Ozone Design Values in Southern California's Air Basins: Temporal Evolution and U.S. Background Contribution

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Key points:

- The temporal evolution of maximum ozone concentrations in southern California is accurately described by a simple mathematical function.
- The U.S. background ozone contribution of 62.0 ± 1.9 ppb is the lower limit achievable for the concentrations upon which the NAAQS is based.
- Projections indicate ~35 years of additional emission control efforts will be required to reach the NAAQS in the Los Angeles area.

ABSTRACT: California's ambient ozone concentrations have two principal contributions: U.S. background ozone and enhancements produced from anthropogenic precursor emissions; only the latter effectively respond to California emission controls. From 1980-2015 ozone has been monitored in eight air basins in Southern California. The temporal evolution of the largest measured concentrations, i.e. those that define the ozone design value (ODV) upon which the National Ambient Air Quality Standard (NAAQS) is based, is described very well by an exponential decrease on top of a positive offset. We identify this offset as the ODV due to the U.S. background ozone (i.e., the concentration that would be present if U.S. anthropogenic precursor emissions were reduced to zero), and is estimated to be 62.0 ± 1.9 ppb in six of the basins. California's emission control efforts have reduced the anthropogenic ozone enhancements by a factor of ~5 since 1980. However, assuming that the current rate of exponential decrease is maintained and that U.S. background ODV remains constant, projections of the past decrease suggests that ~35 years of additional emission control efforts will be required to reach the new NAAQS of 70 ppb in the Los Angeles area. The growing predominance of U.S. background ozone contributions has shifted the maximum ozone concentrations in all air basins from later to earlier in the summer. Comparisons indicate that currently accepted model estimates of U.S. background ozone concentrations in southern California are somewhat underestimated; thus reducing ozone in this region to the 2015 NAAQS may be more difficult than currently expected.

1. Introduction

In 1970 the U.S. passed the Clean Air Act, which required states to develop plans to improve air quality. Since its introduction, comprehensive efforts have been made to reduce emissions of the ozone precursors, oxides of nitrogen ($NO_X = NO + NO_2$) and volatile organic compounds (VOCs), in order to meet the ozone National Ambient Air Quality Standard (NAAQS). The resulting emission reductions have produced substantial decreases in ambient ozone concentrations throughout the Nation, including southern California, which is the focus of this work. Quantification of these decreases and comparison of the decreases between different regions can potentially provide useful information for 1) partitioning ambient ozone concentrations between that produced locally and regionally from that transported from elsewhere, 2) forecasting likely possible evolution of these concentrations, 3) providing metrics for evaluating photochemical models designed to reproduce ambient ozone concentrations, and 4) determining the most effective approach for further reducing the concentrations. Our goal in this paper is to develop a mathematical description of the temporal evolution of the maximum observed ozone concentrations in southern California, and to discuss the implications of the results.

The ozone NAAQS is based on the relatively rare, highest observed ozone concentrations, i.e. the 4th highest maximum daily 8-hour average (MDA8) ozone concentration measured in a given year at a sampling site. The Ozone 8-Hour Design Value (ODV) is defined as the 3-year running mean of this 4th highest annual concentration; it must not exceed the ozone NAAQS, currently set at 70 ppb. Assuming that the highest ozone concentrations occur during the 6-month (May - October) warm season, the 4th highest represents approximately the 98th percentile of the observed MDA8 ozone concentrations. The ODV is calculated each year for each monitoring site with measurements over that year and the preceding two years that meet completeness criteria. The ODV is defined each year for each of southern California's eight air basins (Figure 1) as equal to the largest ODV for any site within the basin. Our primary focus is on these basin ODVs.

One challenge to meeting the ozone NAAQS is that ozone transported into the U.S. from outside its borders contributes a significant fraction to the total ambient concentrations (*Lin et al.*, 2015a; *Cooper et al.*, 2015). This contribution does not effectively respond to reductions in U.S. ozone precursor emissions, but does significantly reduce the margin for locally and regionally produced ozone before the NAAQS is exceeded. In this work, and consistent with other references (e.g., *U.S. EPA* 2015), we identify this transported component plus any ozone produced from local natural emissions as U.S. background ozone, i.e., the concentration that would be present if U.S. anthropogenic emissions of ozone precursors were reduced to zero. The analysis presented in this paper provides an estimate for the lowest NAAQS that could possibly be achieved in southern California's air basins by reducing U.S. anthropogenic ozone precursor emissions to zero, leaving only the U.S. background concentrations. We refer to this lowest NAAQS as the U.S. background ODV.

Other terms have been used to quantify the ozone concentrations transported into the U.S. We will also refer to baseline ozone concentrations (*Cooper et al.,* 2015), which are those completely unaffected by continental influences. They can be directly measured at sites sufficiently isolated such that the ozone transported ashore from the Pacific arrives without significant perturbation from continental influences. U.S. background ozone concentrations (as defined by the U.S. EPA and used in this work) differ from baseline ozone concentrations, because the former are affected by continental influences, including deposition to continental surfaces, especially vegetation, and production from natural ozone precursors, such as those emitted from soils, trees and lightning; the U.S. background ozone concentrations thus vary with location throughout the U.S. depending on the influence of these continental effects. Additional definitions of background ozone will be discussed when we compare our results with modeling results in a later section of this paper.

An important characteristic of baseline ozone concentrations transported into California is their strong dependence on altitude. Figure 1 shows this altitude dependence at Trinidad Head, which is on the California coast approximately 300 km north of the top edge of the map in Figure 1. The strong vertical gradient below about 1 km is caused by relatively rapid photochemical destruction of ozone in the humid marine boundary layer (MBL), where the concentrations of ozone precursors are sufficiently low that photochemical ozone formation cannot compensate for destruction (e.g., *Ayers et al.,* 1992; *Oltmans and Levy,* 1992; 1994). Importantly, baseline ozone at 2 km altitude is 53 ± 15 ppb (average ± 1 standard deviation), so that baseline ozone often approaches the NAAQS of 70 ppb at this altitude. Although Trinidad Head is located north of the region considered in this work, these results are representative of southern California baseline ozone, because there is very little latitudinal variation in average baseline ozone concentrations along the California coast (*Pfister et al*., 2011).

Our analysis in this paper examines the temporal evolution of the ODVs in the eight air basins defined for southern California (Figure 1). We choose to focus on this region for three reasons: first, the largest ozone concentrations in the nation have been, and continue to be, observed here; second, the prevailing winds are from the Pacific Ocean, so that air transported into the region largely brings baseline ozone concentrations relatively unaffected by ozone produced elsewhere in the U.S., so that interpretation of ozone concentrations is less complicated than in other U.S. regions; and third, ozone measurements have been made over the past several decades throughout the region. We first develop a mathematical description of the evolution of the ODVs for the southern California air basins, and then discuss the implications of this description.

2. Methods and Results

Three approaches are used to investigate the temporal trends of the ODVs in the Southern California air basins. Our first task is to define for each air basin the set of basin ODVs to be examined (Section 2.1). The first analysis approach applies a general mathematical functional form to approximate the temporal ODV trends for the individual air basins in Southern California (Section 2.2). The second analysis compares the temporal trends in different air basins by means of correlations of ODVs between air basins (Section 2.3). Finally, a multivariate, least-squares analysis provides as complete a description as possible for the temporal evolution of the ODVs in seven of the southern California air basins (Section 2.4). The results of this third analysis will provide the primary basis for the discussion in Section 3.

2.1. Selection of Air Basin Ozone Design Values

For air quality monitoring and policy development, southern California has been divided into eight air basins (Figure 1). Routine monitoring of ambient ozone concentrations began in the late 1960s in the South Coast Air Basin and was rapidly expanded to the other basins. The California Air Resources Board (CARB) maintains a publicly accessible archive (https://www.arb.ca.gov/adam/index.html) of ODVs calculated from the results of this monitoring for all of California's individual monitoring sites and air basins for the years 1975 - 2015. In this work we use these ODVs to examine the temporal evolution of ozone concentrations in the Southern California air basins.

The temporal evolution of the ODVs in a given air basin is affected not only by temporal changes in the ozone concentrations within the air basin, but also by changes in the monitoring sites that are operational in the basin. We wish to investigate the former without obscuring effects from the latter, so we must control for monitoring sites beginning or ending measurements over the measurement record. Figures S1-S8 illustrate the basin ODVs and show the ODVs from the sites that determine each basin's ODV in each year. Maps are included showing the locations of those sites in three air basins. In most basins, maximum ODVs were reached by 1980, so our analysis begins in that year when possible. In two air basins, North Central Coast and Mojave Desert (Figures S4 and S5), the ODVs in 1989 and 1987, respectively, were significantly higher than observed in previous years; these increases in observed ozone were due to recently initiated sites, so we begin analysis for these two air basins in those years. In one air basin (South Central Coast, Figure S3) in 1986 the site ODVs are missing from the two Simi Valley sites that determine the basin ODV in nearly all other years, so 1986 is excluded from the analysis of this site. Finally, monitoring began later in the Great Basin Valleys Air Basin (Figure S8) so ODVs are not available until 1986. As summarized in Table 1, our analysis considers all ODVs for the eight air basins from 1980 to 2015, with the exceptions discussed above.

In addition to the ODVs we will also investigate the dates of each year that the highest MDA8 ozone concentrations were recorded in each of the eight Southern California air basins. This analysis will include both the four highest and the thirty highest MDA8 concentrations. The former are available from the publicly accessible archive given above; the latter were provided to us through a request to CARB staff.

2.2. Mathematical Description of Temporal Evolution of Air Basin Ozone Design Values

In each of the eight southern California air basins ozone concentrations have significantly decreased as is evident in Figures S1-S8. An exponential function with a constant positive offset (Equation 1) is used to quantify the temporal evolution of the ODVs in each air basin:

$$\mathrm{ODV} = y_0 + A \exp\{-(\mathrm{year}-1980)/\tau\}. \qquad (1)$$

Mathematically, the first term, y_0, is the asymptotic value toward which the basin ODVs are approaching, and the second term is the enhancement of the ODVs above y_0, which is assumed to be decreasing exponentially with an e-folding time constant of τ years. Thus, A is the enhancement of the ODVs above y_0 in 1980. A least-squares fitting routine is used to fit Equation 1 to any time series of ODVs.

If the time evolution of the ODVs for an air basin followed Equation 1 exactly, then a least-squares fit could accurately and precisely determine the three parameters y_0, τ, and A. However, deviations from Equation 1, resulting from interannual variability or other "noise" in the ODVs, generally prevent a precise determination of all three parameters from a single regression fit. Consequently, we apply the following procedure to derive estimates of all three parameters. First, three-parameter fits were examined for the ODVs, as well as for several percentiles of the MDA8 ozone concentrations, in many of the air basins (Figure 2 of *Parrish et al.,* 2016a give some example fits). In favorable cases, relatively precise determinations of all three parameters are possible. In these cases, all determinations of τ agreed within their 95% confidence limits, although some of the confidence limits were quite wide. The weighted average of all of the results was 22.3 ± 4.0 years (95% confidence limits are indicated here and elsewhere), which is taken as the initial best estimate for the value of τ. This best estimate is assumed to apply to all of the air basins; the validity of this assumption will be discussed in the analysis that follows. Substitution of this value of τ into Equation 1 allows the other two parameters, y_0 and A, to be determined for any particular time series of ODV values. Figures S1-S6 and Figure 2 show these two-parameter fits for the six southern California air basins whose ODVs have evolved approximately as described by Equation 1, and the derived parameters are given in Table 1. Also included in the table are root-mean-square deviations in ppb (σ) between the observed ODVs and the derived fits. Note that the North Central Coast Air Basin has relatively small observed trends in the ODVs, which leads to large relative uncertainties in even the two-parameter fit. To improve the precision of the *A* determination for this air basin, y_0 is set equal to that derived for the adjacent South Central Coast Air Basin, i.e. 62.9 pbbv.

The success of the quantification of the ODV evolution by Equation 1 in each air basin can be evaluated by examining the second term on the right side of Equation 1 (i.e., subtracting the derived y_0 value from the observed ODVs) on a logarithmic scale; Figure 3 presents this evaluation for the same six air basins considered in Figure 2. In this format, linear regressions to the data give the values of τ and *A* for each air basin as the inverse of the slopes and the inverse log of the 1980 intercepts, respectively. Table 2 gives the results of this analysis; here the σ values give the relative root-mean-square deviation (in %) between the ODV enhancements and the derived fits.

The analyses illustrated in Figures 2 and 3 provide an excellent mathematical description of the temporal evolution of the ODVs in all six air basins. The large r^2 values included in Table 2 ($\geq$ 0.95 except for the North Central Coast where the enhancements above y_0 are relatively small) indicate that the fit to Equation 1 captures the large majority of the total variance in the data sets (approximately equal to r^2); the root-mean-square deviations are also small (3 to 5 ppb) compared to the range of observed ODVs (~ 200 ppb) shown in Figure 2. In all cases the derived values of τ agree within the indicated confidence limits with the originally assumed value of 22.3 years, and the values of *A* similarly agree between the two analyses. This agreement of τ and *A* is expected, since the analysis illustrated in Figure 3 requires the y_0 values derived in the fitted curves illustrated in Figure 2. One interesting result indicated in Table 1 is the agreement of y_0 within their statistical uncertainties between five of the air basins (58 to 64 ppb); only y_0 for the Salton Sea Air Basin (76 ppb) is significantly greater than the range of the other five.

The uncertainties indicated for the derived parameter values in Tables 1 and 2 and elsewhere in this paper are estimated 95% confidence limits derived from the least squares regression analyses. It should be noted that since the ODVs are the 3-year running means of 4th highest MDA8 ozone concentration measured in a given year at a particular sampling site, the ODVs have a significant degree of autocorrelation. This serves to reduce the number of statistically independent ODV values (i.e., the degree of freedom) of a data set by as much as a factor of 3 from the number of years included in the data set. In all cases the tabulated 95% confidence limits are a factor of $\sqrt{3}$ greater than the confidence limits returned from the least squares analyses in order to properly account for this reduction in the degrees of freedom due to this autocorrelation.

2.3. Correlation of Ozone Design Values between Air Basins.

A somewhat different and more general approach can be applied to define the temporal trends of the ODVs of seven of the southern California air basins. This approach is based upon correlation of the ODVs from other basins with those of the South Coast Air Basin. In this approach, defining a functional form for the temporal evolution of the ODVs (such as given in Equation 1) is not required. The South Coast Air Basin is selected as a reference because Equation 1 most closely fits the temporal trend of that basin's ODVs, as indicated by the r^2 value of 0.99 obtained from the linear regression in Figure 3. Figures S9-S15 and Figure 4 illustrate the correlations of the basin ODVs; the supplemental figures indicate the years of data included in Figure 4. A reduced major axis regression procedure gave the linear fits. In these fits the x and y variables were weighted equally with that weighting based on an assumed 2.6 ppb 1-sigma uncertainty for ozone in all basins; this uncertainty was calculated from a representative root-mean-square deviation of data from the fits in the figures. The intercept and the slope of each correlation (which are annotated in Figures S9-S15) provide second determinations of the y_0 value and the A value of the respective air basin. The vertical dotted lines in Figure 4 indicate the y_0 value of 58.9 ppb derived for the South Coast Air Basin, so the intercept of each linear fit with this vertical line provides an estimate of the corresponding y_0 value for that basin. The slope of each correlation provides an estimate of the ratio of the corresponding A value to that of the South Coast Air Basin. Table 3 gives the results of this analysis.

The results in Table 3 are nearly identical to the previous results included in Tables 1 and 2, so this correlation approach simply provides another consistency test for the six air basins included in the earlier analysis. Here again the large r^2 values (≥ 0.95 except for the North Central Coast) indicate that correlation of a basin's ODVs with those of the South Coast Air Basin provides an excellent mathematical description of the temporal evolution of those ODVs. In addition, this correlation approach allows the investigation of two additional air basins that are not well described by Equation 1. Figure 4b includes all of the ODVs from the Great Basin Valleys Air Basin; a weak correlation with the South Coast Air Basin is apparent ($r^2 = 0.38$), but the significance of the derived parameters is not clear; the temporal evolution of the ODVs in this air basin will not be considered further. Figure S7 and S14 show that before the year 2000, the ODVs in the San Joaquin Valley Air Basin decreased quite slowly with only a weak correlation

($r^2 = 0.28$), with the ODVs of the South Coast Air Basin. However, after 2000 the San Joaquin Valley ODVs decreased much more rapidly, and with a good correlation ($r^2 = 0.94$) with the ODVs of the South Coast Air Basin. For the San Joaquin Valley Air Basin, the ODVs included in Figure 4, the results in Table 3 and the following discussion only include the period after 2000.

Despite the close agreement in magnitude of the parameters in Tables 1 and 3, the confidence limits are systematically smaller in the latter. The analysis based on Equation 1 compares the data of each basin to that exponential function, and calculates the uncertainty of the derived parameters from the scatter of the data about the curve defined by Equation 1. The results in Table 3 are derived from the correlation between each basin's data with the South Coast Basin data. Some of the interannual variability in each basin's data correlates with the interannual variability in the South Coast data. This correlation reduces the scatter of the data about the linear fits in Figures S9-S15, resulting in a reduced uncertainty in the parameters derived in Table 3. Importantly, neither of these approaches captures the full uncertainty of the derived parameters, because both approaches assume an exact value of one critical parameter; the first approach sets $\tau = 22.3$ years, and the second approach sets $y_0 = 58.9$ ppb for the South Coast Air Basin. The multivariate approach described in the next section does not have this limitation, as the values of all parameters of Equation 1 are derived simultaneously.

The correlation analysis developed in this section reinforces the conclusion of the previous section that Equation 1 provides an excellent description of the temporal evolution of the basin ODVs. Notably, the correlations for five of the air basins with the South Coast Air Basin all intersect the vertical dotted line at ODVs that correspond to an average y_0 value of 61.8 ppb for the six air basins; only the Salton Sea Air Basin has a significantly higher (76 ± 5 ppb) intercept and corresponding y_0 value.

2.4. Multivariate Least-Squares Analysis of Ozone Design Values in Seven Air Basins

The results from the preceding sections summarized in Tables 1-3 show a great deal of consistency between analyses as well as similarity between seven air basins. The ODVs in all air basins are approaching the same asymptote, y_0 (within the statistical confidence limits), except in the Salton Sea Air Basin where the ODVs are approaching a significantly higher value. A single e-folding time, $\tau = 22.3$ years, fits the temporal evolution of each basin, and the τ results derived from Figure 3 and given in Table 2 agree with this value within the statistical confidence limits. Finally, each basin has its own distinct value of *A* that agrees in all three analyses within the statistical confidence limits.

In this section we simultaneously optimize the parameters describing the ODV temporal evolution in all southern California air basins (excluding the Great Basin Valleys Air Basin) for all years given in Table 1, except only after year 2000 in San Joaquin Valley Air Basin; this selection provides 214 total data points. The optimization approach iteratively varied the parameters of Equation 1 for each air basin to optimize the fit for the entire data set in a process following that described in Chapter 8 of *Bevington and Robinson* [2003]. More details of this multivariate analysis are given in the Supporting Information. In principle, this process can derive separate values with confidence limits for A, τ and y_0 for each of the seven air basins for a total of 21 parameter values. However, in practice only ten distinct parameters were necessary to describe nearly all of the systematic variance in the ODV data set. These ten parameter values are consistent with the previous analyses: a single τ, a common y_0 for six basins plus a separate y_0 for the Salton Sea Air Basin, and seven values of A, one for each of the seven air basins. Table 4 gives the results of this analysis and Figure 5 compares the observed ODVs with those calculated from the derived parameters. While the results of this multivariate analysis agree with those from the previous analyses, simultaneous consideration of all data provides significantly smaller confidence limits, indicating a more precise determination of all parameter values. The square of the correlation coefficient ($r^2 = 0.984$) provides an estimate of the faction of the variance in the total log-transformed data set that is captured by the ten derived parameters; this large r^2 value indicates that Equation 1 with the parameters of Table 4 provides an excellent description of the temporal evolution of the ODVs in all seven air basins.

Two further aspects of the multivariate analysis should be noted. First, the results for the San Joaquin Valley Air Basin are based on 2001-2015 ODVs. The value of A given in Table 4 (and in Table 3) is indicated in parentheses because A indicates the 1980 ODV enhancement above y_0, but the ODVs in this air basin followed a very different temporal evolution from 1980 to 2000 (see Figure S7); thus the indicated A value has no relation to the actual ODV in 1980 in that air basin. For the other six air basins the indicated A values do give fits to the actual or extrapolated ODV enhancement in 1980. Second, the remaining fraction of the variance of the data (~1.6%) not captured by the multivariate analysis with ten parameters is largely due to interannual variability and other noise about the regression fit. Attempts to extract more information from the data set (i.e., inclusion of additional parameters to capture additional systematic differences in y_0 or in τ between air basins) give results that fail to converge or converge to physically unreasonable results. In summary, the results in Table 4 are believed to provide all of the statistically significant information regarding the temporal evolution of the ODVs in the seven air basins over the time periods considered. However, it may become possible to extract further information as additional years of ozone monitoring data become available.

3. Discussion

3.1. Physical Interpretation of Derived Parameters

The analysis in the preceding section is purely mathematical; it shows that Equation 1 with the ten parameters included in Table 4 gives an excellent description of the temporal evolution of the air basin ODVs in southern California, but provides no physical basis for that equation. In this section we discuss this physical basis, and provide hypotheses for the physical interpretation of the ten parameters.

The long-term decrease in ODVs in southern California is the result of emission control efforts that have reduced ambient concentrations of ozone precursors by large fractions. In the five decades from 1960 to 2010 the ambient volatile organic carbon (VOC) concentrations in the Los Angeles region were reduced by about 98% (i.e., a factor of ~50) (*Warneke et al.,* 2012), and the concentrations of ambient nitrogen oxides (NOx) were reduced by about 75% (i.e., a factor of ~4) (*Pollack et al.,* 2013; *Parrish et al.,* 2016a). These large fractional reductions of the primary precursors of photochemical ozone production suggest that extrapolation of the past ozone decrease through the imagined elimination of the relatively small remaining fraction of anthropogenic emissions provides a quantification of the ODVs resulting solely from U.S. background ozone concentrations. Thus, we identify the parameter y_0 (the asymptote toward which the ODVs are converging) as an estimate of the U.S. background ODV, i.e., the minimum ODV that could be achieved in a given air basin if US background ozone concentrations were not enhanced by North American anthropogenic emissions.

In each of California's air basins, emissions of ozone precursors from U.S. anthropogenic sources provide fuel for local and regional photochemical production of ozone that increases the ODV above y_0. Thus, the parameter A is interpreted as the magnitude of the enhancement of the

ODV above y_0 in 1980. The magnitude and mix of the precursor emissions differ between air basins and transport of ozone between basins affects ambient ozone concentrations, so each basin has a characteristic value of A. The reductions in California anthropogenic emissions have driven a decrease in the magnitude of each basin's enhancement, which is well described as an exponential decrease with a time constant quantified by the parameter $\tau = 21.9 \pm 1.2$ years. This value corresponds to a factor of 2 decrease in the ODV enhancement every 15.2 ± 0.8 years for a total decrease of a factor of ~5 from 1980 to 2015. Based on the analysis presented above, a similar value of τ is found for all air basins, which may be reasonably expected since its magnitude reflects the history of emission controls, and these controls generally have been applied concurrently in all of the air basins. For example, vehicle emission control programs have been implemented simultaneously throughout California. While similar emission control programs may have had different effects in different air basins, such differences are not discernable in this analysis.

An important aspect of these results is the large magnitude derived for the U.S. background ODVs: 62.0 ± 1.9 ppb in six of the air basins. The even larger value (75.6 ± 2.5 ppb) in the Salton Sea Air Basin will be discussed separately below. Two issues are important for understanding these high values. First, in the absence of enhancement of ozone from anthropogenic precursors, it is the very highest, i.e. ~98th percentile, of the U.S. background ozone concentrations that would be responsible for the ODVs. Second, baseline ozone transported ashore from the Pacific is the primary source of U.S. background ozone in California, and these baseline concentrations increase rapidly with altitude (Figure 1). Figure 6a compares the six basin U.S. background ODV determined here (i.e., y_0) with the altitude dependence of the 98th percentile of the baseline ozone concentrations measured at the surface and by sondes at Trinidad Head, the northern California coastal site discussed earlier. The average of these highest baseline ozone concentrations in the 0 to 2 km altitude range are comparable to the basin y_0 values derived in this analysis. We conclude that vertical mixing over California, and the altitude distribution of measurement sites within the air basins, may both contribute to the relatively large value of 62.0 ± 1.9 ppb for the six basin U.S. background ODV derived here. These effects are discussed in more detail below. The impact of vertical mixing on surface air quality in northern California has been discussed previously (*Parrish et al.,* 2010).

Consideration of ODVs at specific sites can further clarify the magnitude of the U.S. background ODVs. With τ set at 21.9 years, a fit of Equation 1 to the time series of ODVs at the Vandenberg Air Force Base site (see Figure S16 of the Supporting Information for details) gives $y_0 = 52.7 \pm 6.4$ ppb. This is the most isolated coastal site in southern California due to its location near sea level on the southwest corner of the South Central Coast Air Basin (location indicated in Figure 1), although pollution ozone from the Los Angeles urban area is occasionally transported to this site. The y_0 at this site is significantly smaller than the U.S. background ODV for the basin (62.0 ± 1.9 ppb from Table 4), reflecting the site's low elevation, coastal location, which is where the smallest baseline ozone concentrations are expected. The surface site at Trinidad Head is a similarly isolated, near sea level coastal site in northern California that has been used to quantify baseline ozone concentrations (Figure 6a). ODVs have not been reported for this site, but the 98th percentile of the MDA8 ozone concentrations (i.e., approximately equal to the ODVs) during baseline conditions is 49 ppb, which is not statistically significantly different from the y_0 value found for the Vandenberg Air Force Base site. Lassen Volcanic NP is a higher elevation (1.76 km) site in northern California that has also been used to quantify baseline ozone concentrations due to its relatively isolated location (*Jaffe et al.,* 2003; *Oltmans et* *al.,* 2008; *Parrish et al.,* 2009; 2012). The U.S. background ODV derived at this site (68.5 ± 9.0 ppb, Figure S17) is significantly larger than at Trinidad Head, and is not statistically significantly different from the 62.0 ± 1.9 ppb found for the six southern California air basins.

The above comparison indicates that the U.S. background ODVs at sites in southern California air basins vary from about 50 ppb to 62 ppb (and even higher in the Salton Sea Air Basin). This variability is also clear in Figures S1-S8, which show the temporal evolution at a variety of sites within the eight air basins. This variability arises from variation in both the sources and sinks of U.S. background ozone. First, the vertical gradient in baseline ozone (Figures 1 and 6a) combined with the elevation distribution of the monitoring sites and with the varying influence of mixing larger ozone concentrations to the surface results in variations in baseline ozone transported to different sites. For example, the South Coast Air Basin contains all of the Los Angeles near-sea level urban sites, but also the rural Crestline site at an elevation of 1390 m. This latter site frequently records the largest ozone concentrations in the air basin, and because of its elevation may receive larger baseline ozone concentrations than lower elevation sites. Further, as air moves from the marine environment onto the continent, vertical mixing is enhanced, so the U.S. background ozone concentration at any particular surface location and time is affected by the average of the baseline ozone concentrations in all of the air parcels mixed to the surface. Vertical transport occurs through convection driven by solar heating of the land surface that causes the boundary layer to grow through entrainment of air from above. Winds interacting with the complex terrain of the California coast, where the coastal mountain ranges are in close proximity to the ocean, drive additional vertical mixing. The concentration of baseline ozone transported to a particular continental site is further modified by ozone loss to surfaces (particularly vegetation) and photochemical production from natural ozone precursors.

The net result is that surface U.S. background ozone concentrations are generally higher over the continent compared to coastal sea level sites; however the effects of vertical mixing and ozone production and loss processes vary significantly depending on site elevation, the character of the local and regional vertical mixing mechanisms, and the ozone loss and natural production processes, which are strong functions of the sites continental environment.

The time evolution of the ODVs in the Salton Sea and San Joaquin Valley air basins differs significantly from the other air basins. The reasons for these differences have not been established, but possible contributing factors can be mentioned. First, both the San Joaquin Valley and the Imperial Valley in the Salton Sea Air Basin are home to the most intensive agricultural activity in California; the State's emission control efforts have addressed emissions from the agricultural sector separately from emissions from other sectors such as mobile sources, electrical generation and industry. *Pusede and Cohen* (2012) emphasize the importance of a temperature dependent VOC source in the San Joaquin Valley that may be associated with agricultural emissions, and they argue that the region has or is transitioning to NOx-limited chemistry when temperatures are hottest and high ozone most probable. This transition may account for the different temporal evolution of the ODVs in the San Joaquin Valley Air Basin (Figures S7 and S14). Before the year 2000, little systematic change occurred in the ODVs, but from 2001-2015, the ODVs decreased at an exponential rate consistent with the other six air basins. A second contributing factor may help explain the larger y_0 value (75.6 ± 2.5 ppb) in the Salton Sea Air Basin. That basin is adjacent to Mexico, and cross border transport of ozone or ozone precursors from emissions in Mexico, which are not subject to U.S. emission control efforts, may account for the elevated U.S. background ODV in that basin.

One complication in the identification of the parameter y_0 as an estimate of the U.S. background ODV is that y_0 is assumed constant in Equation 1; however systematic increases in baseline ozone concentrations at the North American west coast have been documented (*Jaffe et al.,* 2003; *Parrish et al.,* 2009; 2012; *Cooper et al.,* 2010). In order to investigate the impact of these changes in baseline ozone, we have updated the previous analysis of baseline ozone concentrations for near sea level, coastal sites along the North American west coast, primarily Trinidad Head California (*Parrish et al.,* 2009) and at the Lassen Volcanic NP site in the northern California mountains (*Parrish et al.,* 2012). The slowing and potential reversal of the increasing trend in seasonal average baseline ozone concentrations at these sites was quantified (*Parrish et al.,* 2012) by fitting 2nd order polynomials (e.g., curves in Figure 1) to the seasonal average data. The quadratic coefficients from the fits to the data then available (through 2010) were negative, indicating slowing of the increase, but were not statistically significant. Extension of the analysis through 2015 (manuscript in preparation, 2017) shows that with the five additional years of data included in the fits, the quadratic coefficients are indeed negative and statistically significant in all seasons, and that these coefficients agree (within their confidence limits) at the two sites. It is now clear that the increase in seasonal average baseline ozone concentrations discussed in previous work ended with maxima in the mid-2000s, and that the concentrations have begun to decrease in all seasons. The standard deviations of the seasonal baseline ozone concentrations over the complete data record vary from 2.3 to 3.6 ppb, which reflects both interannual variability (e.g., *Lin et al.,* 2015b) and the systematic trends. Compared to the change in ODVs discussed in this work, the systematic changes in baseline ozone concentrations are minor; thus, the assumption that the parameter y_0 is constant is a good approximation. y_0 should be interpreted as the average of the U.S. background ODV over the

1980 to 2015 period, with recognition that there have been small systematic changes in its magnitude.

One additional cautionary note should be considered in the physical interpretation of the parameter y_0. If there were a class of ozone precursor emissions not addressed by the emission control efforts implemented in California over the past decades, then ozone produced from these emissions would not have been reduced. Thus, this contribution to ambient ozone concentrations would serve to elevate y_0 above the actual U.S. background ODV. However, since emission controls have been designed to reduce all known emission classes, it is unlikely that such a class of unknown ozone precursor emissions exists in all of the six air basins that exhibit a common value of y_0. Controls of agricultural emissions have not been implemented as extensively as for other anthropogenic emissions. The Imperial Valley in the Salton Sea Air Basin, the San Joaquin Valley, and the Salinas Valley in the North Coast Air Basin have intense agricultural activity, so y_0 may be elevated above U.S. background ODVs in these basins, as discussed above for the San Joaquin Valley and Salton Sea Air Basins. Other basins have much less agricultural activity, so significant contributions from these emissions are not expected to generally raise all y_0 magnitudes,

3.2. Shift of Seasonal Maximum Ozone Concentrations

The physical interpretation of the derived parameters discussed in the preceding section has one implication that can be examined through ambient ozone concentration data. Baseline ozone transported into California, which is the primary source of U.S. background ozone, has a maximum in spring in the lower troposphere (e.g., *Oltmans et al*., 2008), while local and regional ozone production from anthropogenic precursor emissions is expected to peak in the summer. Thus, as enhancement of ODVs from anthropogenic precursors has been reduced, we expect the seasonal maximum in observed ozone concentrations to have shifted from summer toward spring. Figure 7 shows such a shift in all of the Southern California air basins. Data from the South Coast Air Basin are shown as an example in Figure 7a; here the dates of occurrence of the four highest MDA8 ozone concentrations are plotted. The color-coding indicates the decrease in ODV magnitude, and the slope of the linear regression to these data indicates that the seasonal maximum has moved to earlier in the year at an average rate of 0.55 ± 0.37 day/year. When measurements were begun in the early 1970s, the seasonal maximum was on average in late July, and by 2015 it moved to early July. Figures S18 - S21 show similar plots for all eight air basins for both the four highest and the thirty highest MDA8 ozone concentrations recorded in each year; Figure 7b summarizes the results. Qualitatively similar shifts are found for all eight air basins, without significant differences between the four and thirty highest analyses. Quantitatively, the seasonal shift varies from near zero to approximately one day per year; further investigation is required to account for these differences between air basins. The near lack of a seasonal shift in the South Central Coast Basin is of particular interest.

The dates of the seasonal ozone maximum can be compared across the air basins by focusing on a particular year. Figure 7c shows the year 2000 intercept of the linear regressions in Figures S18 - S21. Here the four coastal air basins are shown on the left in light blue symbols, the two desert basins in orange symbols on the right, with the two other basins in between. The four coastal air basins all have maxima from mid to late July. The latest seasonal maximum is found in early August in the San Joaquin Valley Air Basin, with the earliest maxima in early July in the Salton Sea and the two desert air basins. These systematic differences in the seasonal maxima between air basins may provide useful metrics for investigating the performance of photochemical grid models of ozone formation in southern California. It is likely that models must correctly reproduce the relative contributions of ozone from different sources to correctly reproduce these different seasonal cycles and their shifts in the different air basins. One particularly useful comparison may be the seasonal ozone maxima in the Mojave Desert and South Coast air basins. The former is very sparsely populated, so local photochemical production is expected to be quite limited, yet this basin exhibits large anthropogenic enhancements of ozone (see *A* value in Tables 1-4). These enhancements are believed to reflect transport of ozone from other air basins, primarily the South Coast and secondarily the San Joaquin Valley (e.g., *VanCuren*, 2015), yet the seasonal maximum occurs in the Mojave Desert well before those in these two source air basins. *Neuman et al*. (2012) noted this same difference in the ozone seasonality comparing Redlands (a site in the eastern South Coast Air Basin) with Joshua Tree NP (a site in the Mojave Desert Air Basin).

Similar shifts in the ozone seasonal cycle have been discussed previously. *Parrish et al.* [2013] show that the observed seasonal ozone maximum has shifted to earlier in the year over remote northern mid-latitudes during past decades. The sites considered in this work are primarily in Europe, but did include the Lassen NP site in northern California discussed above. The reported rates of change at these remote sites (3 to 6 days per decade) are similar to the rates shown in Figure 6b. However, the greater importance of background ozone at the more remote sites is reflected in the seasonal maxima occurring earlier in the summer than in southern California, generally mid to late June at sites outside of the MBL. A recent modeling study (*Clifton et al*., 2014) suggests that the ozone seasonal maximum will continue to shift so that the seasonal cycle reverses (to a winter maximum) by late in the 21st century, at least in the northeast and the intermountain west regions of the U.S., although this work suggests that climate change as well as anthropogenic ozone emission reductions cause this shift.

3.3. Projection of Future Basin ODVs and Relation to NAAQS

In 2015 the basin ODVs in most of southern California exceeded the current NAAQS of 70 ppb, in some cases by wide margins. Here we address an important policy-relevant question: How long will be required to reach the NAAQS in the southern California air basins? Equation 1 provides an approximate answer to this question providing two key assumptions are valid: U.S. background ODV remains constant, and local emissions control strategies can continue the exponential decrease of the anthropogenic ozone enhancements into the future. The South Coast Air Basin had the highest basin ODV in 2015, so our initial focus is here. The reduction of ODVs in this basin over the past 35 years has been substantial - from 273 ppb in 1980 to 102 ppb in 2015 corresponding to a decrease of 171 ppb. A further reduction of 32 ppb (about 19% of the past reduction) will lower the ODV to the NAAQS. If the average absolute rate of decrease over the past 35 years (4.9 ppb/year) were to continue into the future, the NAAQS would be reached in seven years, or by 2022. However, projecting the past exponential decrease with the parameters from Table 4 suggests that a substantially longer time will be required. The ODV elevation above the U.S. background ODV (i.e., y_0 = 62 ppb) has been reduced from 211 ppb in 1980 to 40 ppb in 2015, amounting to a factor of ~5 reduction. Reducing the remaining 40 ppb ODV elevation to the 8 ppb elevation necessary to reach the NAAQS will require a further factor of 5 reduction, which is projected to require an additional 35 years of control efforts, i.e. until 2050. Figure 8 illustrates this projection for the South Coast and similar projections for the other six southern California air basins. The annotations in the figure indicate the year that the ODV in each basin will drop to the NAAQS. The projected ODV in one basin is already at or near 70 ppb, but the projected years in five other basins are between 2030 and 2050. Since y_0 in the Salton Sea Air Basin is greater than 70 ppb, this basin is projected to never reach the NAAQS; to change this projection will require an understanding of why y_0 is so high and strategies to reduce its magnitude. The 95 percent confidence limits on these projected years, based solely on the confidence limits of the parameters of Equation 1, vary from 1 year in the North Central Coast Air Basin to 5 years in the South Coast Air Basin.

Equation 1 gives precise projections for the future evolution of air basin ODVs, but the true uncertainty of future projections are undoubtedly larger than indicated by the above confidence limits. Even though Equation 1 provides an excellent description of past changes, there is no guarantee that future evolution will necessarily follow the same functional form. Still, since Equation 1 accurately fits 35 years of past ODV evolution, the projections do provide a useful guide for further thought., It should also be noted that detailed analyses of the temporal evolution of ambient concentrations of primary and secondary pollutants in the South Coast Air Basin demonstrate that many species, including VOCs, CO, NO_X, HNO_3, PAN, SO_2, and $PM_{2.5}$ (*Warneke et al.,* 2012; *Pollack et al.,* 2013; *Parrish et al.,* 2016a) as well as ozone follow approximately exponential behavior. Evidently, the continuous efforts to reduce emissions maintained over multi-decadal time scales in southern California have yielded approximately exponential decreases.

3.4 Comparison of derived parameters with model results

An ideal model able to fully and accurately quantify the ozone budget in southern California would be able to reproduce the temporal evolution of the ODVs in each of the eight air basins considered in this work. The ten derived parameters included in Table 4 can serve as metrics to judge the performance of any model attempting to approach this ideal. To our knowledge, no modeling effort has attempted to reproduce the 36 years of ODV evolution considered here, so such a comprehensive evaluation is not yet possible. However, model studies have quantified

U.S. background ODVs, or closely related quantities, for southern California air basins; our goal here is to provide a brief, preliminary comparison of our U.S. background ODVs derived from observations with model results reported in the literature, and to discuss why disagreement may be expected.

Prior to this work, model calculations have provided the only means to estimate U.S. background ozone concentrations. In setting the new NAAQS, the U.S. EPA relied upon two different regional air quality models to estimate U.S. background ozone concentrations throughout the nation (*U.S. EPA*, 2015; *Dolwick et al.*, 2015). However, both of those regional models relied upon the GEOS-Chem global model to define the boundary conditions, i.e. the ozone concentrations entering the regional model domains. Another global model has calculated baseline ozone concentrations higher than those from GEOS-Chem (*Fiore et al.,* 2014), so a concern remains that the boundary conditions provided by GEOS-Chem may underestimate the ozone transported into the model domain. Thus, the regional air quality models in turn may have underestimated the U.S. background ozone concentrations, so that achieving the NAAQS may be more difficult than currently expected in some regions of the U.S. These issues emphasize the need for more rigorous evaluation of the global models that are used to provide the boundary conditions for regulatory ozone modeling.

Comparison of our observationally derived U.S. background ODVs with model results is somewhat ambiguous because most reported model results are based upon definitions of background ozone that differ from the U.S. background ODVs that we report in this work, and specific results are not generally reported for the southern California air basins considered in this work. Section S1 of the Supporting Information discusses how we interpreted the reported model results to arrive at the corresponding U.S. background ODVs we consider here.

The model results included in Figure 6b exhibit large variability, but taken as a whole are smaller than the U.S. background ozone ODVs estimated in this work; this difference suggests that the actual contribution of U.S. background ozone in southern California air basins may be larger than currently indicated by most model calculations. In contrast, one modeling study did give much higher estimates of U.S. background ODVs.

In addition to the large variability in the model results in Figure 6b, there are two additional reasons to question the reliability of model results designed to define U.S. background ozone concentrations. First, many models have unexplained systematic biases in the magnitude of calculated ozone concentrations compared to observations. *Dolwick et al.* (2015) use comparisons of model results to observations in an attempt to reduce the influence of such a bias, and *Fiore et al.* (2014) discuss a significant positive bias in the AM3 model total ozone concentration results (see their Figure 6). *Lin et al.* (2012), using a closely related AM3 model, were forced to correct for a related bias issue in the result included here in Figure 6b.

A second reason to question the accuracy of model derived ozone background concentrations is that quantitative comparisons of some global models with metrics derived from observations at baseline representative sites find substantial disagreements between models and measurements, and between different models (*Parrish et al.,* 2014; 2016b; *Derwent et al.,* 2016). These disagreements include significant model biases in absolute ozone concentrations, poor reproduction of ozone concentration changes over multi-decadal time periods, poor reproduction of ozone seasonal cycles within the MBL, and lack of adequate isolation of the MBL, at least at the U.S. west coast. For example, *Derwent et al.* (2016) compare results from fifteen global models with observations at the Trinidad Head surface site discussed in this paper; all models overestimated the observed annual mean ozone concentration of 31 ppb by 2 to 19 ppb, and the observed amplitude of the fundamental of the seasonal cycle (5.7 ± 0.9 ppb) was poorly reproduced, with models giving amplitudes from 1.2 to 10.5 ppb. Difficulties in reproducing the ozone seasonal cycle over the U.S. are apparent in the one study cited here that compared two independent global models (*Fiore et al.,* 2014); one model simulated a large seasonal decline in mean NAB concentrations from springtime into summer, while the other found little seasonality. These comparisons suggest that global model results currently reported in the literature have substantial shortcomings that prevent their consistent and quantitatively accurate reproduction of important aspects of the global ozone distribution, and it is this distribution that determines U.S. background ozone.

In this work we have emphasized that vertical mixing over continental sites and its interaction with the strong vertical gradient of baseline ozone concentrations transported into California are important for determining U.S. background ozone concentrations. *Parrish et al*. (2016b) found that the treatment of the MBL dynamics in the three chemistry-climate models they considered was not adequate to reproduce the isolation of the MBL indicated by the observations at Trinidad Head. *Angevine et al*. (2012) demonstrate that mesoscale meteorological models have a difficult time accurately reproducing boundary layer heights and vertical mixing in California. Thus, to improve model calculations of U.S. background ozone concentrations in southern California, it may be useful to pay particular attention to the treatment of the vertical structure and transport in the lower troposphere.

4. Conclusions and Recommendations

The ozone NAAQS is based on a metric called the "ozone design value" (ODV); it is defined as the 3-year running mean of each year's 4th highest maximum daily 8-hour average (MDA8) ozone concentration measured at a monitoring site. To achieve compliance, the ODV must not exceed the NAAQS, currently set at 70 ppb. We have investigated a set of ODVs for the eight air basins in southern California (Figure 1); each basin ODV is equal to the highest ODV calculated for any of the sites in the basin. These basin ODVs span the 36-year 1980-2015 period, and in response to air quality improvement efforts, show strong systematic temporal decreases, although the 2015 ODVs still exceed the NAAQS in most of these air basins, some by wide margins. The temporal evolution of these ODVs has been investigated through several related approaches, and the results are summarized in Figures 2-5 and Tables 1-4. These approaches all show that a simple mathematical function (Equation 1) provides an excellent description of the temporal evolution of the ODVs. Figure 5 shows that 98.4% of the variability in a set of 214 ODV values from seven of the air basins is captured by Equation 1 with a total of 10 parameter values, which are given in Table 4. Only three parameters of these parameters are required to define the temporal variability of the ODVs in all basins, with the other seven required to define the differences in the relative magnitudes of the ODVs between the air basins.

The parameter values in Table 4 are interpreted as providing estimates of physically significant quantities. The parameter y_0 provides a quantification of the lower limit of the basin ODVs, toward which the measured ODVs are approaching. The value of y_0 for an air basin is then an estimate of the lowest NAAQS that could possibly be achieved in that basin by reducing U.S. anthropogenic ozone precursor emissions to zero, leaving only y_0, which we call the U.S. background ODV. However, as seen in the Salton Sea Air Basin, y_0 may be elevated above the true U.S. background ODV if there are impacts from a heretofore uncontrolled or less controlled emissions sector, such as agriculture. It follows that the parameter A is then interpreted as the enhancement of the basin ODV above y_0 in 1980, and that τ is the time constant for the exponential decrease of this ODV enhancement. A single value of $\tau = 21.9 \pm 1.2$ years fits all seven air basins; this value indicates that a factor of 2 decrease in the basin ODV enhancements occurred every 15.2 ± 0.8 years for a total decrease of a factor of ~5 from 1980 to 2015. A single value of y_0 = 62.0 ± 1.9 ppb fit six air basins, with a significantly higher value (75.6 ± 2.5 ppb) required for the Salton Sea air basin. A different value of *A* is found for each air basin. The 1.6% of the variability not captured with the 10-parameter fit to Equation 1 is primarily due to interannual variability about the fit, so that it has not been possible to further differentiate between the common values of y_0 and τ derived for these seven air basins. The U.S. background ODVs derived here are larger than generally appreciated; their large magnitudes emphasize the importance of vertical mixing bringing higher ozone concentrations to the surface from aloft, as emphasized by the results in Figure 6a.

Two implications of the derived description of the temporal evolution of the basin ODVs are investigated. First, a change in the seasonal cycle of ozone in southern California over the 1980-2015 period is expected, as the predominant contribution to observed ozone concentrations shifted from photochemical production driven by anthropogenic precursors (with a summer maximum) to predominately the U.S. background contribution (with a spring maximum). Figure 7 shows that the seasonal cycle of ozone has indeed shifted to earlier in the year in all eight air basins in accord with this expectation; the rate of this shift has varied from near zero to ~1 day/year. Second, Equation 1 provides the basis for a projection of future evolution of the basin ODVs illustrated in Figure 8. This projections depends on two key assumptions: emission control efforts can maintain the past exponential decrease of the anthropogenic ozone enhancements with the same value of τ, and the U.S. background ODV (y_0) remains constant. The resulting projection is rather pessimistic. For example, over the 1980 to 2015 data record, the ODV enhancement above y_0 in the South Coast Air basin decreased markedly - from 211 ppb in 1980 to 40 ppb in 2015 (a factor of ~5 reduction); however, reducing the remaining 40 ppb ODV enhancement to the 8 ppb enhancement necessary to reach the 70 ppb NAAQS requires a further factor of 5 reduction, which is projected to require an additional 35 years of control efforts, i.e. until 2050. The other air basins with smaller anthropogenic ozone enhancements are projected to reach the NAAQS in earlier years as illustrated in Figure 8.

Some features of the basin ODVs and their temporal evolution remain unexplained; investigating the causes of these features may provide fruitful foci for future research.

- The derived value of y_0 for the Salton Sea air basin is significantly larger (75. 6 ± 2.3 ppb) than for the other air basins (62.0 ± 1.9 ppb). The influence of agricultural emissions and transport of precursors and/or ozone from Mexico are suggested as possible causes.
- The temporal decrease of the ODVs for the San Joaquin Air Basin was quite slow before the year 2000, but since that year the decrease has proceeded at a rate similar to the other air basins. The influence of agricultural emissions is again suggested as a cause.
- The rate of the shift in the ozone seasonal cycle and the timing of the seasonal maximum differ significantly between basins; these differences are not understood.

A brief, preliminary comparison of the U.S. background ODVs derived here from observations with results from models reported in the literature is given in Section 3.4 and Figure 6b. For the most part, there are not large differences, although most models seem to give smaller estimates; in contrast *Mueller and Mallard* (2011) calculated significantly larger North American background ODVs. In addition, comparisons of calculations by several global models with measured ambient concentrations at Trinidad Head, a baseline site on the northern California coast, found poor agreement with absolute ozone concentrations, the ozone seasonal cycle, and the isolation of the MBL (*Parrish et al.,* 2014; 2016b; *Derwent et al.,* 2016). These comparisons suggest that the ability of current modeling systems to provide consistent and accurate calculations of U.S. background ozone concentrations is limited.

It may be possible to significantly advance modeling systems in order to improve our understanding of U.S. and North American background ozone concentrations in southern California's air basins. Equation 1 with the parameter values listed in Table 4 provides an excellent description of the temporal evolution of southern California's air basins. Analogous parameter values can be extracted from model calculations designed to reproduce this temporal evolution, and these derived parameters can be compared to those in Table 4, which would serve as comparison metrics. The characterization of the ozone seasonal cycle in Section 3.2 gives the parameters illustrated in Figure 7, which constitute additional comparison metrics. The comparisons of global model results with measurements at Trinidad Head, CA provide further metrics for comparison (*Parrish et al.,* 2014; 2016b; *Derwent et al.,* 2016). A concerted, systematic effort to improve current modeling systems, so that accurate reproduction of all of these metrics is improved, may yield an improved tool for quantifying U.S. background ozone concentrations and the temporal evolution of observed ambient ozone concentrations, at least in California and perhaps other regions of the country.

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TABLES.

Table 1. Time period of basin ozone design values included in analysis and results of least-squares fits to Equation (1) with τ set to 22.3 years. These parameters are from the least square fits illustrated in Figure 2 and Figures S1-S6.

Air Basin	years	y_0 (ppb)	*A* (ppb)	σ (ppbv)
South Coast	1980 - 2015	58.9 ± 7.0	204 ± 13	4.9
San Diego	1980 - 2015	63.9 ± 5.8	83 ± 10	4.1
South Central Coast	1980 - 2015[1]	62.9 ± 6.6	94 ± 12	4.7
North Central Coast[2]	1989 - 2015	62.9	40	3.1
Mojave Desert	1987 - 2015	58.4 ± 7.7	145 ± 17	4.1
San Joaquin Valley	1980 - 2015	----	----	----
Salton Sea	1980 - 2015	75.8 ± 4.8	74 ± 9	3.4
Great Basin Valleys	1986 - 2015	----	----	----

[1] 1986 excluded from the fit as discussed in the text.

[2] The functional fit to the North Central Coast ODVs gives y_0 = 64. 9 ± 6.3 and *A* = 24 ± 15. The values in the table are for y_0 set equal to that of the South Central Coast as discussed in the text.

Table 2. Results of evaluation of least-squares fits to Equation (1). These parameters are from the linear regressions illustrated in Figure 3.

Air Basin	τ (years)	*A* (ppb)	r^2	σ (%)[2]
South Coast	22.2 ± 1.3	204 ± 11	0.99	5
San Diego	21.0 ± 2.5	86 ± 10	0.96	10
South Central Coast	19.8 ± 2.5	101 ± 13	0.96	11
North Central Coast[1]	20.6 ± 8.2	43 ± 20	0.76	22
Mojave Desert	23.0 ± 3.2	139 ± 19	0.96	8
Salton Sea	21.9 ± 3.0	74 ± 9	0.95	11

[1] The values in the table are for y_0 set equal to that of the South Central Coast as discussed in the text.

[2] The σ values give approximate relative root-mean-square deviation (in %), which are calculated from $(\chi^2/(n-2))^{1/2}$, where χ^2 is the sum of the squares of the deviations of the log-transformed data from the linear fits in Figure 3, and n is the number of data points.

Table 3. Results of correlation of air basin ODVs with those of the South Coast Air Basin. These parameters are from the linear regressions illustrated in Figure 4 and Figures S9-S15.

Air Basin	y_0 (ppb)	A (ppb)	r^2
South Coast	58.9	204	----
San Diego	63.9 ± 3.9	83 ± 7	0.96
South Central Coast	62.8 ± 4.0	94 ± 7	0.95
North Central Coast	64.9 ± 5.4	36 ± 13	0.73
Mojave Desert	59.5 ± 5.7	142 ± 13	0.98
San Joaquin Valley[1]	61 ± 18	(155 ± 62)	0.92
Salton Sea	75.9 ± 3.8	73 ± 7	0.96
Great Basin Valleys	----	----	0.38

[1] Only the years 2001-2015 are included in the fits to this air basin as discussed in the text.

Table 4. Results of multivariate least-squares analysis illustrated in Figure 5. The ten parameters extracted from that analysis are included, along with the absolute root-mean-square deviations between the observed ODVs and the derived fits.

Air Basin	τ (years)	y_0 (ppb)	A (ppb)	σ (ppb)
South Coast	21.9 ± 1.2	62.0 ± 1.9	197 ± 8	5.3
San Diego	[2]	[2]	86 ± 5	4.2
South Central Coast	[2]	[2]	95 ± 5	4.7
North Central Coast	[2]	[2]	41 ± 5	3.1
Mojave Desert	[2]	[2]	136 ± 7	4.3
San Joaquin Valley[1]	[2]	[2]	(149 ± 12)	3.4
Salton Sea	[2]	75.6 ± 2.5	73 ± 5	3.6

[1] Only the years 2001-2015 are included in the fits to this air basin as discussed in the text.
[2] Value given for South Coast Air Basin applies to this air basin as well.

FIGURES

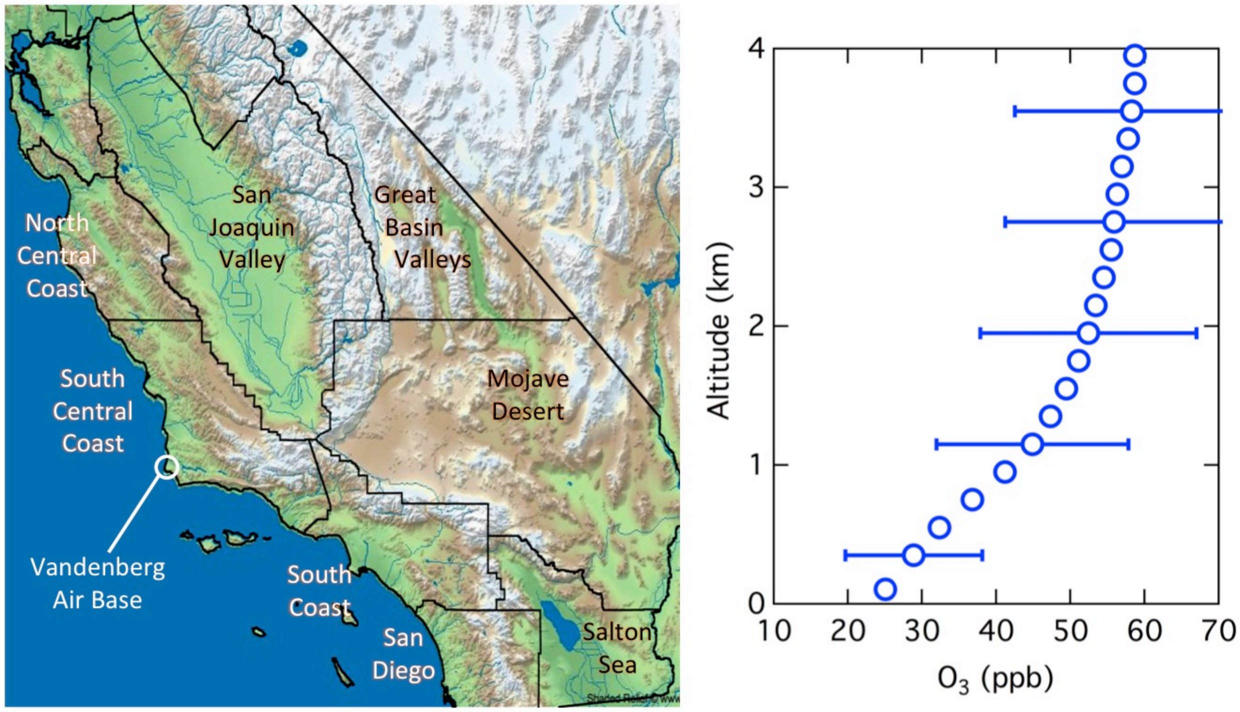
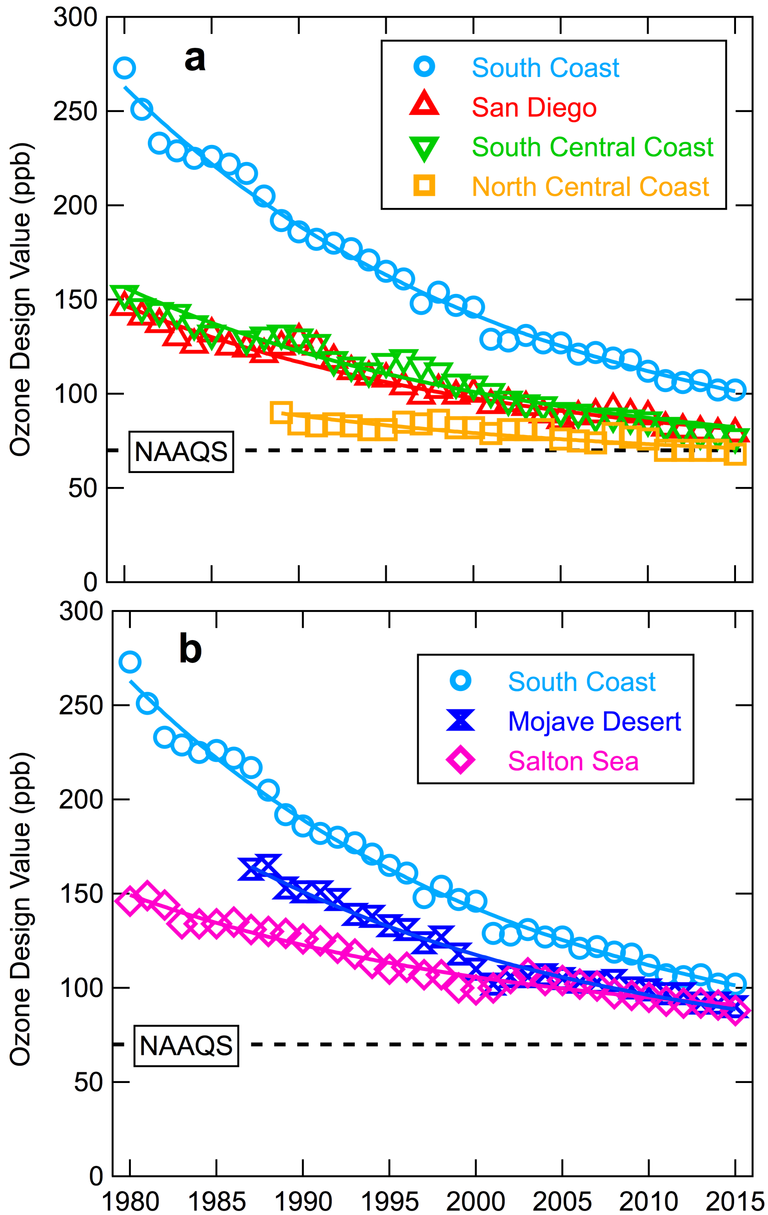


Figure 1. Map of the eight southern California air basins and plot of the vertical profile of baseline ozone concentrations measured by 471 ozone sondes released at Trinidad Head, a northern California coastal site (*Oltmans et al*., 2008) during the 5-month (May-September) ozone season from 1997 through 2014., The symbols show averages over 200 m altitude increments with error bars giving example standard deviations.



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880 **Figure 2.** Evolution of the ozone design values over the past 36 years in **a)** the four southern
881 California coastal air basins and **b)** two inland air basins with the South Coast included for
882 comparison. The symbols give the annual ODVs for each air basin, and the solid curves indicate
883 the fits of Equation 1 to the corresponding ODVs. The dashed line indicates the 2015 NAAQS.

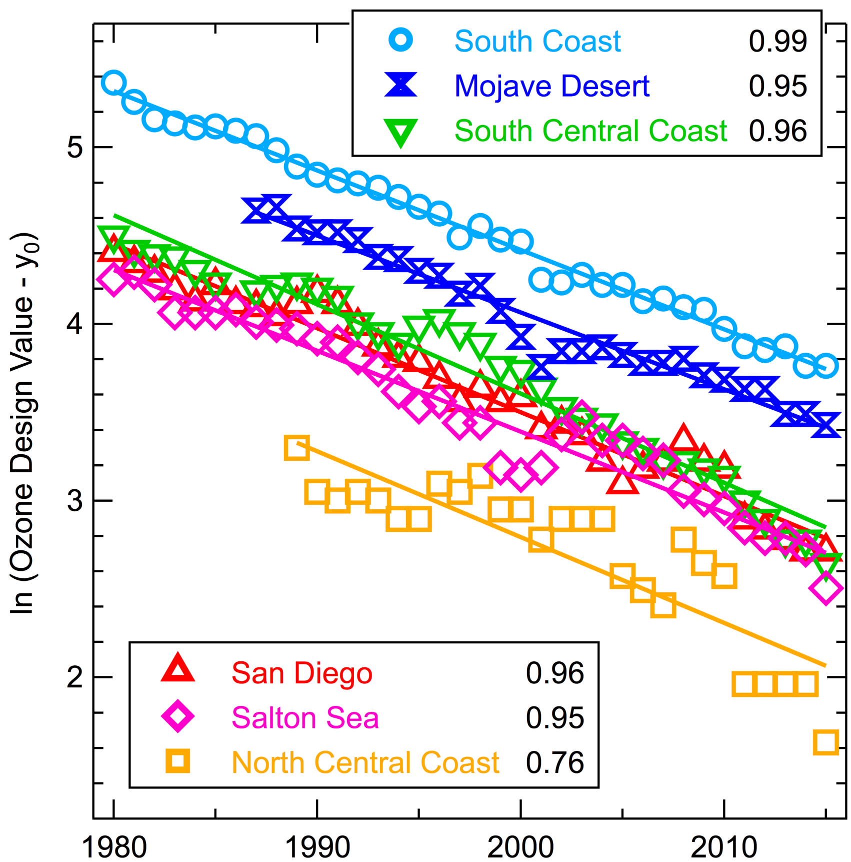

Figure 3. Evolution of the natural logarithm of the ODV enhancement above y_0 over the past 36 years in six southern California air basins. The straight lines indicate linear regression fits to the symbols, with the r^2 of those fits indicated in the annotations.

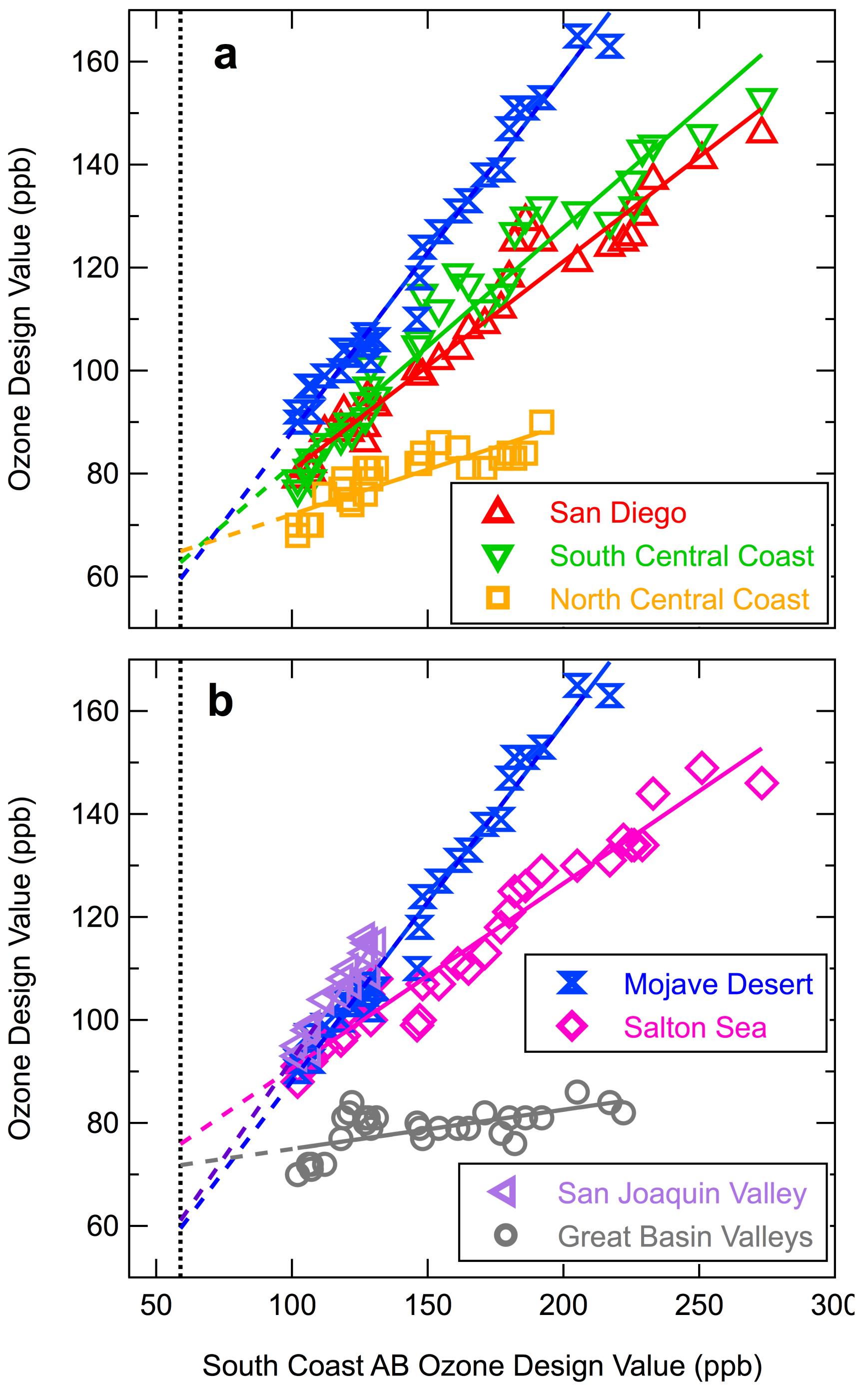

Figure 4. Correlations of ODVs between Southern California air basins and the South Coast Air Basin. The solid lines indicate linear regressions to the symbols. The dashed lines are extrapolations of the linear fits to the y_0 value = 58.9 ppb determined for the South Coast Air Basin (vertical dotted line).

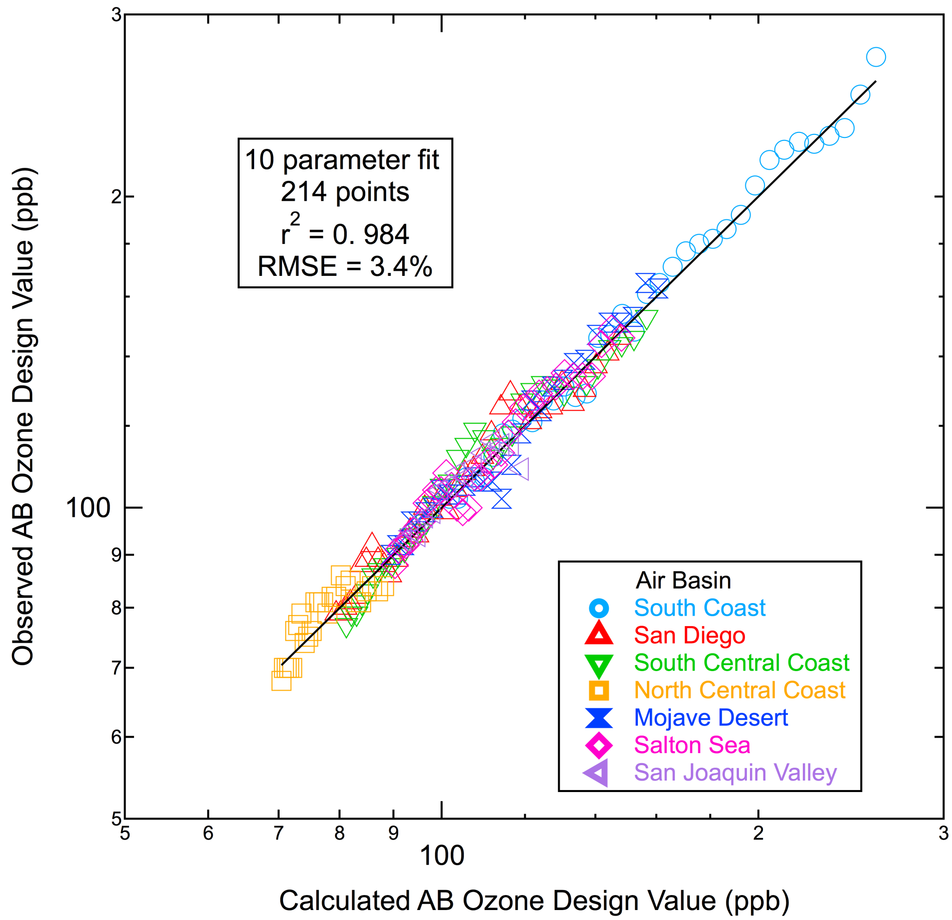

Figure 5. Comparison of observed ODVs with those calculated from Equation (1) based upon a multivariate regression with ten parameters for seven air basins (Table 4). The solid line indicates the 1:1 relationship. The total number of data points, the square of the correlation coefficient for the log-transformed data, and the root-mean-square relative deviations of the calculated ODVs are indicated.

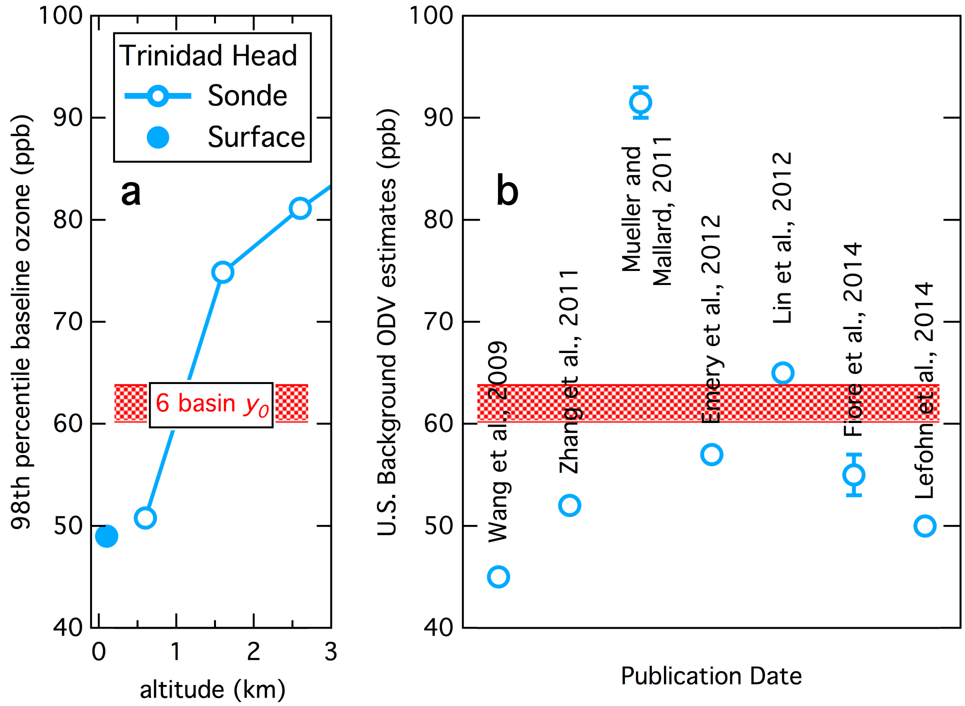

Figure 6. Comparison of y_0 determined for six air basins with **a)** the 98th percentile of the baseline ozone concentrations measured at Trinidad Head in May through September and **b)** estimates of the U.S. background ODV from modeling studies. The red hatched bar indicates the six basin $y_0 \pm$ confidence limits in both plots. In **a)** the solid symbol gives the Trinidad Head surface result and the open symbols give the results from the sonde data (also included in Figure 1) averaged over 1 km thick layers beginning at 0.1 km. The symbols in **b)** give the results from model calculations estimated from the indicated literature references; Section S1 of the Supplementary Information gives details of the interpretation of these model results.

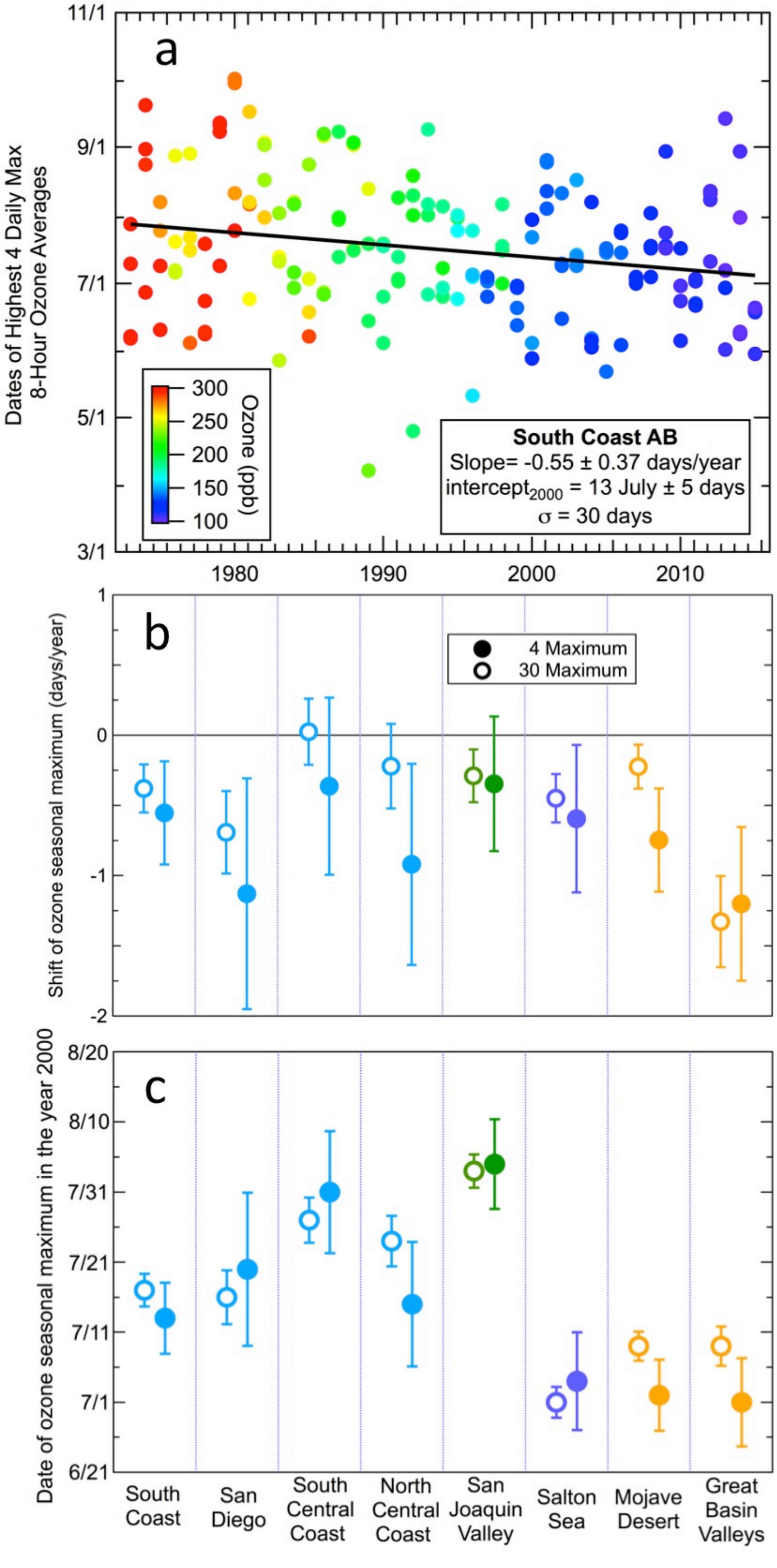
a
Dates of Highest 4 Daily Max 8-Hour Ozone Averages
11/1
9/1
7/1
5/1
3/1
1980
1990
2000
2010
Ozone (ppb)
300
250
200
150
100
South Coast AB
Slope= -0.55 ± 0.37 days/year
intercept$_{2000}$ = 13 July ± 5 days
σ = 30 days
b
Shift of ozone seasonal maximum (days/year)
4 Maximum
30 Maximum
1
0
-1
-2
c
Date of ozone seasonal maximum in the year 2000
8/20
8/10
7/31
7/21
7/11
7/1
6/21
South Coast
San Diego
South Central Coast
North Central Coast
San Joaquin Valley
Salton Sea
Mojave Desert
Great Basin Valleys

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Figure 7. Evolution of the dates of occurrence of the highest maximum daily 8-hour average (MDA8) ozone concentrations over the past 42 years in the Southern California air basins. **a)** Symbols indicate the dates that the four highest maxima were recorded in the South Coast Air Basin each year, and are color-coded according to the ozone concentration. The solid line gives the linear regression fit to the symbols; slopes and intercepts with 95% confidence limits and the root mean square deviation from the fit are annotated. Comparison of **b)** rate of change of ozone seasonal maximum and **c)** the date of the seasonal maximum in the year 2000 in the eight southern California air basins. The results for the four (closed symbols) and the thirty (open symbols) highest MDA8 concentrations in each year are shown with 95% confidence limits.

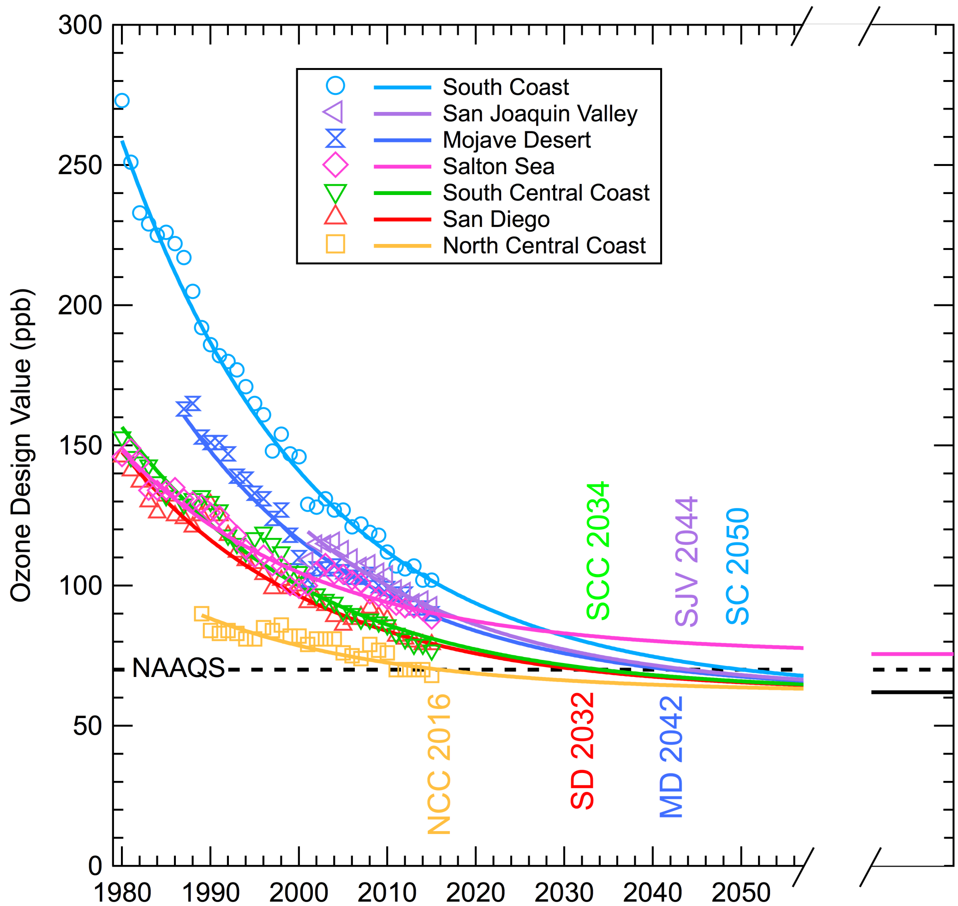

Figure 8. Past and projected evolution of the basin ozone design values in seven southern California air basins. The symbols give the annual ODVs for each air basin, and the solid curves indicate the fits of Equation 1 with the parameters from Table 4 to the corresponding ODVs with projections to the year 2058. The line segments at right indicate the asymptotes (i.e., the parameter y_0) toward which the ODVs are converging (six basins to a common value in black, and the Salton Sea Air Basin approaching its own limit in its corresponding color). The dashed line indicates the NAAQS. The six annotated years in the colors with initials corresponding to the respective basins indicate the projected date that the basin ODV will drop to the NAAQS.