly varied in space and time due to differing chemical and meteorological environments that influence O<sub>3</sub> formation (3, 4, 6, 8, 18). The aggregate effects that make up this relationship (the total derivative,  $d[O_3]/dT$ ) are thought to include at least three components:

$$\frac{d[O_3]}{dT} = \frac{\partial[O_3]}{\partial[stagnation]} * \frac{d[stagnation]}{dT} + \frac{\partial[O_3]}{\partial[reaction]} * \frac{d[reaction]}{dT} + \frac{\partial[O_3]}{\partial[BVOC]} * \frac{d[BVOC]}{dT} + \dots$$

<sup>&</sup>lt;sup>1</sup>American Lung Association, State of the Air Report. 2013; http://www.stateoftheair.org/2012/city-rankings/most-polluted-cities.html

The first term accounts for the association of warm temperatures with stagnant air masses that facilitate the accumulation of  $O_3$  precursor species (19); the second term accounts for the increase in chemical reaction rates for different species, including the thermal decomposition of alkyl nitrates (AN) and subspecies peroxyacetylnitrate (PAN), reservoirs for both NO<sub>x</sub> and HO<sub>x</sub> at low temperatures (7); the third term accounts for temperature dependent variations in biogenic emissions of VOCs (BVOCs), which act as a significant source of precursors for O<sub>3</sub> formation under high-NO<sub>x</sub> conditions and tend to increase with temperature for many species (20, 21). The ellipsis indicates several additional contributing temperature-dependent processes of varying sign that may not be dominant under the assumptions of the current study, including wildfires in the western US (22) and humidity in the Mid Atlantic (23) (see Table 1 in ref. 24 for a comprehensive list). Model perturbation studies resolve the climate penalty partial derivatives, while observations ascertain the total derivative. Extrapolation of present day O<sub>3</sub>-temperature relationships to future climate to estimate changes in O<sub>3</sub> air quality assumes invariable emission rates and ignores complex chemistry-climate interactions (13, 24, 25).

#### Historical trend in O<sub>3</sub>-climate penalty in California

Fig. 1 shows the trend in average daily NO<sub>x</sub> and VOC emissions in the SoCAB and the SJV, along with the corresponding decadal trend in the climate penalty from previous model perturbation and observational studies. The climate penalty is strongly correlated with  $NO_x$ and VOC emissions in both the SoCAB and the SJV. From 1980 to 2010, average daily emissions of NO<sub>x</sub> and VOCs in the SoCAB decreased roughly two and fourfold, respectively; in the SJV NO<sub>x</sub> and VOC emissions decreased by a factor of one-and-a-half and three, respectively (26). The dramatic decrease in these emissions reflects the success of California's statewide emission control programs. Over this same period, the mean value of climate penalty in the SoCAB decreased from +8.0 ppb K<sup>-1</sup> in the 1980s to a present-day value of +2.7 ppb K<sup>-1</sup>, while the climate penalty in the SJV decreased from a value of +2.8ppb K<sup>-1</sup> in the 1980s to a current value of +1.8 ppb K<sup>-1</sup> (3, 4, 6, 8, 18). Similar NO<sub>x</sub>-climate penalty trends have been observed elsewhere. In the eastern U.S., a 43% reduction in power plant NO<sub>x</sub> emissions between 1995 and 2002 was shown to correspond to a 1.0 ppb  $K^{-1}$ decrease in the  $O_3$ -climate penalty (18, 27). Over the next decade, emissions of  $NO_x$  and VOCs are expected to continue to decrease in both the SoCAB and the SJV raising the question: will the O<sub>3</sub>-climate penalty effectively diminish to zero, or does a particular emissions strategy exist that minimizes the O<sub>3</sub>-climate penalty?

### Methods

#### Model description

The UC-Davis-California Institute of Technology (UCD-CIT) air quality model is a 3D Eulerian, photochemical model that simulates reactive chemical transport in the atmosphere and predicts the concentration of both primary and secondary pollutants in the gas and particle phase. Relevant chemical reactions are modeled with the SAPRC11 mechanism (28). A coupled online UV radiative extinction calculation accounts for the scattering and absorption of light due to high airborne particulate matter concentrations to give a more

accurate representation of actinic flux. A more thorough description of the UCD-CIT airshed model and its evolution has been presented previously (16, 29–32).

Due to variations in the physical characteristics of each air basin, different model configurations were used to simulate each pollution episode. The horizontal resolution used in the SoCAB simulations was 5 km  $\times$  5 km. The vertical domain was divided into 5 levels (thickness of 38.5, 115.5, 154, 363, and 429m), extending from the surface to 1.1 km above ground. This relatively shallow model depth is only appropriate in well-defined air basins, such as the SoCAB, where pollutants have a residence time of only a few days. The horizontal resolution in the SJV simulations was  $8 \text{ km} \times 8 \text{ km}$ , and the vertical distance from the surface to 5 km above ground was divided into 16 levels (the surface to 1.1 km above ground for the SJV simulations is comprised of 11 levels). In the SoCAB, hourly 2D and 3D meteorological fields (temperature, absolute humidity, wind speed and direction, and solar intensity) were interpolated from observations using the method described by refs. 33 and 34, while the SJV simulations used hourly meteorological fields generated over California at  $4 \text{ km} \times 4 \text{ km}$  horizontal resolution with the Weather Research and Forecasting model (WRF) v3.4 (35), driven by the North American Regional Reanalysis (NARR) (36). Four dimensional data assimilation (FDDA) is further used to nudge WRF model estimates closer to observed conditions. The WRF meteorological fields were averaged to  $8 \text{ km} \times 8 \text{ km}$  to reduce model simulation times. Previous studies have shown these configurations to well reproduce measured pollutant concentrations (16, 37).

The base case emission inventories for the SoCAB and SJV episodes were obtained from the South Coast Air Quality Management District (SCAOMD) and the California Air Resources Board (ARB) and are summarized in refs. 38 and 39, respectively. Boundary conditions at the western edge of each modeling domain were based on measured background concentrations of pollutants that are transported to California (40, 41) and remained constant while emission perturbations were applied. Biogenic emissions were generated at  $8 \text{ km} \times 8$ km spatial resolution using the Biogenic Emission Inventory Geographic Information System (BEIGIS) model (42). A year 2000 land-use pattern generated by the Moderateresolution Imaging Spectroradiometer (MODIS) satellite is used to determine vegetation types and leaf area indices. Hourly averaged surface air temperature and shortwave radiation from the meteorology is used to calculate emissions of isoprene, monoterpenes, and 2methyl-3-buten-2-ol (MBO) (20, 21). In the SJV, livestock feed VOC emissions were estimated using the method described by ref. 43 and are mapped to the spatial distribution of livestock ammonia emissions. Predicted O<sub>3</sub> concentrations for both pollution episodes in this study had performance statistics that met U.S. Environmental Protection Agency (EPA) guidance for air quality models (44).

## Calculating the O<sub>3</sub>-climate penalty

To generate an  $O_3$  isopleth diagram, the episode base case emissions of  $NO_x$  and anthropogenic VOCs were uniformly scaled up (more emissions) or down (less emissions) to represent a hypothetical range of pollution control strategies in each air basin. Here, the air quality model explicitly simulates 121 and 64  $NO_x$  and VOC emissions scenarios in the SoCAB and SJV, respectively. These simulations are then repeated after applying a

temperature perturbation for a total of 370 model runs. In this study, a spatially uniform temperature perturbation was applied to every hour during both multi-day pollution events to calculate a value of the climate penalty at each  $NO_x$  and VOC emissions point. This technique explores the  $O_3$ -climate penalty under base case conditions to better understand important relationships between emissions and climate. Further work would be required to account for detailed future emissions trends and projected climate patterns if the effects of these secondary factors on future  $O_3$ -climate penalties are of interest.

The O<sub>3</sub>-climate penalty was calculated as the difference between the O<sub>3</sub> concentrations predicted with the base case temperature profile and the base case temperature profile plus a -5 K perturbation, divided by the magnitude of the temperature perturbation (ppb K<sup>-1</sup>). The magnitude of the perturbation is arbitrary and is not intended to reflect a projection of future temperature change. Previous work has shown the O<sub>3</sub>-climate penalty is not strongly sensitive to the absolute magnitude of the temperature perturbation used (3). A negative (rather than positive) temperature perturbation was chosen in the present study because maximum daily temperatures from the base case episodes were greater than 40°C and the contributions to  $d[O_3]/dT$  from PAN decomposition and isoprene emissions have been shown to diminish at temperatures >39°C (8). Not fully accounting for these contributions could lead to an under prediction of the base case O<sub>3</sub> sensitivity to temperature. The negative perturbation produces temperatures that are more in line with historical temperature ranges and therefore yields values of  $[O_3]/T$  that are more directly comparable to  $d[O_3]/dT$ calculated from long-term measurements of O<sub>3</sub> and temperature (e.g. (6, 8, 18, 45)).

In this study, the temperature perturbation affects chemical kinetic reaction rates and biogenic emissions of isoprene, monoterpenes, and MBO (20, 21). The temperature perturbation does not alter the evaporation of anthropogenic VOCs (46) or the emission rate of soil NO<sub>x</sub> and is uncoupled from temperature dependent meteorological variables such as mixed layer depth, solar insolation, wind speed and wind direction; model perturbation studies have shown that mixed layer depth has weak positive and negative effects on O<sub>3</sub> concentrations in polluted regions (1, 3). Temperature driven changes to atmospheric circulation are not considered and could be important in defining the exact meteorological characteristics of peak O<sub>3</sub> episodes. Vegetation and land use data remain constant.

The Clausius-Clapeyron relation predicts exponential increases in the atmosphere's capacity to hold water vapor with increasing temperature. Increases in water vapor can lead to greater  $HO_x$  production which may affect  $O_3$  formation differently depending on the region and the atmospheric conditions (1, 2, 4, 47). The temperature perturbations applied in the current study were coupled with different assumptions about humidity for each air basin depending on their geographical features. The majority of the SoCAB is close to the Pacific Ocean where an unlimited water reservoir maintains an approximately constant relative humidity (RH) with increasing temperature. The RH was therefore held constant in the SoCAB when temperature was perturbed. In the SJV, the supply of moisture is limited, and it was therefore assumed that absolute humidity would remain constant with increasing temperature, leading to a decrease in RH. Additional SJV modeling simulations that assumed constant RH resulted in O<sub>3</sub>-climate penalty values nearly identical to those that fixed absolute humidity.

### Results and discussion

#### Decreases in NO<sub>x</sub> and VOC emissions and the O<sub>3</sub>-climate penalty response

Isopleths of 8-h. average  $O_3$  (10:00–18:00 LDT) (ppb) and  $O_3$ -climate penalty (ppb K<sup>-1</sup>) for NO<sub>x</sub> and VOC emissions rates relative to conditions on September 8–9, 1993 are shown in Fig. 2 at Downtown Los Angeles, Azusa, Claremont, and Anaheim in the SoCAB. Ozone isopleth diagrams generated for Visalia, Fresno, Hanford, and Bakersfield in the SJV for conditions on July 27, 2005 are shown in Fig. 3. The SoCAB is an urban environment that is NO<sub>x</sub>-saturated during weekdays (48), while both the SJV and the eastern U.S. are predominantly NO<sub>x</sub>-limited at all times (49). Each isopleth shows the modeled base case  $O_3$  concentration under a particular set of NO<sub>x</sub> and VOC emissions rates with the same meteorology. In these simulations, NO<sub>x</sub> is emitted from both soil and anthropogenic sources and VOC is emitted from anthropogenic and natural sources. For both air basins, NO<sub>x</sub> and only anthropogenic VOC emissions are scaled. The scaling factors are the fraction of NO<sub>x</sub> and VOC emissions relative to the base years. The base year for the SJV episode is 2005 and the base year for the SoCAB episode is 1993. Base years have a scaling factor of 1. The range of scaling factors was chosen to capture the range of both historical and projected emissions.

The colors overlaid on each  $O_3$  isopleth diagram in Figs. 2 and 3 show the magnitude of  $O_3$ climate penalty (ppb K<sup>-1</sup>). The maximum in the  $O_3$ -climate penalty occurs at a NO<sub>x</sub> emission level slightly greater than that which produces the maximum  $O_3$  under the base case temperature simulation and at the highest VOC emission rates. This is coincident with the "O<sub>3</sub> isopleth ridge", or the line of maximum O<sub>3</sub> formation. The minimum in O<sub>3</sub>-climate penalty occurs in conditions that are appreciably NO<sub>x</sub>-saturated. The simulations here suggest that when NO<sub>x</sub> emissions are much greater than VOC emissions, the O<sub>3</sub>-climate penalty may become strongly negative (i.e. a climate "benefit") at Downtown LA and Anaheim (-0.1 to -0.4 ppb K<sup>-1</sup>) (O<sub>3</sub> decreases with increasing temperature), suggestive of O<sub>3</sub> titration by NO from further NO<sub>x</sub>-saturation that results from the thermal decomposition of PAN at hotter temperatures (7).

The historical and projected trend (1990—2020) in average daily anthropogenic NO<sub>x</sub> and VOC emissions rates, relative to the respective base case inventory, is drawn on each isopleth diagram as black (historical) and grey (projected) dots connected by a dashed black line, taken together to constitute an emissions "trajectory". Receptors in each air basin are assumed to experience an equivalent rate of NO<sub>x</sub> and VOC emissions reductions. The O<sub>3</sub> values along the NO<sub>x</sub>-VOC emissions trajectory are an estimate of the maximum amount of O<sub>3</sub> pollution that could be formed during a severe pollution event with similar meteorology. Substantially NO<sub>x</sub>-saturated conditions are not predicted by the emissions trajectory at any of the SoCAB or SJV receptors over the next decade (Figs. 2 and 3).

In both air basins, the  $O_3$  isopleth diagrams suggest that  $NO_x$  and VOC emission reductions between 1990 and 2010 have been effective at abating  $O_3$  during weekday severe pollution events, especially in eastern LA and the SJV, confirming previous findings (10, 26). Reductions in  $O_3$  in the SoCAB were accomplished through reductions in emissions of both  $NO_x$  and VOCs. Fig. 2 shows that reductions in  $NO_x$  emissions alone over this 20-year

period would have increased  $O_3$  concentrations in the SoCAB. Little change in  $O_3$  is seen at both Anaheim and Downtown LA (Fig. 2a, d) because reductions in  $NO_x$  and VOC emissions produce a trajectory that stays within a zone of approximately constant  $O_3$ . In the SJV, reductions in  $O_3$  have primarily occurred through reductions in  $NO_x$  emissions.

Over the next decade, the ARB projects that  $NO_x$  and VOC emissions will continue to decrease in both air basins, with  $NO_x$  emissions declining more rapidly. Projections for the SoCAB indicate that this emissions trajectory may not be optimal, with slight increases in  $O_3$  concentrations (+20–30 ppb under the meteorological conditions studied). This result is consistent with findings from other investigators; Fujita et al. find that reductions in  $NO_x$  emissions without concurrent VOC emission reductions over the next decade will cause  $O_3$  to increase in central portions of the SoCAB during weekdays (9). No such effect is predicted for the SJV in the present study; the  $O_3$  isopleths for the SJV predict continued decreases in  $O_3$  over the next decade under meteorological conditions conducive to  $O_3$  formation (Fig. 3).

The historical and projected trend in the O<sub>3</sub>-climate penalty can be inferred from the NO<sub>x</sub>-VOC emission trajectory on the isopleths (Figs. 2 and 3). Both NO<sub>x</sub> and VOC emissions appear to play a role in determining the O<sub>3</sub>-climate penalty in the SoCAB, contrary to previous findings that suggest NO<sub>x</sub> emissions are the primary explanatory variable in the observed decreasing trend in the O<sub>3</sub>-climate penalty (18). Reducing NO<sub>x</sub> emissions, primarily emitted as nitric oxide (NO), in a NO<sub>x</sub>-saturated environment can exacerbate O<sub>3</sub> pollution by both decreasing O<sub>3</sub> loss by NO titration and increasing the ratio of VOCs to NO<sub>x</sub>, favoring peroxy (HO<sub>2</sub>) and alkylperoxy (RO<sub>2</sub>) formation, both of which propagate the chain reaction mechanism that produces O<sub>3</sub> in the troposphere (50). While NO<sub>x</sub> emission controls may be effective at decreasing the O<sub>3</sub>-climate penalty in the NO<sub>x</sub>-limited eastern U.S. and SJV (18, 49), the results of the current study suggest that further decreases in VOC emissions over the next decade in the SoCAB (NO<sub>x</sub>-saturated) may be beneficial to reducing base case O<sub>3</sub> pollution and may additionally be effective at minimizing the O<sub>3</sub>-climate penalty.

## Future trend in the O<sub>3</sub>-climate penalty and implications

The O<sub>3</sub> isopleth diagrams illustrate climate penalty-emissions relationships at individual receptor sites, but do not readily facilitate an air-basin wide assessment of historical and projected trends in the O<sub>3</sub>-climate penalty along the emissions trajectory. To characterize an air-basin wide climate penalty, we use 18 urban receptor sites in the SJV and 26 urban receptor sites in the SoCAB. The location of these receptors are shown in supporting information, Fig. S1, and are analogous to the receptor sites that are used by ref. 8. Fig. 4 shows the modeled historical (1985—2010) and projected (2015—2020) trend in O<sub>3</sub>-climate penalty (ppb K<sup>-1</sup>) at these receptor sites in the SoCAB (left) and the SJV (right). Modeled results are presented as box-and-whisker plots ( $25^{th}$ , median, and  $75^{th}$  percentiles) where the whiskers are the mean (not shown) ± the standard deviation. Values outside of the whiskers are plotted as crosses. Historical values of the O<sub>3</sub>-climate penalty from the literature (as both air basin averages and at individual receptors) are drawn as solid black symbols. Values

given by ref. 8 are decadal air basin averages constructed from long-term measurements and likely capture the full O<sub>3</sub>-temperature relationship.

The observed trend of the O<sub>3</sub>-climate penalty from all literature sources are generally well reproduced by the air quality model using the meteorology from severe pollution events that are characterized by very hot surface temperatures ( $r^2=0.98$  in the SoCAB;  $r^2=0.69$  in the SJV). The median model prediction is systematically lower than the measured climate penalty from ref. 8 by, at most, 0.8 ppb  $K^{-1}$  in the SoCAB over the past three decades, but is reproduced to within  $\pm 0.3$  ppb K<sup>-1</sup> in the SJV from the 1990s to the 2000s. In the SJV, siteby-site differences in the  $O_3$ -climate penalty are more pronounced (> 1 ppb K<sup>-1</sup>), including between the current and past model perturbation studies (3, 5) and may reflect differing assumptions therein. Differences between modeled and observed values may reflect emissions sector changes (i.e. changes to VOC reactivity (51)) during the past three decades that are not captured using the uniform emissions scaling approach employed here, or other contributions that are not captured with the simple temperature perturbation approach that only affects kinetic rate constants, biogenic emission rates, and water vapor concentrations in a representative episode. For example, calculation of the O<sub>3</sub>-climate penalty from longterm modeled  $O_3$  and surface temperature may yield different sensitivities than those derived from a single severe pollution event as some contributing components of the full O<sub>3</sub>temperature relationship may be driven by intra-seasonal weather patterns and events. The choice of biogenic emissions models and chemical mechanisms may also influence the predicted climate penalty. The sensitivity of the results to these modeling options should be investigated in future work.

The range of climate penalties at receptors in the SoCAB in 1985 varies by about a factor of 30, +0.7 ppb  $K^{-1}$  to +26.2 ppb  $K^{-1}$ , a substantially wider range of variability compared to the SJV, +0.6 ppb  $K^{-1}$  to +3.9 ppb  $K^{-1}$ . Receptors east of Los Angeles that are adjacent to the San Gabriel Mountains (a large source of biogenic VOCs) have the largest climate penalties through out the simulation period (1985–2020)(Fig. S2a). These sites are likely sensitive to increased biogenic VOC emissions through rises in temperature. The central and coastal receptors in the SoCAB consistently have the lowest climate penalty, as they may be saturated with fresh NO emissions that titrate O<sub>3</sub>. While the future median O<sub>3</sub>-climate penalty is projected to decrease steadily in both air basins, some receptors in the SoCAB near the San Gabriel Mountains (e.g. Azusa and Claremont, Fig. 2b-c) are expected to experience a rise in the climate penalty due to the strengthening sensitivity of  $O_3$  to strong biogenic emissions in a region where NO<sub>x</sub> decreases much more rapidly than VOC emissions. The 2020 median  $O_3$ -climate penalty is projected to be +0.8 ppb K<sup>-1</sup> in the SoCAB (basin-wide range of -0.8 ppb K<sup>-1</sup> to +11.8 ppb K<sup>-1</sup>) and +0.9 ppb K<sup>-1</sup> in the SJV (basin-wide range of 0.0 ppb  $K^{-1}$  to +1.5 ppb  $K^{-1}$ ), suggesting under the projected emissions pathway, increases in temperature due to climate change may continue to have deleterious effects on  $O_3$  control programs. Although average daily  $NO_x$  and VOC emissions are projected to decrease 37% and 12%, respectively, over the next decade in the SoCAB (26), potential concomitant anthropogenic VOC emissions reductions may be beneficial to reduce both base case O<sub>3</sub> and to further diminish the O<sub>3</sub>-climate penalty.

In NO<sub>x</sub> limited regions such as the SJV and the eastern US, continued decreases in NO<sub>x</sub> emissions are anticipated and may continue to lower the O<sub>3</sub>-climate penalty. The exact O<sub>3</sub>-temperature relationship at other locations should be evaluated for a representative episode of interest (peak or average) using an appropriate reference year (historical or present-day). Future studies should also account for climate-driven changes to atmospheric circulation, changes in land use, choice of boundary conditions that reflect changes to long range transport of pollutants, and scaling individual emissions sectors to accurately reflect emission control targets.

### Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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#### Figure 1.

(a) Historical and projected average daily anthropogenic  $NO_x$  (yellow) and VOC (gray) emissions (tons day<sup>-1</sup>) versus emissions year for the South Coast Air Basin and (b) the observed decadal trend in the O<sub>3</sub>-climate penalty for the Southern California Air Basin attributed to emissions changes during the 1980s (orange), the 1990s (green), and the 2000s (blue). Dashed lines give the range of both observed and modeled O<sub>3</sub>-climate penalty values in the South Coast Air Basin from the literature; solid squares are the mean O<sub>3</sub>-climate penalty calculated from values given in the literature. Symbols beneath each range correspond to literature references: † is Mahmud et al., 2008 (statistical downscaling based on measured trends), § is Steiner et al., 2010 (observations), ¶ is Kleeman, 2008 (model perturbation), *#* is Millstein and Harley, 2009, (model perturbation), and ‡ is Steiner et al., 2006 (model perturbation); (c) as for (a) but for the San Joaquin Valley; (d) as for (b) but for the San Joaquin Valley.



#### Figure 2.

Isopleths of 8 hr. average  $O_3$  (ppb)(solid black lines) and  $O_3$ -climate penalty (ppb K<sup>-1</sup>) (colors) generated from a -5 K temperature perturbation for (a) Downtown Los Angeles, (b) Azusa, (c) Claremont, and (d) Anaheim. All calculations are for the conditions on September 8–9, 1993. Estimated anthropogenic emissions trend relative to the 1993 base year is shown as a dashed black line. A different color scale is used for each panel.



#### Figure 3.

Isopleths of 8 hr. average  $O_3$  (ppb)(solid black lines) and  $O_3$ -climate penalty (ppb K<sup>-1</sup>) (colors) generated from a -5 K temperature perturbation for (a) Hanford, (b) Fresno, (c) Bakersfield, and (d) Visalia. All calculations are for the conditions on July 27, 2005. Estimated anthropogenic emissions trend relative to the 2005 base year is shown as a dashed black line. A different color scale is used for each panel.

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#### Figure 4.

Historical (colored markers) and modeled  $O_3$ -climate penalty (ppb K<sup>-1</sup>) for emissions years from 1985 to 2020 for the South Coast Air Basin (SoCAB) (left) and the San Joaquin Valley Air Basin (SJV) (right). The box-and-whisker plots (mean minus the standard deviation,  $25^{th}$ ,  $50^{th}$ ,  $75^{th}$ , and mean plus the standard deviation) give statistics of the modeled  $O_3$ climate penalty at 26 urban receptors in the South Coast Air Basin and at 18 urban receptors in the San Joaquin Valley (*see* supporting information, Fig. S1). Values greater or less than the mean  $\pm$  the standard deviation are shown as crosses. All modeled calculations are for the conditions on September 8–9, 1993 (SoCAB) and July 27, 2005 (SJV).