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How the atmosphere responds to the regulation efforts-observation-constrained historical changes in ozone production characteristics

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**Abstract**

The ultimate purpose in air quality research is to establish the most legitimate regulation policies requiring larger spatio-temporal-scale understanding which can be achieved via logical simplifications, integration, and thus generalization of precise and accurate process level knowledge. In this regards, phenomenal interpretation based on state-of-the-art knowledge is beneficial. Here, we show observational evidence of the responsiveness of ozone production characteristics which reveal tight link with real-world regulation efforts, by investigating the time rate of change in ozone concentrations under maximum local production condition; South Coast Air Basin (SCAB), California results show clear regulation shift from predominantly VOC-focused to NOx-focused after 2009. Sole NOx regulation policies may pose challenges for near-future attainment in National Ambient Air Quality Standards since SCAB just entered the NOx-transitioning regime. Our approach provides a valuable reference with good amount of long-term data which are available in many regions in the world.

**Significance**

As ozone (O3) reduction strategies are tricky, this study highlights the importance of determining how the atmosphere responds to the ozone mitigation strategies being implemented. As applied to South Coast Air Basin (SCAB), California, where intensive mandated O3 controls are carried out but still violates the O3 regulatory requirements, our analysis shows an observational proof of the regulation shift from VOC- to NOx-focused; while NOx reduction is a straight-forward approach, concurrent VOC reduction is still necessary. This study has important implications on how O3 controls could be effectively designed. It is timely as well, given that there is an increasing availability of long-term observational database, not only in California but also in other regions in the world battling ozone problems.

**Introduction**

Living in the Anthropocene, tackling human impact on nature is very important but not trivial. As much as fancy, fast, and sensitive techniques are being developed and employed for understanding the mechanistic processes, long-term, continuous robust datasets through careful analysis must also be equally paid attention too as these can provide good insights on regulation policies. Tropospheric ozone (O3) is one good example pollutant since (1) well-established intensive technique exists for high temporal and spatial coverage monitoring and (2) it is a worldwide concern that has regulation complexities.

Surface O3 is a major pollutant that is air quality and climate-relevant. It directly and indirectly affects the climate by influencing radiative forcing and by controlling the lifetimes of other greenhouse gases (1–3). In addition, O3 is a primary constituent of photochemical smog; it is harmful to human health based on toxicologic and epidemiologic evidences (4–8) and poses adverse effects to vegetation (9, 10). Thus, it has been classified as one of the 6 criteria air pollutants by the U.S. Environmental Pollution Agency (EPA) which is subjected to regulations in many areas in the globe (11).

O3 is not directly emitted into the air but is only formed from the net results of radical formation and termination processes among 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 with respect to precursors reductions is not intuitive due to the non-linearity of O3 formation, thus, reducing precursors do not always lead to reduced O3 concentrations (13, 14). Ozone production sensitivity (OPS) classifies how O3 production responds to changes in precursors emissions in terms of photochemical regimes, either NOx-saturated (also called as VOC-limited, VOC-sensitive, or radical-limited) or NOx-limited (NOx-sensitive) regime (15, 16).

Comprehensive direct measurements and/or detailed modelling works provided the major insights in OPR and OPS evaluation which helped in establishing regulation policies. First and second-generation Measurement of Ozone Production Sensor (MOPS) (17–20) and modified instruments (21, 22) directly measured OPR. Indicators such as LN/Q (ratio of radical loss by reactions with NOx to the total primary radical production), NOx/VOC, and proxies such as $\frac{H\_{2}O\_{2}}{HNO\_{3}}$, $\frac{HCHO}{NO\_{y}}$ , and $\frac{O\_{3}}{NO\_{y}}$ (13, 23–27) expressed OPS. These are good tools but hardly show us how the atmosphere responds to our regulation efforts over the decades and rarely predict where we are going, unless supported by model prediction. In addition, due to intensive measurement, these are bounded in terms of spatio-temporal coverage.

The time rate of change in O3 concentration under specific conditions to focus on analysis of maximized local process influence can represent the O3 forming characteristics. In this regard, changes in $PO\_{3}$\*, a proxy set for OPR based on already existing datasets of O3, NOx, including several speciated VOCs, and meteorological parameters from routine air quality monitoring stations, can be used to show how O3 photochemistry has changed along with implementation of O3 control strategies. This approach which uses pair of days in a week with varying NOx while holding VOC reactivity relatively constant to represent comparable radical production conditions enables us to analyze the long-term trends of O3 production rate and determine its functional dependence on precursors. Additionally, it allows us to promptly predict the quantitative effectiveness of precursors reductions toward mitigating ozone production over a specific area and period.

**Results and Discussion**

As a test bed for tracing decadal O3 production characteristic changes, California South Coast Air Basin (SCAB) is selected not only due to availability of long-term datasets but also to its high population density (1700 people/square mile) and favorable photochemistry conditions in conjunction with intensive regulation efforts. The combined effects of emissions, topography, and meteorology of the basin lead to air quality problems like high ozone levels, especially in inland areas (28, 29). Over the past decades, O3 problems has been significantly dealt with through stringent implementation of NOx and VOCs reductions, however, the basin still suffers from O3 with extreme non-attainment.

In inferring photochemical O3 production quantitatively, “odd-oxygen”, $O\_{x} $($O\_{x}=O\_{3}+NO\_{2})$ is preferred over O3$ $due to its production and destruction are independent of the fast photochemical reactions that convert O3 to NO2 and vice versa (30, 31). We estimated $PO\_{x}$\* using the mass balance approach $\frac{d [O\_{x }]}{dt}=PO\_{x}-LO\_{x}+AO\_{x}-DO\_{x}$). $PO\_{x}$\* becomes directly proportional to the time rate of change in ambient $O\_{x}$ concentrations under the assumptions that during the selected time window when the photochemical activity is high, $O\_{x}$ production ($PO\_{x}$) outweighs $O\_{x}$chemical loss$(LO\_{x})$, and advection ($AO\_{x}$) in horizontal direction is negligible. To fulfill these criteria, $PO\_{x}$ time window was carefully chosen for each Air Quality Monitoring Stations (AQMS) site (*SI Appendix*, Fig. S1). Days with perturbations in local photochemistry (i.e. rain, cloud cover and fire events, etc.) were filtered out. Data with high wind speed were excluded as well to minimize the influence of advected features and to hold deposition $(DO\_{x})$ relatively constant, which also depends on the roughness of surface, and thus atmospheric turbulence hardly changes in different days in a week under similar wind condition. 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 achieve the required assumptions are provided in the supplementary materials.

Table 1 summarizes the $PO\_{x}$\* values over the last two decades of various areas in SCAB which we grouped following the identified sub-regions of California Air Resources Board (*SI Appendix*, table S1) as coastal (we additionally separate CST1 and CST2 based on the distance from the coast), San Gabriel Valley (SGV), Inland Empire (INL), Riverside County (RIV), San Fernando Valley (SFV), and Santa Clarita (SCL) . $PO\_{x}$\* were weighted for 3-year averaging period from 2001 to 2018 with number of observations, to describe the changes in O3 characteristics due to regulation efforts. Our study focused on months of May to September when O3 maximizes. As a validation, we compared our $PO\_{x}$\* with PO3 from NASA Langley Research Center (LaRC) photochemical model constrained by Arctic Research of the Composition of the Troposphere from Aircraft and Satellites-CARB (ARCTAS-CARB) flights, and they are in good agreement (within13 %, *SI Appendix*, Fig. S4), the difference can be explained by $PO\_{x}$\* and $PO\_{3}$ comparison as well as possible offsets of depositional loss (1.2 to 2.2 ppb/hr; details for offset estimation are found in *Methods*); our $PO\_{x}$\* shows larger variabilities than the modeled, 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. Majority of the sub-regions, (except CST1 and RIV) tend to be lower during weekday (high NOx) and higher during weekend (low NOx), indicating that these regions have been in the NOx-saturated regime, but in succeeding years, SFV and INL have subtly entered the transition region. On the other hand, SGV and CST2 sub-regions still remain as NOx-saturated regions where NOx emissions are high, as typical of urban cores environment. Interestingly, RIV is nearing the NOx-limited regime far before 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 under steady state HOx assumption (32, 33) with various HOx radical production rate (PHOx) which ranges from 0.24 to 1.24 ppt/s. The relative magnitude of tuned PHOx for matching OPS of individual sites generally agrees well with temperature that was used as a proxy for PHOx and organic reactivity (here after, VOCR) due to its direct/indirect relationship with VOC concentration, as previous studies suggested (16, 34, 35), and explains well the precursor dependence in OPR; CST1 and LAK in RIV have the lowest PHOx ,(0.24 to 0.44 ppt/s) with VOCR, thus, lowest $PO\_{x}$\* and are or near the NOx-limited regime while SCL, INL, and RIV have higher PHOx (0.44 to1.24 ppt/s) with relatively similar VOCR, consequently, higher $PO\_{x}$\* and are at the transitional regime. There are few exceptions like SGV with lower temperature but higher PHOx, likely due to urban characteristics and LAN of CST2 with lower PHOx but higher temperature, likely due to being a megacity affected by land use type and higher VOCR could be due to the measured aldehydes with high reactivity contribution but not measured in other sites.

Calculated OPS (*SI Appendix*, Table S3) evidently reflects the aggressive efforts of SCAB in mitigating O3 precursors in the past years. The basin successfully reduced NOx all throughout the study period, but with VOC, reductions were more apparent in 2001-2009 (Fig. 2A). Our OPS analysis reveals how local O3 production responds to such changes in precursors. Thus, our OPS plot is an observational proof of regime changes; historically, SCAB has been in NOx-saturated regime, but as it implemented emissions mitigation strategies, precursors related to mechanisms controlling O3 formation and abundance have changed (29).

In recent years, in spite of substantial reductions in precursor emissions, O3 and $PO\_{x}$\* did not significantly decrease as expected and still violates the regulatory requirements (*SI Appendix*, Fig. S6 and Table S4); a dramatic reduction in NOX (-1.6 ppb/yr, p-value=0.0085), but no significant changes in $PO\_{x}$\* (-0.085 ppb/hr/yr, p-value=0.060) and thus, O3 (95th percentile concentration -0.55 ppb/yr, p-value=0.13, α=0. 05), both even increased in 2016-2018. This momentary slowing rate may be an indication of regional non-linear transitioning from NOx-saturated to NOx-limited regime, as also predicted by photochemical modeling analyses (29). Consistent with two decadal trend of NOx, O3 and $PO\_{x}$\*, our OPS analysis has captured as the basin began to enter the transitional zone, as shown in Fig. 2A. Transition to NOx-limited regime may sound like NOx-focused control would be a more strategic approach, but our projection with OPS shows that attaining the standard is still questionable.

Currently, the percentage of exceedance days for 3-yr average of maximum 8-hr O3 is predicted as ~30% (Fig. 2B), from the back calculation of O3 concentration using $PO\_{x}$\* , $LO\_{x}$,with background changes along with correction for depositional loss (*Methods*), which agrees well with the fraction of corresponding violation days (slope:0.92, R2:0.79, *SI Appendix*, Fig. S7). Via this estimation method, our prediction shows that an additional reduction of ~2.0 and ~ 3.4 ppb/hr $PO\_{x}$\* are required to result to 20% and 10 % exceedance, which would be challenging to achieve solely from NOx reduction strategy (57% and 72% from current level, Fig 2A) under the current energy production scheme; reduction in PHOx (47% and 64%) may be a complementary tactic for near-future attainment. Overall, continuous NOx-focused control strategy is an effective approach, however, since the basin is still at the transitional regime, attaining the NAAQS for O3 might be more difficult than expected without being supported by concurrent VOC reductions.

Our prediction could have been limited by O3 mixing in vertical direction especially for residual layer intrusion in the morning hours (36). Even with the fact that our method is more realistic since it is based on real phenomenon behaviors of O3, however, to estimate the limit of improvement magnitude in localized regulation efforts, O3 concentration influenced by local production and meteorological factors need to be separated. The readily available O3 vertical gradient information with larger spatio- temporal coverage will be beneficial. Moreover, efforts on development of direct or indirect PHOx gauging techniques and/or larger coverage in VOC speciation measurements will be necessary for more precise strategies for VOC reduction.

The results of this work not only strengthen our understanding of O3 production but also provides an insight on the effectiveness of emission control strategies. With the new OPS indicator developed based on the proxy for estimating the local ozone production rate, taking advantage of the extensive network data available since 2001, we determined the photochemical regime of SCAB and its different air mass groups. In future reductions, not only in SCAB but also in other regions in the world working toward achieving better air quality with O3 abatement strategies, the rate of O3 improvement is expected to vary due to implementation of controls and changing regimes. Hence, OPS indicators play a vital role in establishing the efficiency of control strategies and used as a gauge of effectiveness in regulation.

**Materials and Methods**

**Site and Data Description.** Nineteen Air Quality Monitoring Stations (AQMS) grouped into 7 sub-regions were considered in this study, as shown in *SI* *Appendix,* Table S1with their detailed site information: CST1- 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 near the coast, CST2- La Habra (LAH), Los Angeles North Main Street (LAN\*), Pico Rivera 4144 San Gabriel (PIC\*), located in the central part and urban core, SFV-Burbank Palm Avenue (BPA\*), Reseda (RES), Santa Clarita (SCL), SGV-Azusa (AZU\*), Glendora-Laurel (GLE), and Pasadena (PAS), INL-Fontana, Pomona (POM), and Upland (UPL\*), and Riverside Rubidoux (RIV\*) on the eastern side of the basin; \* marks the 7 stations where VOC data are available. The air quality and meteorological data coverage is from May to September of 2001 to 2018 and are available for download from Air Quality and Meteorological Information System (AQMIS) section of California Air Resources Board (CARB) website (<https://www.arb.ca.gov/aqmis2/aqmis2.php>) (37). The speciated VOCs were also provided by CARB. Hourly air quality data (O3, NO2, NOx, and CO) were used. A total of 56 to 62 VOC species, measured every 6 days, ranging from alkanes to biogenics, as listed in *SI* *Appendix,* Table S5 with their OH reaction rate constant, were also used. Oxidation of VOCs by OH leads to radical production which is one of the major factors in determination of ozone production rate (OPR), and individual VOCs have different effects depending on the levels of reactivity (38). But it is only at a certain amount 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 VOC mixture is calculated as,

$VOCR = \sum\_{}^{}k\_{i}\left⌊VOC\_{i}\right⌋$ (Eq. 1)

where,

$i$ stands for each VOC species, $\left⌊VOC\_{i}\right⌋$stands for ith VOC concentration

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

Moreover, hourly data of meteorological parameters such as temperature, pressure, wind speed, and precipitation were utilized for filtering and sensitivity test. The closest AQMS meteorological data were used for the sites without them, as shown with \*\* marker in *SI* *Appendix,* Table S1.

This study aimed to focus on local ozone production rate, thus, considering different NOx conditions (day-of-the-week (DOW) pair) and defining data analysis criteria were critical to narrow down the data set when local ozone formation processes are maximum. Days with perturbations in local photochemistry such as rain due to greater cloud cover and fire events were filtered out with the filtering criteria of precipitation (greater than 0 mm) and 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 advected features and deposition.

**Ozone Production Rate Proxy.** The mass balance approach shown in equation 2 is used for determining the rate of $O\_{x} $production. As the equation shows, ambient $O\_{x}$ depends on the combined effects of chemical production $PO\_{x}$ and destruction of $O\_{x}$($LO\_{x}$) and meteorological factors that drive $O\_{x}$ transport- advection ($AO\_{x}$) and deposition ($DO\_{x}$) . In this study, the time window was crucial for computing $PO\_{x}$\* and it was chosen based on the diurnal plots of O3 and NOx (*SI* *Appendix,* Fig. S1); each site exhibits unimodal distribution for O3 but with different peaking time based on their relative position in an air shed; upwind and urban areas show peaking time around noon while the downwind area likely shows delayed peaking time. Thus, the time window varies but similarly selected when $O\_{x}$ concentration linearly increases with time; when local photochemical production is high and boundary layer is well-developed, chemical loss of $O\_{x} $is outweighed by production. Additionally, 2-3 hours after NOx peaking time and before it starts to rise again was considered to not include the effect of NOx titration. Deposition mainly depends on wind speed and roughness of surface and thus atmospheric turbulence is also assumed to be relatively the same in different days being compared since in a specific area, these parameters hardly change within a week under similar wind and temperature condition. Moreover, advection is 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 $O\_{x}$ with respect to time is proportional to $PO\_{x}$\* , as shown in Eq. 3, it is determined using linear regression, by computing the change in $O\_{x}$ concentration with respect to the time window selected, and used as a proxy for OPR. $PO\_{x}$\* for each group was weighted based on the number of data observations.

$\frac{d [O\_{x }]}{dt}=PO\_{x}-LO\_{x}+A-D$ (Eq. 2)

$\frac{d[O\_{x}]}{dt}∝PO\_{x}\* $ (Eq. 3)

**Ozone Production Sensitivity.** In this study, OPS for every 3-year period is determined by calculating the $PO\_{x}$\* changes with respect to NOx changes, as shown in Eq. 4. High and low NOx conditions are represented by weekday (WD) and weekend (WE), respectively. In NOx-limited region, $PO\_{x}$\* decreases as NOx decreases (positive slope) or vice versa, while in NOx-saturated region, $PO\_{x}$\* decreases as NOx increases (negative slope). Enlarged OPS plots for SCAB sub-regions are shown in *SI* *Appendix,* Fig. S8.

$slope =\frac{[(PO\_{x}\*)\_{WD }-(PO\_{x})\_{WE }]}{[(NO\_{x})\_{WD }-(NO\_{x})\_{WE }]}$ (Eq. 4)

**Sensitivity Tests.** To check the robustness of our results, time window, day-of-the-week pair, and wind speed threshold parameters were subjected to sensitivity tests. Time window selection was done 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. Pair of days with constant VOCR but significantly different NOx conditions was selected to represent change in emissions-related activities (mainly due to reduced motor vehicle emissions) during weekday and weekend, particularly in urban areas (40, 41). The analysis is similar to weekend effect (32, 38) but with unchanging VOCR. Although the available VOC data is limited to 7 sites, it was still used since weekday and weekend were comparable in terms of data points. It was observed that Saturday is more suited to represent weekend and is paired with Wednesday as weekday representative (*SI* *Appendix,* Fig. S2). LAN has a more comparable VOCR with Sunday (weekend), but OPS of Sunday-Wednesday and Saturday-Wednesday pairs have no significant difference (p-value=0.59); since we are analyzing sub-regions as well, CST2 still shows that Saturday is a better weekend representative. Except for LAW with no significant difference in NOx, all the other sites with available VOC data have weekdays that are not significantly (VOCR) and significantly different (NOx) from Saturday at α = 0.05 level of significance (*SI* *Appendix,* Table S2), indicating that the method will not be affected by whichever weekday is chosen. To further test the effect of changing weekday pair, sensitivity test was done by plotting the OPS of Saturday with 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, 30% discarded threshold was selected as this minimizes the influence of advected features and still covers sufficient data.

$PO\_{x}$**\*** **comparison with Modelled** $PO\_{3}$ **(**$PO\_{3}$**mod).** To check the validity of the proxy we estimated for $PO\_{x}$\*, we extracted and computed June 18-26, 2008 $PO\_{x}$\* of SCAB and compared it with the instantaneous $PO\_{3}$ data computed using NASA Langley Research Center (LaRC) photochemical box model constrained by measurements taken aboard the NASA DC-8 aircraft during Arctic Research of the Composition of the Troposphere from Aircraft and Satellites-CARB (ARCTAS-CARB). Such 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 $PO\_{3}$ ($PO\_{3}$mod) values that fall within the spatial coordinates of the study area, 09:00 to 14:00 time window, and within 2 km pressure altitude were compared with $PO\_{x}$\* (June 18, 22, and 24, 2008). $PO\_{x}$\* is approximately 1.13 times larger but it is within the range and not significantly different from model-calculated $PO\_{3}$ (p-value: 0.25, α =0.010) (*SI* *Appendix,* Fig. S4). The observed discrepancy could be associated to the difference in measurement altitude, overpass time, and heterogeneity originating from the variety of nearfield sources at the surface. Moreover, since we have not included the effects of deposition and advection losses, such could have been offsets as well.

**Prediction of Percent Exceedance Days.** The fraction of exceedance days was predicted using the mass balance approach (Eq. 2). The background concentration $(O\_{3})\_{B}$ considered is 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 8-hr average is needed and $PO\_{x}$\* only covers 4-hr average, the next 4 hours are used to determine the 8-hr averaged max O3 concentration, estimated as -2.4 ppb/hr by computing the change in O3 concentration over the time window (in the same manner how $PO\_{x}$\* was computed) when O3 linearly decreases, and the rate of deposition (D) offset is computed as 1.2 to 2.2 ppb/hr using Eq. 5, where deposition velocity ($V\_{D}$) is assumed to be ~0.37 to 0.74 cm/s based from the model results of previous studies in urban setting which used different O3 dry deposition schemes (44, 45), mean summer afternoon mixing layer height is 770 m (46), and weighted mean of 95th O3 percentile is 66.9 ppb. The predicted maximum 8-hr O3 was compared to the observed maximum 8-hr O3 and shows good agreement (8% difference in slope with 0.79 R2, fig. S7). Histogram fit of the 3-yr maximum 8-hr O3 and the corresponding $PO\_{x}$ were plotted and the current percentage exceedance days was computed to be 30%. $PO\_{x}$\* is reduced by a factor of 0.18 and 0.30, and the corresponding O3 was back calculated which resulted to 20% and 10% exceedance days, respectively.

$D=\frac{V\_{D} }{MLH}(O\_{3})$ (Eq. 5)