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Observing Severe Drought Influences on Ozone Air Pollution in California

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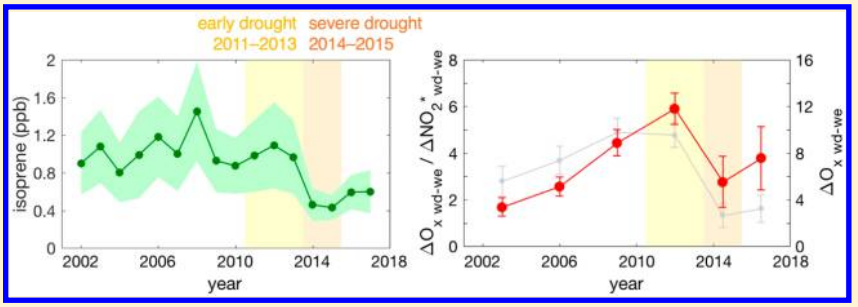
Supporting Information



ABSTRACT: Drought conditions affect ozone air quality, potentially altering multiple terms in the O_3 mass balance equation. Here, we present a multiyear observational analysis using data collected before, during, and after the record-breaking California drought (2011−2015) at the O_3-polluted locations of Fresno and Bakersfield near the Sierra Nevada foothills. We separately assess drought influences on O_3 chemical production (PO_3) from O_3 concentration. We show that isoprene concentrations, which are a source of O_3-forming organic reactivity, were relatively insensitive to early drought conditions but decreased by more than 50% during the most severe drought years (2014−2015), with recovery a function of location. We find drought−isoprene effects are temperature-dependent, even after accounting for changes in leaf area, consistent with laboratory studies but not previously observed at landscape scales with atmospheric observations. Drought-driven decreases in organic reactivity are contemporaneous with a change in dominant oxidation mechanism, with PO_3 becoming more NO_x-suppressed, leading to a decrease in PO_3 of ∼20%. We infer reductions in atmospheric O_3 loss of ∼15% during the most severe drought period, consistent with past observations of decreases in O_3 uptake by plants. We consider drought-related trends in O_3 variability on synoptic time scales by analyzing statistics of multiday high-O_3 events. We discuss implications for regulating O_3 air pollution in California and other locations under more prevalent drought conditions.

INTRODUCTION

Climate change is expected to increase the frequency and severity of drought in the future.[1−5] Drought conditions can potentially affect air quality, including concentrations of tropospheric ozone (O_3),[6−8] a pollutant harmful to humans, plants, and ecosystems.[9,10] While effective future pollution control strategies will require improved understanding of drought−O_3 coupling, these influences are challenging to discern, as drought conditions alter multiple terms in the O_3 mass balance equation simultaneously: emission of biogenic O_3 precursors and chemical production rate (PO_3), chemical and depositional loss rate (LO_3), and change in O_3 concentration on synoptic time scales with atmospheric transport and mixing (eq 1).

$$\frac{\partial[O_3]}{\partial t} = PO_3 + LO_3 \pm \text{transport/mixing} \quad (1)$$

The response of any individual term in $\partial[O_3]/\partial t$ to drought may vary in sign and magnitude as a function of drought duration, drought severity, availability of nonrainwater sources, and PO_3

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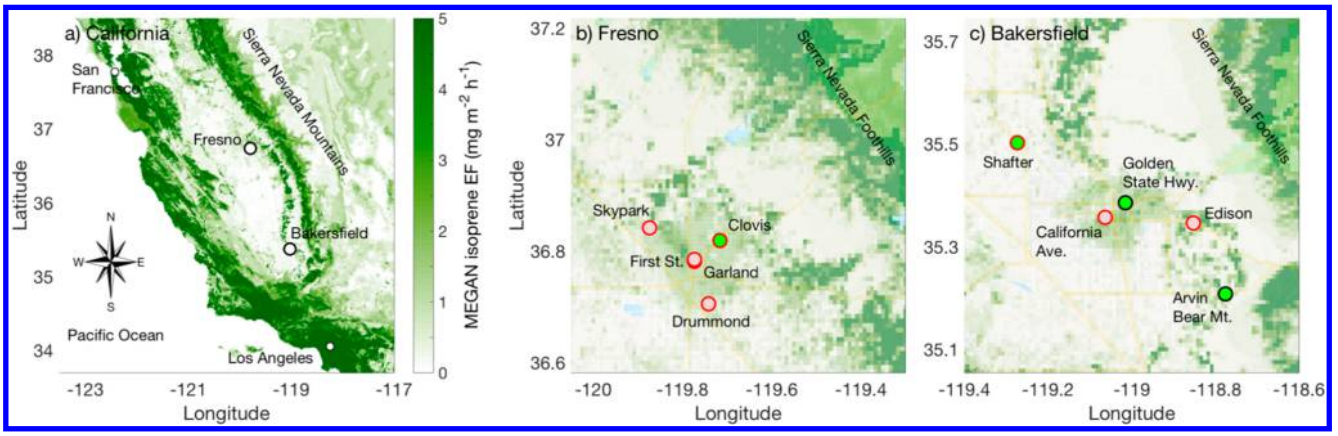

Figure 1. California (a) with MEGAN isoprene emission factors (MEGAN v2.1, version 2011).[40] Fresno (b) and Bakersfield (c) areas and monitoring station locations with isoprene (green) and O_3 and NO_2* (red outline) measurements available, with MEGAN isoprene emission factors in same color scale as panel a.

chemical regime. Moreover, because droughts may extend over multimonth to multiyear time scales, emissions regulations, seasonal patterns, and climatic events (e.g., El Nino Southern Oscillation) may confound interpretation, causing simultaneous variations in the $\partial[O_3]/\partial t$terms influencing O_3 mixing ratios.

Past research has focused on two key drought−$\partial[O_3]/\partial t$ perturbations: decreased isoprene emissions as they affect PO_3 and reduced stomatal conductance with regard to LO_3. In many locations, plants emit the majority of O_3-forming organic compounds reactive with the hydroxyl radical (OH).[11−13] Isoprene is the most abundant source of organic OH reactivity in the terrestrial atmosphere,[14] a significant contributor to PO_3 in the summertime even in cities,[15] and among the most-studied biogenic reactive carbon species. Detailed laboratory studies have demonstrated that on time scales of hours to weeks, water deficits initially enhance isoprene emissions under mild drought[16−18] but ultimately suppress isoprene fluxes under sustained, severe water stress.[19,20] Both types of drought−isoprene response have been inferred at landscape scales,[8,21−25] and soil moisture (i.e., plant water status) has been found to control a major portion of the interannual variability in isoprene flux in many locations.[21]

Plant stomatal O_3 uptake is a major LO_3 pathway that is also drought-sensitive.[26,27] Drought lowers stomatal deposition rates because apertures close to prevent water loss via transpiration and because, at longer time scales, overall leaf area is reduced. Decreased LO_3 has been directly observed using O_3 flux measurements in the late summer/early fall in Mediterranean climates, when water-deficient conditions are prevalent, including the Sierra Nevada Mountains of California.[28−31] Chemical transport and chemistry-climate models, which allow isolation of LO_3 from $\partial[O_3]/\partial t$, indicate drought-driven LO_3 decreases may be large enough to enhance O_3 concentrations.[7,32] Huang et al.[7] found monthly mean O_3 deposition velocities (v_d), where LO_3 to deposition equals $v_d[O_3]$, decreased over Texas forests during a 2011 drought leading to higher O_3 concentrations. In simulating the 1988 North American Drought, Lin et al.[32] reduced v_d by 35%, increasing O_3 concentrations and improving model-measurement agreement. By contrast, while Wang et al.[8] found elevated O_3 mixing ratios during drought periods, v_d was relatively insensitive to drought conditions.

In 2011−2015, California experienced the most severe drought over the 120-year observational record[5,33,34] and the last millennium.[35] During this period, California saw a historic combination of annual high temperatures[5] and precipitation deficits.[33,34] California is also home to poor O_3 air quality, with many of the most O_3-polluted cities in the U.S. located in the state.[36] Here, we present observations of isoprene, O_3, and nitrogen dioxide concentrations before, during, and after the California drought (2002−2017) to investigate the influence of drought conditions on O_3 air quality. Data were collected in California in the San Joaquin Valley (SJV), with monitoring sites proximate to isoprene-emitting oak savanna regions in the Sierra Nevada Mountain foothills (Figure 1). We combine interpretation of variability in interannual, weekday−weekend, and day-to-day O_3 concentrations to observationally distinguish effects temporally corresponding to drought on PO_3 from other influences on O_3 concentration. We infer changes in LO_3 and analyze multiyear trends in synoptic-time scale high-O_3 events and meteorological variables. We discuss the implications of our results for regulating O_3 air pollution in a potentially more drought-prone future in California and in locations where isoprene dominates OH reactivity.

OBSERVATIONS

Isoprene mixing ratio data are 3 h integrated samples collected in pressurized stainless-steel canisters and analyzed offline by gas chromatography-flame-ionization-mass spectrometric detection with preconcentration (EPA method code 177)[37] as part of the U.S. Environmental Protection Agency (EPA) Photochemical Assessment Monitoring Stations (PAMS) program. A near-continuous data record (2002−2017) for "Fresno" is reported at Clovis-N Villa Avenue (36.819° N, 119.716° W). We produce a "Bakersfield" record by combining isoprene observations at Shafter-Walker Street (35.503° N, 119.273° W) (2002−2010 and 2012−2017), Arvin Bear Mountain Boulevard (35.208° N, 118.776° W) (2002−2009), and Bakersfield Golden State Highway (35.386° N, 119.015° W) (2012−2017). In accordance with PAMS protocols, isoprene observations are made for three months each year during O_3 season, typically spanning June−September. At most sites, data collection occurred in June−August for the years 2002−2007, 2009, and 2014 and in July−September for the years 2008, 2010−2013, and 2015−2017, with exceptions: Shafter, 2012−2013 in June−August; Arvin, 2008 in June−August; and Arvin, 2002−2007 and 2009 in August−September. Isoprene data were down-

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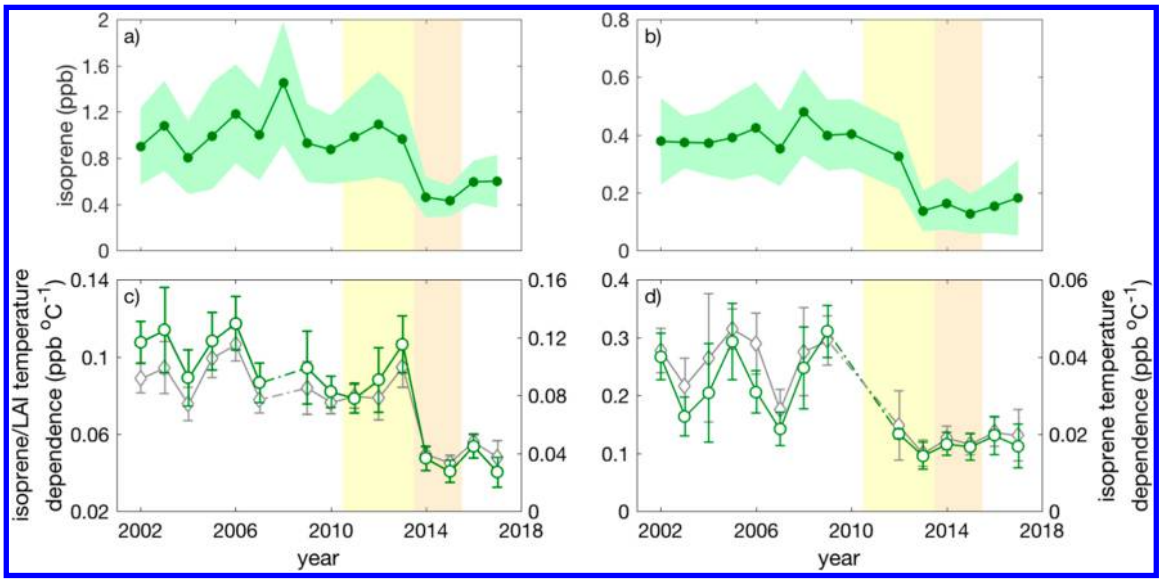

Figure 2. Daytime (8 am−8 pm, LT) isoprene mixing ratios (ppb) during O_3-season in Fresno (a) and Bakersfield (b). Envelopes define the 2σ standard deviation, not the measurement uncertainty. Slopes of the correlation between daily maximum temperature (°C) and isoprene/LAI (green, left axis) or isoprene (gray, right axis) in Fresno (c) and Bakersfield (d) with slope errors. Plot fields are tinted to indicate the 2011−2013 early drought (light yellow) and 2014−2015 severe drought (light orange) time periods.

loaded from the U.S. Environmental Protection Agency (EPA) AQS Data Mart (https://aqs.epa.gov/api).

Hourly O_3 and NO_2* measurements are made by UV absorption and chemiluminescence, respectively, and provided to the public by the California Air Resources Board (CARB) (https://www.arb.ca.gov/aqmis2/aqdselect.php). NO_2* data have a well-known positive interference from higher nitrogen oxides,[38] which have been shown to add uncertainty to absolute, but not relative NO_2* concentrations.[39] We acknowledge this interference by using NO_2* rather than NO_2. "Fresno" data are the mean of available hourly observations from Clovis-N Villa Avenue, Skypark (36.842° N, 119.874° W), Drummond (36.706° N, 119.741° W), Fresno-Garland (36.785° N, 119.773° W), and First Street (36.782° N, 119.773° W) stations (Figure 1b). "Bakersfield" data are mean of available hourly measurements from Shafter-Walker Street, California Avenue (35.357° N, 119.063° W), and Edison (35.346° N, 118.852° W) stations (Figure 1c). In Fresno, extremely elevated NO_2* mixing ratios were observed corresponding to the time period of the nearby Lion Fire (beginning September 27, 2017); these O_3 and NO_2* data were excluded from the analysis. In 2014, at California Avenue, NO_2* measurements prior to September 16 are missing; at Edison, NO_2* measurements prior to July 24 are either missing or were removed because of an apparent persistent negative offset. Hourly temperature, relative humidity, and winds (speed and direction) are also provided by CARB (https://www.arb.ca.gov/aqmis2/metselect.php). We use data from Clovis to represent Fresno. Full annual wind data are not available in Clovis in 2002, 2007, and 2008. In Bakersfield, we combine temperature records at California Avenue (2002−2012, 2015−2016) and Bakersfield Municipal Airport (35.332° N, 119.000° W) (2013−2014, 2017), where temperature measurements were well-correlated (r^2 of 0.99 for 2017 data).

The leaf area index (LAI) product is generated using satellite observations from the Moderate Resolution Imaging Spectrometer (MODIS) instruments and available for download as part of MOD15A2H Version 6. LAI (8-day intervals at 500 m resolution) were averaged for June−September over a series of rectangles that focus observations on the Sierra Nevada foothills adjacent to the Fresno and Bakersfield areas (Figure S1).

RESULTS AND DISCUSSION

Severe Drought Alters Biogenic Isoprene Emissions and Concentrations. A wide variety of plant species produce isoprene within the leaves by the protein isoprene synthase (IsoS) using carbon from the Calvin cycle as the primary carbon source.[41−43] Isoprene is emitted to the atmosphere as a function of sunlight, leaf temperature, leaf area, and species identity. Longer-term field studies indicate emissions are independent of stomatal conductance,[20,44] while short-term greenhouse experiments suggest a weak dependence on stomatal conductance, attributed to reduced CO_2 uptake and internal CO_2 concentrations that are associated with enhanced isoprene emissions.[45] While drought stress immediately decreases plant photosynthetic activity, laboratory studies have found disproportionately smaller corresponding reductions in isoprene emission rates, implying nonphotosynthetic carbon pools are available.[16,43,46−48] Severe and/or sustained drought conditions do lead to lower emissions, but only when these alternative pools are depleted[47] and IsoS activity is suppressed.[19] In laboratory studies, recovery is observed to be rapid following soil rewatering, with isoprene emissions temporarily exceeding predrought rates in some cases.[16,18]

Isoprene mixing ratios have been measured in California for the last two decades. In Figure 2a,b, mean daytime (8 am−8 pm local time, LT) isoprene is shown throughout the predrought (2002−2010), early drought (2011−2013), severe drought (2014−2015), and postdrought (2016−2017) periods in Fresno and Bakersfield during O_3-season (June−September). Mixing ratios are enveloped by the 2σ summertime variability; standard mean error uncertainties are given in Table 1. Comparable trends with time are observed if months included in the averages are varied (June−August versus July−September). Our categorization of the severe drought is consistent with Exceptional Drought (D4) classification by U.S. Drought Monitor[49] and the lowest Tulare Basin water-year

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Table 1. Statistics during the Pre- (2002−2010), Early (2001−2013), Severe (2014−215), and Postdrought (2016−2017) Time Periods for Fresno, Bakersfield, and the Tulare Basin during O_3 Season (June−September)[a]

	predrought *2008−2010* 2002−2010	early drought 2011−2013	severe drought 2014−2015	postdrought 2016−2017
		Fresno		
isoprene mixing ratio (ppb)	1.00 ± 0.03	1.00 ± 0.04	0.45 ± 0.02	0.60 ± 0.02
isoprene/LAI vs temperature slope (ppb °C^{-1})	0.10 ± 0.01	0.10 ± 0.02	0.04 ± 0.01	0.05 ± 0.01
LAI	0.84 ± 0.03	0.89 ± 0.04	0.84 ± 0.04	0.91 ± 0.02
$\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$	*4.5 ± 0.6* 2.9 ± 0.5	5.9 ± 0.7	2.8 ± 1.1	3.8 ± 1.4
percent $\Delta NO_2{}^*_{wd-we}$ (%)	*42* 42	36	24	23
O_x mixing ratio (ppb)	*75.7 ± 0.4* 78.2 ± 0.4	73.6 ± 0.3	69.5 ± 0.3	72.9 ± 0.2
NO_2* mixing ratio (ppb)	*4.9 (4.3) ± 0.1* 6.0 (5.5) ± 0.1	4.1 (3.7) ± 0.1	3.4 (3.1) ± 0.1	3.4 (3.2) ± 0.1
daily maximum temperature (°C)	34.6 ± 0.1	35.2 ± 0.1	35.1 ± 0.1	35.7 ± 0.1
relative humidity (%)	25 (22)	24 (22)	26 (24)	24 (23)
wind speed (m s^{-1})	6.4 ± 0.1	6.0 ± 0.1	5.7 ± 0.1	5.9 ± 0.1
stagnation severity (O_3 ppb day^{-1})	6.3 (5.4) ± 0.2	6.0 (5.3) ± 0.3	5.7 (5.8) ± 0.3	5.3 (4.8) ± 0.3
stagnation event duration (days)	5.4 (5) ± 0.1	5.4 (5) ± 0.1	5.5 (5) ± 0.2	5.8 (5) ± 0.2
stagnation accumulation (O_3 ppb event^{-1})	26.8 (23.3) ± 0.8	25.7 (23.1) ± 1.3	24.7 (24.0) ± 1.4	24.9 (23.1) ± 1.4
		Bakersfield		
isoprene mixing ratio (ppb)	0.40 ± 0.01	0.21 ± 0.02	0.15 ± 0.01	0.17 ± 0.01
isoprene/LAI vs temperature slope (ppb °C^{-1})	0.23 ± 0.05	0.11 ± 0.02	0.06 ± 0.01	0.12 ± 0.04
LAI	0.16 ± 0.03	0.20 ± 0.01	0.18 ± 0.02	0.22 ± 0.01
$\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$	*6.7 ± 0.6* 4.4 ± 0.6	5.5 ± 0.7	3.9 ± 1.5	3.3 ± 1.1
percent $\Delta NO_2{}^*_{wd-we}$ (%)	*36* 31	32	23	29
O_x mixing ratio (ppb)	*76.0 ± 0.2* 79.0 ± 0.1	71.5 ± 0.2	67.0 ± 0.2	72.5 ± 0.2
NO_2* mixing ratio (ppb)	*4.2 (4.0) ± 0.1* 5.3 (4.7) ± 0.1	3.7 (3.4) ± 0.1	2.6 (2.6) ± 0.1	2.9 (2.7) ± 0.1
daily maximum temperature (°C)	34.4 ± 0.1	34.1 ± 0.1	34.9 ± 0.1	35.8 ± 0.1
relative humidity (%)	25 (22)	24 (23)	21 (19)	18 (17)
wind speed (m s^{-1})	3.2 ± 0.4	3.4 ± 0.3	3.1 ± 0.2	3.1 ± 0.2
stagnation severity (O_3 ppb day^{-1})	6.0 (5.2) ± 0.2	5.6 (5.1) ± 0.3	6.1 (5.4) ± 0.4	4.8 (4.3) ± 0.3
stagnation event duration (days)	5.5 (5) ± 0.1	5.5 (5) ± 0.2	5.5 (5) ± 0.2	5.8 (5) ± 0.2
stagnation accumulation (O_3 ppb event^{-1})	25.7 (22.7) ± 0.8	23.7 (23.7) ± 1.0	25.7 (24.9) ± 1.2	23.0 (20.5) ± 1.4
		Tulare Basin		
water-year rainfall (inches)	56.1	55.2	27.8	72.7

[a]For O_x and NO_2* metrics, we also include predrought defined as 2008−2010 (italics). Data are reported as means if distributions are generally Gaussian and include medians in parentheses if non-normal. Normality was determined through visual examination of histograms and quantile−quantile plots. Isoprene metrics are daily means (8 am−8 pm, LT); all other metrics are afternoon observations (12−5 pm, LT). Uncertainties are 1σ standard mean errors, with the exception of the isoprene/LAI versus daily maximum temperature slopes, which are slope errors. The number of days with measurements included in each metric is reported in Table S1.

(October−September) rainfall totals over the study period (Table 1).[50]

In Fresno, isoprene concentrations during the pre- and early drought were statistically indistinguishable (p = 0.362, Wilcoxon rank-sum test). During the severe drought, isoprene decreased by 54% from predrought levels. In the postdrought, isoprene concentrations recovered by 34%, amounting to a 39% return to predrought levels. In Bakersfield, predrought isoprene abundances were steady through 2012 but fell by 65% in 2013, suggesting drought-driven emissions decreases occurred earlier in the Southern Sierra Nevada foothills area than in Fresno. While isoprene mixing ratios in Fresno do not appear to decline in 2013, isoprene concentrations fell precipitously in August 2013 (not shown). In Bakersfield, isoprene decreased by an additional 29% during the severe drought. In the postdrought period, isoprene concentrations may have recovered by 16%, but differences between 2014−2015 and 2016−2017 are not significant to the 5% level (p = 0.112). Isoprene mixing ratios are a function of both emissions and chemical loss. When photochemistry is active (summer days), isoprene's loss rate ($k_{isoprene+OH}$[OH][isoprene]) is proportional to the OH concentration. Isoprene exerts a positive feedback on its own lifetime, as decreased isoprene and consequent higher OH lead to faster isoprene loss rates and, hence, lower isoprene concentrations. As a result, observed differences in isoprene

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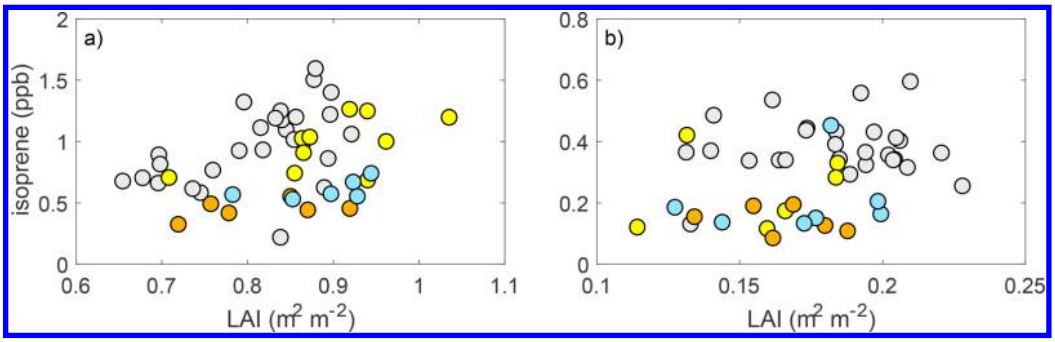

Figure 3. Monthly mean isoprene mixing ratios (ppb) versus MODIS-derived LAI (m^2 m^{-2}) in Fresno (a) and Bakersfield (b). Coloration indicates predrought (gray), early drought (yellow), severe-drought (orange), and postdrought (light blue) time periods.

mixing ratio represent an upper bound on changes in isoprene emissions.

Isoprene emissions have a well-known temperature dependence,[14,54,55] with critical implications for PO_3 on hot days.[56] A recent laboratory experiment produced evidence that drought stress may alter this temperature dependence for at least weeks after rewetting.[19] They found that while photosynthetic rates rebound fully from drought stress across the range of atmospheric temperatures, IsoS recovery was temperature-dependent, with full recovery of emission rates at lower temperatures, but only partial recovery at higher temperatures. The net result was that isoprene fluxes at high and low-temperatures were comparable and the temperature dependence was no longer a simple monotonic relationship. While this complex temperature relationship has been seen at leaf and single plant scales previously,[19,57] our results are the first to demonstrate this relationship at landscape scales.

Isoprene emissions also vary with available leaf area.[58] Plants suffering severe water deficits may reduce leaf area to prevent runaway embolism,[22,59,60] as hydraulic conductivity loss in the xylem can inhibit water delivery to leaves.[61] To separate drought effects on the isoprene−temperature response and plant leaf area, in Figures 2c,d we investigate the slope of correlation between daily maximum temperature and isoprene per unit LAI, where LAI is defined as the ratio of top-level leaf surface area relative to ground surface area over 2002−2017. The slope was derived using an ordinary least-squares linear regression, as uncertainties in the *y*-dimension (isoprene) dominate uncertainties in the *x*-dimension (temperature). Individual correlation plots are shown in Figures S2−S3, with on average 32 and 29 daily observations available per year in Fresno and Bakersfield, respectively (Table S1). In year 2008 in Fresno and 2010 in Bakersfield, insufficient dynamic range in the observations prevented determination of the slope (Figures S2−S3).

In Fresno, we find the isoprene−temperature response was similar in the pre- and early drought periods. However, the slope of this correlation (isoprene/LAI versus temperature) fell by 55% during the severe drought, with no apparent postdrought recovery. In Bakersfield, the isoprene−temperature response decreased as early as 2012 (there were no measurements in 2011). During the severe drought, the slope of correlation was 47% lower than in the predrought period, with no rebound in 2016−2017. Panels c and d of Figure 2 are consistent with laboratory observations by Fortunati et al.,[19] offering the first landscape-scale evidence that severe drought alters the temperature dependence of isoprene emissions.

Although we do not find a tight correlation between isoprene and LAI (Figure 3), similar trends in the isoprene temperature-dependence are observed for both isoprene/LAI and isoprene alone (Figure 2c,d). Direct comparison of monthly mean isoprene mixing ratios and LAI suggests reduced isoprene emissions per unit leaf area but no significant decrease in severe-drought LAI compared to predrought (Figure 3). While our MODIS imagery averaging regions (Figure S1) focus on the oak savanna, they also encompass agricultural fields and higher-elevation pine forests, which may obscure drought−LAI effects on isoprene-emitting species specifically.[62] Therefore, the observed correlation is a lower bound on the isoprene-emitting LAI response to severe drought. However, congruent with our findings, canopy-scale isoprene emission studies of poplar (*Populus spp.*) demonstrated that as leaves die, the LAI-dependence of isoprene emission rates decline, and emissions become more sensitive to light and temperature.[63,64] As a constraint on isoprene variation with changes in photosynthesis, solar-induced chlorophyll fluorescence (SIF) observations from the satellite-based Global Ozone Monitoring Experiment-2 (GOME-2) would be a potentially direct proxy for interannual trends of photosynthetic activity;[51,52] however, the sensor has experienced steady degradation over our study window, preventing interpretation of drought impacts.[53]

Observational Constraints on PO_3. PO_3 is a nonlinear function of the abundance of nitrogen oxides ($NO_x \equiv NO + NO_2$) and organic gases reactive with OH (Figure 4). At low

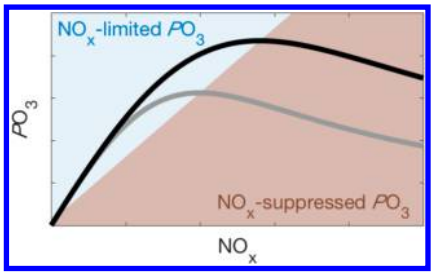

Figure 4. Cartoon illustrating PO_3 versus NO_x concentration at high (black) and low (gray) organic reactivity. NO_x-limited PO_3 is indicated in blue, and NO_x-suppressed PO_3 is indicated in brown.

NO_x concentrations, increases in NO_x increase PO_3, as NO propagates radical recycling and drives PO_3. Under these conditions, organic reactivity to OH (e.g., isoprene) has little effect on PO_3. This chemical regime is known as NO_x-limited and O_3 can be regulated effectively through NO_x emission control. At high NO_x concentrations, NO_x increases reduce PO_3, as NO_2 reacts with OH, yielding closed-shell nitric acid and

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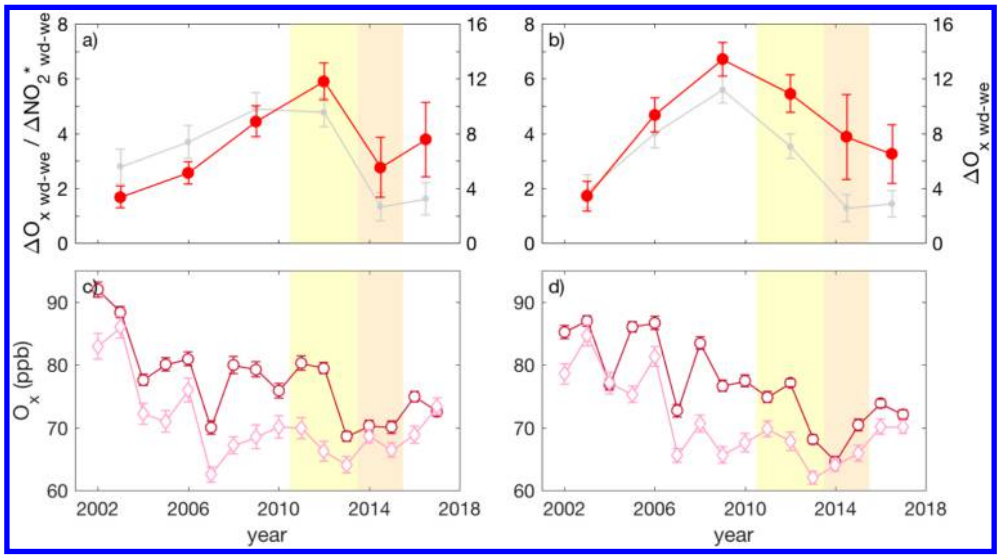

Figure 5. (a and b) Right axis (red): afternoon (12−5 pm, LT) $\Delta O_{x\ wd-we}/\Delta NO_2^*{}_{wd-we}$ during O_3 season (June−September) in Fresno and Bakersfield. Left axis (gray): $\Delta O_{x\ wd-we}$ for the same data with standard mean errors. (c and d) Afternoon (12−5 pm LT) O_x (ppb) during O_3 season on weekdays (burgundy circles) and weekends (pink diamonds) in Fresno (c) and Bakersfield (d). Error bars are 1σ standard mean errors. Tinted areas indicate the 2011−2013 early drought (light yellow) and 2014−2015 severe-drought (light orange) time periods.

terminating radical propagation. This PO_3 regime is known as NO_x-suppressed, with organic emission reductions leading to decreased PO_3 and NO_x reductions leading to worsened O_3 pollution. Changes in organic reactivity not only affect PO_3 at higher NO_x levels; they also alter the NO_x concentration at which PO_3 is maximized (Figure 4). Steady reductions in NO_x emissions over the past few decades in California[39] and across the United States[65] have led to the prevalence of O_3 chemistry that is increasingly NO_x-limited, which has been observed in California[66,67] and cities throughout the United States.[68,69]

Drought effects on the NO_x-dependence of PO_3 can be tested independently from the loss and mixing terms in $\partial[O_3]/\partial t$ (eq 1) using the well-documented weekday−weekend experiment, which takes advantage of known day-of-week patterns in emissions of NO_x and organic reactivity to OH. In U.S. cities, NO_x concentrations have historically been much lower (40−60%) on weekends than weekdays because of reduced weekend traffic from heavy-duty diesel vehicles (HDDVs).[65,70] HDDVs are a major source of NO_x emissions, although they comprise a small fraction (~3%) of the overall U.S. vehicle fleet.[71] Weekend NO_x decreases occur without equivalently large changes in organic reactivity to OH,[72] as HDDVs are a relatively small source of total organic reactivity emissions. This has been demonstrated to be true in California where there are abundant nontraffic organic emission sources.[73−75] When statistics are sufficient to minimize meteorological variability, observed weekday−weekend differences in the mixing ratio of O_x ($\Delta O_{x\ wd-we}$) trace a single PO_3 versus NO_x curve (i.e., constant organic reactivity with varying NO_x).[66] O_x ($O_x \equiv O_3 + NO_2$) includes the portion of O_3 temporarily stored as NO_2.

In 2007, the EPA established more stringent HDDV NO_x emission standards using NO_x selective catalytic reduction (SCR) technology.[76] HDDV regulations affect the weekday−weekend experiment, as reductions mostly occur on weekdays, causing diminishing weekday−weekend differences. HDDVs have long service lifetimes and slow fleet turnover; therefore, their NO_x control will take place gradually over decades. In California, HDDV NO_x reductions have been accelerated through statewide programs requiring all vehicle owners to retrofit or replace older engines with SCRs by 2023.[77] As a result, SCR-equipped vehicles represent a growing fraction of HDDVs on California roads.[78,79] While there have been conflicting reports on the real-world efficiency and durability of SCRs,[80,81] SCR-equipped HDDV fleet infiltration is suggested by decreases in weekday−weekend NO_2^* differences ($\Delta NO_2^*{}_{wd-we}$) in California (Table 1).

Trends toward smaller $\Delta NO_2^*{}_{wd-we}$ are also consistent with increases in the relative contribution of other non-HDDV weekday−weekend-independent NO_x emission sources, for example soils and fires, which are also drought-dependent. Almaraz et al.[82] demonstrated that fertilized soils contributed almost half of NO_x emissions in late July−early August 2016 in Central California (Fresno, Tulare, and Kings counties), and increases in fire activity, and hence NO_x emissions, attributed to greater fuel aridity[83] and the lengthening of the summer fire season,[84] have been observed in the western United States and California over the past several decades.

To investigate drought effects on PO_3 separately from effects on O_x mixing ratios, we present trends in $\Delta O_{x\ wd-we}$ during the pre- (2002−2010), early (2011−2013), severe (2014−2015), and post- (2016−2017) drought periods in Fresno and Bakersfield (Figure 5). To account for simultaneous interannual changes in $\Delta NO_2^*{}_{wd-we}$, we normalize $\Delta O_{x\ wd-we}$ by $\Delta NO_2^*{}_{wd-we}$, which linearly approximates the derivative $\partial PO_3/\partial NO_x$, representing $\Delta O_{x\ wd-we}$ per 1 ppb change in NO_2^*. Comparison of $\Delta O_{x\ wd-we}/\Delta NO_2^*{}_{wd-we}$ and $\Delta O_{x\ wd-we}$ indicates that lack of regard for decreasing $\Delta NO_2^*{}_{wd-we}$ would lead to an interpretation of PO_3 that is more NO_x-limited early in the record (in Fresno) and more NO_x-suppressed later on (in Fresno and Bakersfield) than is observed using $\Delta O_{x\ wd-we}/\Delta NO_2^*{}_{wd-we}$. In Figure 5a,b, $\Delta O_{x\ wd-we}/\Delta NO_2^*{}_{wd-we}$ shown are afternoon (12−5 pm LT) hourly measurements during the June−September O_3 season. Weekdays are defined as Wednesday−Friday and weekends are Sunday to reduce memory effects of the previous day. Any drought influence over PO_3 will have occurred alongside longer-term PO_3 trends ascribed to anthropogenic emission controls. In California, NO_x emission controls have led to decreases in NO_2^* concentrations (Table 1,

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Figure S4) and increasingly NO_x-limited PO_3.[66,67,85,86] This is evident in Figure 5a,b as $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ increased from 1.7 ± 0.4 to 4.5 ± 0.6 during the predrought in Fresno and from 1.7 ± 0.5 to 6.7 ± 0.6 in Bakersfield; at the same time, $NO_2{}^*$ decreased by ∼35% in both locations.

In Fresno, during the early drought, $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ continued to increase compared to the most recent predrought 3-year mean ratio (33%), while in Bakersfield, $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ decreased by ∼20% with respect to 2008−2010 $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$. During the severe drought, $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ fell in Fresno by 53% and in Bakersfield by 29% relative to early drought averages. Average postdrought $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ may have increased in Fresno by ∼35% and decreased slightly by ∼15% in Bakersfield compared to the severe drought period; however, differences are within uncertainties defined as 1σ standard mean errors.

Trends in $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ imply PO_3 became more NO_x-suppressed (although was still NO_x-limited) during the severe drought in Fresno and early and severe drought in Bakersfield. From 2008 to 2017, weekend O_x mixing ratios were comparable, suggesting weekend PO_3 was sufficiently NO_x-limited that drought did not perturb the chemical regime. A shift toward more NO_x-suppressed PO_3 can happen by either an increase in NO_x concentrations or by a decrease in organic reactivity to OH (Figure 4). In Fresno and Bakersfield, afternoon (12−5 pm LT) $NO_2{}^*$ mixing ratios declined by 18% and ∼35%, respectively, from 2008−2010 to 2014−2015. Downward NO_x trends were slower in Fresno, similar to the nationwide trends,[81] decreasing by just 6% between the early and severe drought compared to 30% in Bakersfield (Figure S4). While there may be drought influences over NO_x concentrations, we do not attempt to quantify them here.

Taken together, trends in $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ and $NO_2{}^*$ are consistent with a reduction in a substantial portion of the O_3-forming organic reactivity. Additionally, temporal changes in $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ reflect observed trends in isoprene as a function of location, with lower isoprene mixing ratios observed earlier in Bakersfield than Fresno. Isoprene constitutes just a portion of the total organic reactivity to OH in the region[87] and is known to make a small contribution in Bakersfield.[72] There are currently uncertainties in our knowledge of all specific molecules that comprise the organic reactivity regionally.[72,75] Our results offer evidence that an important fraction of this total reactivity is drought-sensitive and not produced as a simple function of photosynthetic carbon fixation.

A shift toward more NO_x-limited PO_3 caused by reduced organic reactivity requires that absolute PO_3 has also decreased (Figure 4). Here, we approximate the change in PO_3 from the early to severe drought period (ΔPO_3), which we then use (with measured $[O_x]$) to solve eq 1 for the coincident change in LO_3 + transport/mixing. We apply a known set of analytical equations (eqs S1−S3) to calculate instantaneous PO_3.[88,89] The analytical model is built on three assumptions: odd hydrogen ($HO_x \equiv OH + HO_2$) is conserved, peroxy nitrates are in steady state with radical precursors, and radical propagation dominates termination. These assumptions are valid when photochemistry is rapid, for example during hot summer days, and should be drought-independent. The model first solves for OH concentration, followed by PO_3; a full description is provided in the Supporting Information. Inputs to the model are NO_2/NO_x, total organic reactivity to OH, air temperature, PHO_x, and the alkyl nitrate branching ratio (α). Following the temperature-dependent O_3 chemistry analysis in Bakersfield by Pusede et al.,[72] we derive values at 35 °C of $NO_2/NO_x = 0.75$ and $PHO_x = 0.7$ ppt s^{-1} for both Fresno and Bakersfield. Because these terms are largely a function of O_3 concentration, they are likely similar in the two locations over 2002−2017. While there are observational constraints on predrought organic reactivity (at 35 °C) in Bakersfield (7−12 s^{-1}),[72] we have no empirical knowledge of the reactivity in Fresno. For Fresno, we test the range of available data (7−25 s^{-1}), including those collected at the Blodgett Forest Research Station in the Sierra Nevada Mountains, which may not be entirely representative.[90] In Fresno, α was set equal to 0.10 following Beaver et al.[91] for Sierra Nevada foothill Oak-influenced air parcels. In Bakersfield, α was set equal to 0.03 following Pusede et al.[72] We did not vary PHO_x or α between the early and severe drought; however, both may be drought-sensitive. While changes in PHO_x and α alter absolute ΔPO_3, they have a smaller effect on the PO_3 NO_x dependence than organic reactivity.[92,93]

To estimate ΔPO_3, we first determine the decrease in total organic reactivity consistent with measured $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ (an approximate of $\partial PO_3/\partial NO_x$), $\Delta NO_2{}^*_{wd-we}$, and the observation that $\Delta PO_{3\ we} \approx 0$ (Figure 5). This step is necessary because while we know the change in isoprene concentration between early and severe drought (Figure 2), we know neither isoprene's contribution to total organic reactivity nor the drought-sensitive portion of the total, including unknown reactivity. Because of documented $NO_2{}^*$ inaccuracies, the weekend NO_x concentration is determined as the NO_x concentration at which $\Delta PO_{3\ we} \approx 0$ within a 0.5 ppb tolerance. We compute PO_3 with an initial (early drought) total organic reactivity value in the range of 7−20 s^{-1} in Fresno and 7−12 s^{-1} in Bakersfield. We then estimate severe-drought PO_3 by varying "severe-drought" total organic reactivity (rounded to the nearest integer), optimizing agreement in observed $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ and $\partial PO_3/\partial NO_x$ (Figure S5). Calculated ΔPO_3 are weighted by 1 weekend day ($\Delta PO_{3\ we} \approx 0$) and three weekdays, mirroring our weekday−weekend analysis. Regardless of initial reactivity, results were generally consistent (Table S2). Severe-drought reductions in organic reactivity of 65−70% in Fresno and 25−30% in Bakersfield were required to match observations. Because we do not account for drought-related changes in PHO_x or α, calculated reactivity changes are an upper estimate, as they account for the full observed change in $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$. By comparison, isoprene mixing ratios decreased by 54% in Fresno and 29% in Bakersfield (Figure 2). Trends in $\Delta O_{x\ wd-we}/\Delta NO_2{}^*_{wd-we}$ are consistent with increased OH concentrations during the severe drought, which would have also led to reductions in nonbiogenic and/or drought-insensitive reactivity. In this way, we approximate that ΔPO_3 equals −25% in Fresno and −17% in Bakersfield.

Inferring Drought Influences over LO_3 and O_x Synoptic Time-Scale Variability. Despite large reductions in PO_3 between early and severe drought, O_x decreased by just 6% in both Fresno and Bakersfield (Table 1), indicating compensating changes in other terms in $\partial[O_3]/\partial t$. Lower severe-drought O_x mixing ratios compared to early drought were significant to the 1% level (Fresno, $p = 0.010$; Bakersfield, $p < 0.001$). Severe-drought O_x differences were also significant to the 1% level with respect to the early drought ($p < 0.001$) defined as 2008−2010 to reduce the influence of ongoing NO_x controls since 2002. While there were no ongoing direct LO_3 measurements in California, by solving the O_3 mass balance using the calculated change in PO_3 and treating drought-related changes in mixing

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effects on the O_3 concentration as negligible (discussion below), we infer estimates of the magnitude of drought LO_3 decreases.

In the surface boundary layer over vegetation, LO_3 is often dominated by chemical reactions between O_3 and biogenic alkenes ($LO_{3\ chemistry}$) and O_3 deposition through stomatal pores ($LO_{3\ deposition}$),[26,28] although other nonstomatal processes may also be important. Using the isoprene concentration measurements, in Fresno we estimate a decrease in $LO_{3\ chemistry}$ between the early and most severe drought periods of less than 0.3 ppb O_3 day^{-1} ($k_{O_3+isoprene} = 1.3 \times 10^{-17}$ cm^3 $molecules^{-1}$ s^{-1}, integrated over 12−5 pm). Long-term observations of reactive terpenes are not available; as an upper estimate, if drought similarly reduced other reactive organic gases in Fresno (by 0.45 ppb isoprene), and if these gases had an O_3 reaction rate similar to α-pinene ($k_{O_3+\alpha\text{-pinene}} = 8.0 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}), we would calculate that $LO_{3\ chemistry}$ changed by 1.5 ppb O_3 day^{-1} integrated over 24 h, contributing to a ∼ 2.5% increase in O_x concentration. In Bakersfield, we estimate a decrease in $LO_{3\ chemistry}$ from the early to severe drought of 0.03 ppb O_3 day^{-1} due to decreased isoprene mixing ratios and of 0.2 ppb O_3 day^{-1} due to the same hypothetical reduction in other organic gases (0.06 ppb). This suggests a change in $LO_{3\ chemistry}$ during the severe drought of 0.5−3% in Fresno and <0.3% in Bakersfield.

The remainder of the drought-dependent change in LO_3 has been previously attributed to reduced $LO_{3\ deposition}$ to vegetated canopies because of decreased stomatal conductance and leaf area.[7,22,27,94,95] Deposition to ground surfaces may also be suppressed during drought, as reduced resistance to soil deposition has been observed at lower relative humidities.[96] Using eq 1, we estimate drought-driven changes in $LO_{3\ deposition}$ (stomatal, cuticular, and to soil) of ∼18% in Fresno and ∼10% in Bakersfield, which are of the same magnitude as modeled changes over Texas forests, where drought led to $LO_{3\ deposition}$ decreases of 5−15%.[22]

Some models predict drought will result in changes in surface wind speeds and synoptically driven factors such as greater atmospheric stagnation[8,97] leading to enhanced O_3 accumulation over multiple days[98,99] and changes in surface mixing heights.[100] In Fresno and Bakersfield, we find slightly slower daytime (12−5 pm LT) surface wind speeds concurrent with drought years (Table 1). One effect would be to reduce the spatial extent of the upwind footprint. For example, the Clovis monitoring station is located at the eastern edge of the O_3-polluted SJV and 10.5 km northeast of downtown Fresno. Integrated over 6 h, early drought and severe-drought wind speed differences (corresponding with ΔPO_3) amount to a 5% decrease in the mean upwind footprint. Because high O_3 concentrations are prevalent throughout the SJV,[66] small changes in the size of the source region are not expected to cause large variations in O_3 mixing ratios measured in Fresno or Bakersfield.

As a constraint on whether O_3 variation on synoptic time scales is influenced by drought conditions, we compare the severity, length, and total O_3 accumulation of high-O_3 events during the pre-, early, severe, and postdrought periods (Table 1). O_3 events are identified as four or more consecutive days of increasing afternoon (12−5 pm LT) mean O_x mixing ratios during the June−September O_3 season with a 5% tolerance and leading to an O_x increase over the event of at least 10%.[101] Severity and accumulation are defined for each event as the slope of the O_x concentration versus day and the difference between the maximum and minimum measured O_x, respectively.

Through this method, in Fresno, event severity, length, and accumulation in the early ($p = 0.324$, $p = 0.639$, $p = 0.807$) and severe drought ($p = 0.635$, $p = 0.272$, $p = 0.871$) were statistically indistinguishable from the predrought period. While the ensemble event severity distribution is positively skewed over most of the time record, during 2014−2015 the distribution is approximately normal (Table 1). A reduction in the highest severity values is consistent with a reduction in PO_3 during severe-drought O_3 events. Likewise, in Bakersfield, differences in event severity, length, and accumulation in the early ($p = 0.450$, $p = 0.926$, $p = 0.431$) and severe drought ($p = 0.398$, $p = 0.898$, $p = 0.483$) from the predrought period were not significant at the 5% level. While O_3 variations on synoptic time scales (4−13 days over 2002−2017) do not appear to have changed significantly during the severe drought, drought conditions may have still exerted influence over synoptically driven factors.

Air Quality Implications, Future O_3 Ecosystem Impacts. Our results suggest drought-O_3 influences are both more complex than would be inferred from the atmospheric O_3 temperature and humidity dependence and are a function of drought severity and duration. This observational study, based on trace gas concentrations rather than flux measurements, is not sensitive enough to distinguish early drought-driven isoprene enhancements from interannual variability, but decreased isoprene under severe drought conditions (and with early drought in Bakersfield) is unambiguous. Oak trees are drought tolerant,[102,103] in part because of their ability to manage water resource limitation[104] and access groundwater through deep root systems;[105] however, the limits of their drought resilience are not entirely known.[104] We find conditions in the Sierra Nevada foothills during the California drought were sufficiently severe to suppress isoprene emissions regionally. While isoprene mixing ratios rebounded partially in Fresno (∼35%) and possibly in Bakersfield (∼15%) in 2016−2017, recovery was impaired at higher atmospheric temperatures. We anticipate results derived in California should apply to other ecosystems with isoprene-emitting drought-prone vegetation. While O_3−temperature correlations are often presupposed, in many locations, this correlation is caused by the temperature dependence emissions of biogenic organic reactivity to OH, including isoprene.[56]

Decreased isoprene emissions will alter O_3 plant and ecosystem impacts, as isoprene reduces stresses from O_3 pollution.[106] Isoprene and other biogenic alkenes act as within-leaf chemical sinks of oxidants, including O_3, preventing a variety of O_3 plant injuries[107] and suggesting greater O_3 sensitivity for ecosystems postdrought. However, while Sierra Nevada trees can live for hundreds of years, high O_3 concentrations in the western Sierra Nevada foothills, which are common during drought and nondrought years, are only a decades-old phenomenon. The combination of serious O_3 pollution and widespread tree death initiates a landscape scale experiment on O_3 influences over plant community dynamics. There is laboratory evidence that elevated atmospheric O_3 affects plant development and growth, including delayed starch biosynthesis, greater isoprene emissions with a larger portion of photosynthetic carbon allocated to isoprene production, and structural changes leading to increased O_3 resistance.[108] It is also predicted that O_3 pollution favors isoprene-emitting plant species, causing a shift in species composition, which unless otherwise perturbed, would take centuries.[109]

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Climate change is predicted to affect the chemistry and environmental conditions that control atmospheric O_3 concentrations.[6,56,110] There remain critical uncertainties related to effective regulatory design in a warmer and/or otherwise different climate, including more prevalent and extreme drought. Moreover, the magnitude and sign of drought forcing on any individual term in the O_3 mass balance equation will vary as a function of location. Our analysis adds to growing literature indicating severe drought has the potential to alter the abundance and temperature-dependence of O_3-forming biogenic organic reactivity, the dominant chemical mechanisms and absolute rates of PO_3, and the O_3 tropospheric lifetime. While less abundant in Fresno and Bakersfield, California, isoprene is typically the largest source of OH reactivity in the continental boundary layer; as a result, drought−isoprene effects on PO_3 will likely be more pronounced in locations where isoprene dominates. We find severe drought conditions worsen the so-called O_3-climate penalty, defined as diminished NO_x emission control benefits,[67] as biogenic reactivity is reduced to the extent that PO_3 becomes more NO_x suppressed; more substantial decreases in NO_x would be required to have the same effect. In California, drought conditions led to decreased PO_3, but air quality benefits were largely negated by concomitant changes in LO_3, suggesting more aggressive regulatory interventions will be required in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04852.

Geographical areas for LAI, annual isoprene versus temperature correlations, trends in weekday and weekend NO_2* mixing ratios throughout study period, and analytical model description (PDF)

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Notes

The authors declare no competing financial interest.

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