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Atmospheric response to air quality regulations: Observation-constrained assessment of historical changes in ozone production characteristics

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**Abstract**

One of the important goals of air quality research is to provide data that can help in determining the most appropriate regulatory policies. Often, this requires a larger spatio-temporal-scale understanding, which can be obtained by integrating precise and accurate process-level knowledge. In this paper, we find observational evidence of the responsiveness of ozone production characteristics to implemented regulation by investigating the time rate of change in ozone concentrations at peak local production conditions. The South Coast Air Basin (SCAB) in California results indicate a clear shift from predominantly volatile organic compounds (VOC) to nitrogen oxides (NOx) after 2009, when the regulations were enacted. Regulation policies affecting NOx only may pose challenges for the attainment of National Ambient Air Quality Standards (NAAQS) in the near future, as the SCAB recently entered the NOx-transitioning regime. Our approach provides a valuable reference for studies using the long-term data available in many regions in the world.

**Significance**

Because ozone (O3) reduction strategies are complex, this study highlights the importance of determining how the atmosphere responds to implemented ozone mitigation strategies. As applied to the South Coast Air Basin (SCAB) in California, where intensive mandated O3 controls are enforced, but violations of regulations also occur, our analysis shows observational proof of the sought-after shift from VOC- to NOx-predominance. While NOx reduction is a more straight-forward process, concurrent VOC reduction is still necessary. This study has important implications for effectively designing O3 controls. It is timely as well, given the increasing availability of long-term observational databases, not only in California but also in other world regions battling ozone problems.

**Introduction**

Living in what has been termed the Anthropocene Epoch, it is important to study the human impact on our environment. While state-of-the-art techniques continually reveal more of the mechanistic processes of air pollution, long-term, continuous and robust datasets can also provide valuable insights on regulation policies. Tropospheric ozone (O3) is one good example of a pollutant since well-established intensive techniques, with high temporal and spatial coverage, exist for monitoring it. Furthermore, O3 is the subject of widespread concern and poses numerous regulatory complexities.

Surface O3 is a major pollutant with consequences for air quality and the climate. It directly and indirectly affects the climate by influencing radiative forces and by controlling the lifetimes of other greenhouse gases (1–3). In addition, O3 is a primary constituent of photochemical smog; there is toxicological and epidemiological evidence that it is harmful to human health (4–8) and that it poses adverse effects to vegetation (9, 10). Consequently, it has been classified as one of the six criteria air pollutants designated by the U.S. Environmental Pollution Agency (EPA), and is subject to regulations in numerous countries (11).

O3 is not emitted directly into the air. Rather, it is formed via radical formation and termination processes from the reactions of its precursors-nitrogen oxides (NOx = NO + NO2) and volatile organic compounds (VOCs) in the presence of sunlight (12). Moreover, quantifying the exact amount of expected O3 improvement from reducing precursors is complicated by the non-linearity of O3 formation. Thus, reducing precursors does not always lead to reduced O3 concentrations (13, 14). Ozone production sensitivity (OPS) classifies how O3 production responds to changes in precursor emissions in terms of photochemical regimes, either NOx-saturated (also termed VOC-limited, VOC-sensitive, or radical-limited) or NOx-limited (NOx-sensitive) regimes (15, 16).

Comprehensive direct measurements and detailed models have provided major insights into ozone production rates (OPR) and OPS, which have helped in establishing regulatory policies. First and second-generation Measurement of Ozone Production Sensors (MOPS) (17–20) and modified instruments (21, 22) directly measure OPRs. Indicators such as LN/Q (ratio of radical loss by reactions with NOx to the total primary radical production), NOx/VOC ratios, and proxies such as , , and (13, 23–27) reflect OPS. These are useful tools but do not demonstrate the atmospheric response to regulations over decades and rarely provide future projections, unless supported by predictive models. In addition, due to intensive sampling requirements, these tools are limited to areas with ample spatio-temporal data coverage.

The time rate of change in O3 concentrations under specific conditions enables us to analyze O3 formation process on a local scale. The photochemical ozone production rate (PO3\*) is a proxy for OPR based on already existing datasets of O3, NOx, several speciated VOCs, and meteorological parameters from routine air quality monitoring stations. Changes in PO3\* can be used to show how O3 photochemistry has changed following implementation of O3 control strategies. This approach uses pairs of days in a week with varying NOx concentrations, while holding VOC reactivity relatively constant to represent comparable radical production conditions. Thus, long-term trends of the O3 production rate and its dependence on precursors can be analyzed. Additionally, it enables us to quickly predict the effectiveness of precursor reductions towards mitigating ozone production over a specific area and time period.

**Results and Discussion**

California’s South Coast Air Basin (SCAB) was selected as a test case for tracing changes in decadal O3 production characteristics, not only due to the availability of long-term datasets, but also due to its high population density (1700 people/square mile), favorable photochemistry conditions, and intensive regulatory efforts in the region. The combined effects of emissions, topography, and meteorology of the basin lead to a number of air quality problems, including high ozone levels, especially in inland areas (28, 29). Over the past decades, O3 problems have been addressed through stringent implementation of NOx and VOC reductions, However, the basin still falls far short of attaining its ozone reduction goals.

In inferring photochemical O3 production quantitatively, “odd-oxygen”, ( is preferred over O3because its production and decomposition are independent of the rapid photochemical reactions that convert O3 to NO2 and vice versa (30, 31). We estimated the ozone production rate, \*, using the mass balance approach: . \* becomes directly proportional to the time rate of change in ambient concentrations. We assumed that during the selected time window when the photochemical activity is high, production () outweighs chemical loss, and horizontal advection () is negligible. To meet these criteria, a time window was carefully chosen for each Air Quality Monitoring Station (AQMS) site (*SI Appendix*, Fig. S1). Days with perturbations in local photochemistry (i.e., rain, cloud cover, fire events, etc.) were excluded, as were data with high wind, l to minimize the influence of advection and to hold deposition relatively constant, which also depends on the roughness of a surface. The atmospheric turbulence changes minimally within a week, provided that wind conditions are constant. Wednesday and Saturday were chosen to represent high and low NOx conditions, respectively (*SI Appendix*, Fig. S2 and Table S2). Further details on the locations of individual stations (*SI Appendix*, Table S1), filtering (*Methods*), and sensitivity test results (*SI Appendix*, Fig. S3) to reach the assumptions are provided in the supplementary materials.

Table 1 summarizes the \* values over the last two decades in various areas of the SCAB, which we grouped as coastal according to the identified subregions of the California Air Resources Board (*SI Appendix*, table S1) (we additionally distinguish between CST1 and CST2 based on the distance from the coast): the San Gabriel Valley (SGV), the Inland Empire (INL), Riverside County (RIV), the San Fernando Valley (SFV), and Santa Clarita (SCL). To study the changes in O3 characteristics due to regulation efforts, \* values were calculated within three-year averaging periods from 2001 to 2018 and weighted according to the number of observations. Our analysis focused on the months of May to September, when O3 peaks. For validation, we compared our calculated \* with PO3 values from the NASA Langley Research Center (LaRC) photochemical model. The LaRC model is constrained by observations from the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites-CARB (ARCTAS-CARB) flights. Our calculations are consistent with the LaRC model within 13 %, (*SI Appendix*, Fig. S4), and the difference can be explained by a \* and comparison as well as by possible offsets of depositional loss (1.2 to 2.2 ppb/hr; details for offset estimation are found in *Methods*), Our \* calculation shows larger variabilities than the modeled values from LaRC, likely due to the heterogeneity originating from the variety of nearfield sources at the surface.

Fig. 1 shows the spatial and temporal variation of OPS. The majority of the subregions, with the exception of CST1 and RIV, tend to have a lower OPS during the week (high NOx) and a higher OPS during the weekend (low NOx), indicating that these regions have been in a NOx-saturated regime. However, in recent years, SFV and INL have subtly entered the transition region. Nonetheless, SGV and CST2 subregions still remain as NOx-saturated regions where NOx emissions are high, as typical of urban core environments. Interestingly, RIV is nearing the NOx-limited regime far earlier, as OPS slopes become steeper and positive (-0.060, 0.015, 0.0060, 0.30, 0.14, and 0.27, respectively).

The shaded background in Fig. 1 was computed with an analytical model assuming a steady state of hydrogen oxide radicals (HOx) (32, 33) and various HOx radical production rates (PHOx) ranging from 0.24 to 1.24 ppt/s. The relative magnitude of PHOx adjusted for matching the OPS of individual sites generally aligns well with temperature values that were used as a proxy for PHOx and VOC reactivity (VOCR). As previous studies have suggested, PHOx has both a direct and indirect relationship with VOC concentration (16, 34, 35), and helps explain the precursor concentration dependence in OPR. CST1 and LAK in RIV had the lowest PHOx (0.24 to 0.44 ppt/s) and VOCR values. Thus, the lowest \* values were near the NOx-limited regime. In contrast, SCL, INL, and RIV had higher PHOx (0.44 to1.24 ppt/s) and relatively similar VOCR values;consequently, they had higher \* values and were in the transitional regime. There were several exceptions, such as SGV, which had lower temperatures but a higher PHOx, likely due to its urban characteristics. Likewise, LAN of CST2 had a lower PHOx but higher temperatures, presumably due to its large urban area and land use patterns. Furthermore, the higher VOCR found there could be attributable to the measured aldehydes with a high reactivity contribution that were not measured in other sites.

Calculated OPS (*SI Appendix*, Table S3) in the SCAB evidently reflects the aggressive efforts in mitigating O3 precursors in recent years. NOx levels were successfully reduced in the basin throughout the study period, but regarding VOC, reductions were more apparent from 2001 to 2009 (Fig. 2A). Our OPS analysis reveals how local O3 production responded to such changes in precursors. Thus, our OPS plot is an observational proof of regime changes. Historically, the SCAB has been in a NOx-saturated regime, but since emission mitigation strategies have been implemented, precursors related to mechanisms controlling O3 formation and quantity have changed (29).

In spite of substantial reductions in precursor emissions in recent years, O3 and \* have not significantly decreased as expected and continue to violate the regulatory requirements (*SI Appendix*, Fig. S6 and Table S4). A dramatic reduction in NOX levels (-1.6 ppb/yr, p-value=0.0085) did not yield significant changes in \* (-0.085 ppb/hr/yr, p-value=0.060) or O3 (95th percentile concentration -0.55 ppb/yr, p-value=0.13, α=0. 05); rather, both increased between 2016 and 2018. This momentary slowing rate may indicate a regional non-linear transitioning from a NOx-saturated to a NOx-limited regime, as also predicted by photochemical modeling analyses (29). Consistent with this nearly twenty-year trend of NOx, O3 and \*, our OPS analysis has captured when the basin began to enter the transitional zone, as shown in Fig. 2A. Transitioning to a NOx-limited regime may seem to suggest that NOx-focused controls would be a more strategic approach, but our projections with OPS show that attaining the desired standard with NOx-focused controls remains questionable.

Currently, the percentage of exceedance days for the three-year averages of peak 8-hr O3 is predicted as ~30% (Fig. 2B). This is derived from the back calculation of O3 concentration using \* , , background changes, and with correction for depositional loss (*Methods*). This method aligns well with the fraction of corresponding violation days (slope:0.92, R2:0.79, *SI Appendix*, Fig. S7). Using this estimation method, our prediction shows that an additional reduction of ~2.0 and ~ 3.4 ppb/hr \* is required to achieve 20% or 10 % exceedance, respectively. Such a reduction would be challenging to attain solely from NOx reduction strategies of 57% and 72% from the current level (Fig 2A) and under the current energy production scheme. Reduction in PHOx by 47% and 64% may be a complementary tactic for attainment in the near future. Overall, a continuous NOx-focused control strategy is an effective approach. However, since the basin is still in a transitional regime, attaining the NAAQS for O3 might be more difficult than expected without concurrent VOC reductions.

Our prediction may have been limited by vertical mixing of O3, and especially residual layer intrusion during morning hours (36). Although our method is based on observed behaviors of O3, estimating the limit of improvement from localized regulation efforts necessitates separating between O3 concentrations influenced by local production and those affected by meteorological factors. This analysis will benefit from readily available O3 vertical gradient data with larger spatio-temporal coverage. Moreover, the development of direct or indirect PHOx gauging techniques and larger coverage in VOC speciation measurements will be required for more targeted VOC-reduction strategies.

The results of this work not only strengthen our understanding of O3 production, but also provide insight into the effectiveness of emission control strategies. We developed a new OPS indicator based on a proxy for estimating the local ozone production rate. Taking advantage of the extensive network data available since 2001, we determined the photochemical regime of the SCAB and its constituent air mass groups. In the SCAB, as well as other regions in the world, enacting O3 abatement strategies, the rate of O3 improvement is expected to vary according to how controls are implemented and by changes in regulatory regimes. Hence, OPS indicators play a vital role in establishing the efficiency of control strategies and may be used as a gauge of regulations’ effectiveness.

**Materials and Methods**

**Site and Data Description.** Nineteen Air Quality Monitoring Stations (AQMS) grouped into seven subregions were examined in this study. Table S1 in the *SI* *Appendix* summarizes their detailed site information. Region CST1 includes areas near the coast: Anaheim-Pampas Lane (ANA), Costa Mesa-Mesa Verde Drive (COS), Los Angeles Westchester Parkway (LAW\*), North Long Beach (NLB), and West Los Angeles- VA Hospital Region CST2 includes areas in the central basin, urban core, and eastern basin: La Habra (LAH), Los Angeles North Main Street (LAN\*), Pico Rivera 4144 San Gabriel (PIC\*), SFV-Burbank Palm Avenue (BPA\*), Reseda (RES), Santa Clarita (SCL), SGV-Azusa (AZU\*), Glendora-Laurel (GLE), Pasadena (PAS). INL-Fontana, Pomona (POM), Upland (UPL\*), and Riverside Rubidoux (RIV\*). The asterisk denotes the seven stations with available VOC data. The air quality and meteorological data coverage is from May to September of 2001 to 2018, and is available for download from the Air Quality and Meteorological Information System (AQMIS) section of the California Air Resources Board (CARB) website (<https://www.arb.ca.gov/aqmis2/aqmis2.php>) (37). We used speciated VOC profiles from CARB, as well as hourly air quality data for O3, NO2, NOx, and CO. Our analysis utilized a total of 56 to 62 VOC species measured every six days, ranging from alkanes to biogenics, as listed in *SI* *Appendix,* Table S5 with hydroxyl (OH) reaction rate constants. The oxidation of VOCs by OH leads to radical production, a major factor in determining ozone production rates (OPR). Individual VOCs also have reactivity-dependent effects (38). However, it is only at a threshold level of NOx that higher VOCR promotes more O3 formation due to the radical termination processes of self-reactions among HOx radicals (OH, HO2 and RO2). The OH reactivity of a VOC mixture is calculated as:

 (Equation 1)

where,

 stands for each VOC species, stands for ith VOC concentration,

and refers for the rate constant for the reaction of VOC with OH.

Moreover, hourly meteorological data of parameters, such as temperature, air pressure, wind speed, and precipitation were utilized for filtering and for sensitivity tests. For sites without an AQMS, meteorological data from the closest AQMS were used instead,(designated as \*\* in *SI* *Appendix,* Table S1).

This study aimed to investigate local ozone production rates. Consequently, considering different NOx conditions (day-of-the-week (DOW) pairs) and defining inclusion criteria were critical to focus the data set on times of peak local ozone formation processes. Days with perturbations in local photochemistry, such as rain, increased cloud cover, and fire events, were removed. We used the filtering criteria of precipitation greater than 0 mm, and carbon monoxide (CO) values more than three scaled median absolute deviations (MAD) away from the median. Days with high wind speed were also excluded due to the possible influence of advection and deposition.

**Ozone Production Rate Proxy.** The mass balance approach shown in Equation 2 is used for determining the rate of production. As the equation demonstrates, ambient depends on the combined effects of chemical production ( and destruction of (), as well as meteorological factors that drive transport: advection () and deposition (). In this study, the timespan was crucial for computing \*, and was chosen based on the diurnal plots of O3 and NOx (*SI* *Appendix,* Fig. S1). Each site exhibited unimodal distribution for O3, but with different peaking times, based on their relative positions in an airshed. Upwind and urban areas showed peaking times around noon, while the downwind area likely showed delayed peaking times. The time window varies but is similarly selected for when concentration linearly increases with time. When local photochemical production was high and the boundary layer was well-developed, chemical loss of was outweighed by production. Additionally, the time window of two to three hours after the NOx peaking time and prior to it rising again was considered to exclude the effect of NOx titration. Deposition mainly depends on wind speed and roughness of the surface, and thus atmospheric turbulence was also assumed to be relatively constant across day-pairs. In a specific area, these parameters remained stable throughout a week of similar wind and temperature conditions. Moreover, advection was set to be negligible through wind speed filtering. Values greater than the 70% threshold of the histogram data were discarded to minimize the effect of horizontally transported O3. Given these assumptions, the rate of change in ambient with respect to time was proportional to the \*, as shown in Equation 3. It wa determined using linear regression, computing the change in concentration with respect to the time window selected, and, when used as a proxy for the OPR. \* for each group, was weighted based on the number of data observations.

 (Equation 2)

 (Equation 3)

**Ozone Production Sensitivity.** In this study, the OPS for every three-year period is determined by calculating \* changes with respect to NOx changes, as shown in Equation 4. High and low NOx levels are represented by weekday (WD) and weekend (WE), respectively. In NOx-limited regions, \* decreases as NOx decreases (positive slope) or vice versa, while in NOx-saturated regions, \* decreases as NOx increases (negative slope). Enlarged OPS plots for SCAB subregions are shown in *SI* *Appendix,* Fig. S8.

 (Equation 4)

**Sensitivity Tests.** To check the robustness of our results, we performed sensitivity tests on the time window, day-of-the-week pairing, and wind speed threshold parameters. Sensitivity tests on the time window selection were conducted by shifting the starting time an hour earlier and later than the default or original time window selected (*SI* *Appendix,* Fig. S3A). No significant changes in the regime were observed. Pairs of days with constant VOCR but significantly different NOx conditions were selected to represent the change in emissions-related activities (mainly due to reduced motor vehicle emissions) between the business week and weekend, particularly in urban areas (40, 41). The analysis was similar to the weekend effect (32, 38) but with unchanging VOCR. Although the available VOC data was limited to seven sites, it was still used because weekdays and weekends were comparable in terms of data points. It was observed that Saturday and Wednesday were best suited to represent a weekend day and a weekday(*SI* *Appendix,* Fig. S2). LAN has a more comparable VOCR on Sunday, but the OPS of Sunday–Wednesday and Saturday–Wednesday pairs had no significant difference (p-value=0.59). Because we were also analyzing subregions, CST2 still showed Saturday as a better weekend representative. With the exception of LAW, which displayed no significant difference in NOx, weekdays and weekends compared similarly at all other sites with available VOC data. There was an insignificant difference in VOCR, but a significant difference in NOx between the weekdays and Saturday, at α = 0.05 level of significance (*SI* *Appendix,* Table S2), indicating that the method was not affected by the particular weekday chosen. To further test the effect of changing the day-of-week pairs, we plotted the OPS of Saturday with a Wednesday to Friday pairing (*SI* *Appendix,* Fig. S3B). No significant changes in the regime were observed. Similarly, it was examined based on wind speed by discarding 10%, 20%, 30% (default), and 40% of the histogram data (*SI* *Appendix,* Fig. S3C). As no changes in the regimes were observed, the 30% discarded threshold was selected to minimize the influence of advection and still include a sufficient amount of data.

**\*** **comparison with Modelled (mod).** To check the validity of the proxy, we estimated for \*, we extracted data from June 18–26, 2008, computed \* within SCAB, and compared it with the instantaneous data calculated using the NASA Langley Research Center (LaRC) photochemical box model. This model is constrained by measurements taken aboard the NASA DC-8 aircraft during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites-CARB (ARCTAS-CARB) flights. These were downloaded from NASA LaRC ARCTAS archive: <https://www-air.larc.nasa.gov/cgi-bin/ArcView/arctas?DC8-MERGE=1> (42). Only California-focused modelled (mod) values falling within the spatial coordinates of the study area, the 09:00 to 14:00 time window, and within a 2 km pressure altitude were compared with \* (June 18, 22, and 24, 2008). \* was approximately 1.13 times larger, but it was within the range and not significantly different from model-calculated (p-value: 0.25, α =0.010) (*SI* *Appendix,* Fig. S4). The observed discrepancy could be associated with the difference in measurement altitude, overpass time, and heterogeneity originating from the variety of nearfield sources at the surface. Moreover, because the effects of deposition and advection losses have not been included, they could have been offsets as well.

**Prediction of Percent Exceedance Days.** The fraction of exceedance days was predicted using the mass balance approach (Equation 2). The background concentration considered was 45 ppb, using the reported value in literature of 40 to 44 ppb, which has an increasing rate of 0.27 ± 0.13 ppb/yr (43). Since an 8-hr average is needed and \* only covers 4-hr average periods, the next four hours were used to determine the 8-hr averaged peak O3 concentration. We estimated it as -2.4 ppb/hr by computing the change in O3 concentration over the time window when O3 linearly decreases, in the same manner in which \* was computed. The rate of deposition (D) offset was computed as 1.2 to 2.2 ppb/hr using Equation 5, where deposition velocity () was assumed to be ~0.37 to 0.74 cm/s based from the model results of previous studies in urban settings. These used different O3 dry deposition schemes (44, 45), a mean summer afternoon mixing layer height of 770 m (46), and a weighted mean of the 95th O3 percentile at 66.9 ppb. The predicted peak 8-hr O3 and the observed maximum 8-hr O3 show good agreement (8% difference in slope with 0.79 R2, fig. S7). From a histogram fit of the 3-yr peak 8-hr O3 levels and corresponding values, the current percentage of exceedance days was computed to be 30%. \* was reduced by a factor of 0.18 and 0.30, and the corresponding O3 was back calculated which resulted in 20% and 10% exceedance days, respectively.

 (Equation 5)