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

David D. Parrish1,2,3, Lindsay M. Young2,3, Mia H. Newman2,4, Kenneth C. Aikin1,2,4, and Thomas B. Ryerson2

1Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA, 2Chemical Sciences Division, NOAA ESRL, Boulder, CO, USA, 3Now at East High School, Denver, CO, USA, 4Now at Ralston Middle School, Belmont, CA, USA

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 to 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 suggest 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.

Plain Language Summary Over the past decades, ozone air quality in Southern California has been greatly improved, but the National Ambient Air Quality Standard (NAAQS) has not yet been achieved in much of the region. The ozone standard is based on the rare, highest recorded concentrations (~98th percentile). A simple mathematical function is shown to provide an excellent description of the decrease in these ozone concentrations, which allows some implications to be inferred. Since 1980 the anthropogenic contribution to these concentrations has been reduced by a factor of ~5. However, the contribution of background ozone is estimated as ~89% of the NAAQS. Since this background contribution is so large, projection of the past rate of decrease of the anthropogenic contribution into the future suggests that ~35 years of additional emission control efforts will be required to reach the new NAAQS of 70 ppb in the Los Angeles region. The model calculations of the background ozone contribution that were considered in the formulation of the new NAAQS underestimate the background contribution. Thus, reducing Southern California ozone concentrations to the 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 (NOx = NO + NO2) 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 fourth highest maximum daily 8 h 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 fourth 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 fourth 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 2 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 (Cooper et al., 2015; Lin, Fiore, 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. Environmental Protection Agency (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 & 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 in the supporting Information 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 4 highest and the 30 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:

\[ \text{ODV} = y_0 + A \exp\left(-\frac{\text{year} - 1980}{\tau}\right). \]  

(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 \(\tau\) 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 \(y_0\), \(\tau\), 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, Galbally, et al., 2016, give some example fits). In favorable cases, relatively precise determinations of all three parameters are possible. In these cases, all determinations of \(\tau\) agreed within their 95% confidence limits, although some of the confidence limits were quite wide. The weighted average of all of the results was \(22.3 \pm 4.0\) years (95% confidence limits are indicated here and elsewhere), which is taken as the initial best estimate for the value of \(\tau\). 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 \(\tau\) 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 2 show these two-parameter fits for the six Southern California air basins whose ODVs have evolved.

### Table 1

<table>
<thead>
<tr>
<th>Air basin</th>
<th>Years</th>
<th>(y_0) (ppb)</th>
<th>(A) (ppb)</th>
<th>(\sigma) (ppbv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Coast</td>
<td>1980–2015</td>
<td>58.9 ± 7.0</td>
<td>204 ± 13</td>
<td>4.9</td>
</tr>
<tr>
<td>San Diego</td>
<td>1980–2015</td>
<td>63.9 ± 5.8</td>
<td>83 ± 10</td>
<td>4.1</td>
</tr>
<tr>
<td>South Central Coast</td>
<td>1980–2015(^a)</td>
<td>62.9 ± 6.6</td>
<td>94 ± 12</td>
<td>4.7</td>
</tr>
<tr>
<td>North Central Coast</td>
<td>1989–2015</td>
<td>62.9</td>
<td>40</td>
<td>3.1</td>
</tr>
<tr>
<td>Mojave Desert</td>
<td>1987–2015</td>
<td>58.4 ± 7.7</td>
<td>145 ± 17</td>
<td>4.1</td>
</tr>
<tr>
<td>San Joaquin Valley</td>
<td>1980–2015</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Salton Sea</td>
<td>1980–2015</td>
<td>75.8 ± 4.8</td>
<td>74 ± 9</td>
<td>3.4</td>
</tr>
<tr>
<td>Great Basin Valleys</td>
<td>1986–2015</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Note. These parameters are from the least squares fits illustrated in Figures 2 and S1–S6.

\(^a\)1986 excluded from the fit as discussed in the text. \(^b\)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.
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 parts per billion ($\sigma$) 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 ppbv.

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 $\tau$ 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 $\sigma$ 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 $\tau$ 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 $\tau$ 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 fourth 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 4 illustrate the correlations of the basin ODVs; figures in the supporting information indicate
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.

Table 2

<table>
<thead>
<tr>
<th>Air basin</th>
<th>$r$ (years)</th>
<th>$A$ (ppb)</th>
<th>$r^2$</th>
<th>$\sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Coast</td>
<td>22.2 ± 1.3</td>
<td>204 ± 11</td>
<td>0.99</td>
<td>5</td>
</tr>
<tr>
<td>San Diego</td>
<td>21.0 ± 2.5</td>
<td>86 ± 10</td>
<td>0.96</td>
<td>10</td>
</tr>
<tr>
<td>South Central Coast</td>
<td>19.8 ± 2.5</td>
<td>101 ± 13</td>
<td>0.96</td>
<td>11</td>
</tr>
<tr>
<td>North Central Coast</td>
<td>20.6 ± 8.2</td>
<td>43 ± 20</td>
<td>0.76</td>
<td>22</td>
</tr>
<tr>
<td>Mojave Desert</td>
<td>23.0 ± 3.2</td>
<td>139 ± 19</td>
<td>0.96</td>
<td>8</td>
</tr>
<tr>
<td>Salton Sea</td>
<td>21.9 ± 3.0</td>
<td>74 ± 9</td>
<td>0.95</td>
<td>11</td>
</tr>
</tbody>
</table>

Note. These parameters are from the linear regressions illustrated in Figure 3.

The $\sigma$ values give approximate relative root-mean-square deviation (in %), which are calculated from $(\sum(y_i - \bar{y})^2/n)^{1/2}$, where $\bar{y}$ is the sum of the squared of the deviations of the log-transformed data from the linear fits in Figure 3, and $n$ is the number of data points. The values in the table are for $y_0$ set equal to that of the South Central Coast as discussed in the text.

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 ($\geq 0.95$ 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. Figures 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 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.
The dashed lines are extrapolations of the linear South Coast Air Basin. The solid lines indicate linear regressions to the symbols. PARRISH ET AL. SOUTHERN CALIFORNIA OZONE DESIGN VALUES

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).

Table 3
Results of Correlation of Air Basin ODVs With Those of the South Coast Air Basin

<table>
<thead>
<tr>
<th>Air basin</th>
<th>$y_0$ (ppb)</th>
<th>$A$ (ppb)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Coast</td>
<td>58.9</td>
<td>204</td>
<td>–</td>
</tr>
<tr>
<td>San Diego</td>
<td>63.9 ± 3.9</td>
<td>82 ± 7</td>
<td>0.06</td>
</tr>
<tr>
<td>South Central Coast</td>
<td>62.8 ± 4.0</td>
<td>94 ± 7</td>
<td>0.95</td>
</tr>
<tr>
<td>North Central Coast</td>
<td>64.9 ± 5.4</td>
<td>36 ± 13</td>
<td>0.73</td>
</tr>
<tr>
<td>Mojave Desert</td>
<td>59.5 ± 5.7</td>
<td>142 ± 13</td>
<td>0.98</td>
</tr>
<tr>
<td>San Joaquin Valley</td>
<td>61 ± 18</td>
<td>(155 ± 62)</td>
<td>0.92</td>
</tr>
<tr>
<td>Salton Sea</td>
<td>75.9 ± 3.8</td>
<td>73 ± 7</td>
<td>0.96</td>
</tr>
<tr>
<td>Great Basin Valleys</td>
<td>–</td>
<td>–</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Note. These parameters are from the linear regressions illustrated in Figures 4 and 5. A signiﬁcant value of $A$ 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 10 parameters is largely due to interannual variability and other noise about the regression fit. Attempts to extract

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, $\tau = 23.3$ years, fits the temporal evolution of each basin, and the $\tau$ 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 $A$, $\tau$, and $y_0$ for each of the seven air basins for a total of 21 parameter values. However, in practice, only 10 distinct parameters were necessary to describe nearly all of the systematic variance in the ODV data set. These 10 parameter values are consistent with the previous analyses: a single $\tau$, 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 fraction of the variance in the total log-transformed data set that is captured by the 10 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 10 parameters is largely due to interannual variability and other noise about the regression fit. Attempts to extract
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) (Warnke et al., 2012), and the concentrations of ambient nitrogen oxides (NOx) were reduced by about 75% (i.e., a factor of ~4) (Parrish, Galbally, et al., 2016; Pollack et al., 2013). 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 U.S. 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 \( \tau \) 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

---

### Table 4

Results of Multivariate Least Squares Analysis Illustrated in Figure 5

<table>
<thead>
<tr>
<th>Air basin</th>
<th>( \tau ) (years)</th>
<th>( y_0 ) (ppb)</th>
<th>A (ppb)</th>
<th>( \sigma ) (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Coast</td>
<td>21.9 ± 1.2</td>
<td>62.0 ± 1.9</td>
<td>197 ± 8</td>
<td>5.3</td>
</tr>
<tr>
<td>San Diego</td>
<td>b</td>
<td>b</td>
<td>86 ± 5</td>
<td>4.2</td>
</tr>
<tr>
<td>South Central Coast</td>
<td>b</td>
<td>b</td>
<td>95 ± 5</td>
<td>4.7</td>
</tr>
<tr>
<td>North Central Coast</td>
<td>b</td>
<td>b</td>
<td>41 ± 5</td>
<td>3.1</td>
</tr>
<tr>
<td>Mojave Desert</td>
<td>b</td>
<td>b</td>
<td>136 ± 7</td>
<td>4.3</td>
</tr>
<tr>
<td>San Joaquin Valley(^a)</td>
<td>b</td>
<td>b</td>
<td>(149 ± 12)</td>
<td>3.4</td>
</tr>
<tr>
<td>Salton Sea</td>
<td>b</td>
<td>75.6 ± 2.5</td>
<td>73 ± 5</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note. The 10 parameters extracted from that analysis are included, along with the absolute root-mean-square deviations between the observed ODVs and the derived fits.

\(^a\)Only the years 2001–2015 are included in the fits to this air basin as discussed in the text. \(^b\)Value given for South Coast Air Basin applies to this air basin as well.

---

Figure 5. Comparison of observed ODVs with those calculated from equation (1) based upon a multivariate regression with 10 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.
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 $\tau$ 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 in the supporting information for details) gives $y_0 = 52.7 ± 6.4$ 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., 2012; Parrish, Millet, & Goldstein, 2009). 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 NO$_x$-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 S17 and S14). Before the year 2000, little systematic change occurred in the ODVs, but from 2001 to 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 (Cooper et al., 2010; Jaffe et al., 2003; Parrish et al., 2009, 2012). 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 second-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, Horowitz, et al., 2015) 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. The $y_0$ 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 $0.55 \pm 0.37$ 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 4 highest and the 30 highest MDA8 ozone concentrations recorded in each year; Figure 7b summarizes the results. Qualitatively similar shifts are found for all eight basins, without significant differences between the 4 and 30 highest analyses.
Quantitatively, the seasonal shift varies from near zero to approximately 1 day/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 middle 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 midlatitudes 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 middle 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 emission 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/yr) were to continue into the future, the NAAQS would be reached in 7 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
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 parameters from Table 4 to the corresponding ODVs with projections for each air basin, and the solid curves indicate the 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.

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 10 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 (Dolwick et al., 2015; U.S. EPA, 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 in 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 (Derwent et al., 2016; Parrish et al., 2014; Parrish, Xu, et al., 2016). These disagreements include significant model biases in absolute ozone concentrations, poor reproduction of ozone concentration changes over multidecadal 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 15 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, Xu, et al. (2016) 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 fourth highest maximum daily 8 h 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 \( \tau \) 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 \( 15.2 \pm 0.8 \) years for a total decrease of a factor of \( -5 \) from 1980 to 2015. A single value of \( y_0 = 62.0 \pm 1.9 \) ppb fits six air basins, with a significantly higher value \((75.6 \pm 2.5 \) 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 \( \tau \) 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 \( \tau \) 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 \((75.6 \pm 2.3 \) ppb) than for the other air basins \((62.0 \pm 1.9 \) 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 (Derwent et al., 2016; Parrish et al., 2014; Parrish 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 (Derwent et al., 2016; Parrish et al., 2014; Parrish, Xu, 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.

Acknowledgments
The authors acknowledge support from NOAA’s Atmospheric Chemistry, Carbon Cycle, and Climate (AC4) Program. The CareerLaunch Internship Program of Denver Public Schools supported L.M.Y. The STAR (STEM Teacher and Researcher) Program of California State University supported M.H.N. The California Air Resources Board provided maximum 8-hr ozone concentrations. Ozone design values were calculated by the California Air Resources Board and downloaded from http://www.arb.ca.gov/adam/index.html. NOAA Earth System Research Laboratory Global Monitoring Division provided surface and ozone sonde data from Trinidad Head (McClure-Begley, A.; Petropavlovskikh, I.; Oltmans, S., 2014) NOAA Global Monitoring Surface Ozone Network. 2012–2014: National Oceanic and Atmospheric Administration, Earth Systems Research Laboratory Global Monitoring Division. Boulder, CO. http://dx.doi.org/10.7289/V57P8BW8). The National Park Service provided ozone data from Lassen NP. The authors are grateful to Owen R. Cooper and Andrew O. Langford for extensive, helpful discussions. Disclosure: David Parrish also works as an atmospheric chemistry consultant (David D. Parrish, LLC); he has had contracts funded by several state and federal agencies, although they did not support this work. The scientific results and conclusions, as well as any views or opinions expressed herein, are those of the author(s) and do not necessarily reflect the views of NOAA or the Department of Commerce.

References


