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Key Points:

- Long-term changes and seasonal cycles of lower troposphere baseline ozone are similar throughout northern midlatitudes
- At northern midlatitudes baseline ozone increased before 2000, but that increase ended, and average concentrations have since decreased
- The year of the baseline ozone maximum (~2006) does not vary significantly with location, altitude, or season

Supporting Information:

- Supporting Information S1

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Zonal Similarity of Long-Term Changes and Seasonal Cycles of Baseline Ozone at Northern Midlatitudes

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Abstract The lifetime of ozone in the troposphere is approximately 3 weeks. Prevailing westerly winds at northern midlatitudes can transport air around the globe in that time. Hence, within these latitudes zonal similarity is expected in long-term changes and seasonal cycles of concentrations of baseline ozone. We quantify the degree of zonal similarity by examining eight in situ baseline ozone data sets near the west coasts of North America and Europe, that is, upwind of those continents and downwind of the Pacific and Atlantic Oceans, where the impacts of local and regional ozone sources have been largely mixed into the troposphere, giving the best-defined baseline ozone signature. Zonal similarity is found in both long-term changes and seasonal cycles. The decades-long increase in Northern Hemisphere, midlatitude baseline mixing ratios (average ~ 0.60 ppb year⁻¹ from 1980–2000), has ended, with a maximum reached in the mid-2000s, followed by slow decrease (average = -0.09 ± 0.08 ppb year⁻¹ from 2000 to the present). The year of the ozone maximum exhibits little if any statistically significant difference with location, altitude, or season. The ozone seasonal cycle differs markedly between sea-level coastal stations representative of the marine boundary layer and the free troposphere sampled at elevated sites and by sondes and aircraft. However, within each of these broad tropospheric layers, the seasonal cycles are similar at all locations. Vertical profiles of the parameters that define the long-term trends and the seasonal cycle are also similar between North America and Europe.

Plain Language Summary Ozone in the lower atmosphere (i.e., the troposphere) plays important roles in atmospheric chemistry, air pollution, and climate change. Ozone has a wide variety of sources and sinks that vary temporally and spatially, which complicate our efforts to fully understand ozone's temporal and spatial distribution. Strong sources (primarily man-made and natural) and sinks of ozone are located in the lower troposphere (i.e., the boundary layer), and input of ozone from the stratosphere is a strong source to the upper troposphere. Here we use long-term records (~2 decades or more) of measured ozone concentrations at relatively remote locations in the northern midlatitudes (where the majority of man-made ozone sources are located) to quantify as accurately and precisely as possible ozone's long-term changes and seasonal cycles. Consistent with the ~3-week lifetime of ozone in the troposphere, we find substantial similarity in these temporal variations throughout this latitude band. From the start of the measurements in the late 1970s, these concentrations increased until a maximum was reached in the mid-2000s, followed by slowly decreasing concentrations. Decreasing ozone concentrations in the background troposphere is good news from the perspective of ozone's contributions to urban and regional air pollution and climate change.

1. Introduction

Tropospheric ozone (O₃) plays a major role in local, regional, and global air quality (Royal Society, 2008), influences the Earth's radiative budget (IPCC, 2013), and controls tropospheric photochemical processes as a precursor to the hydroxyl radical (OH), which drives the primary removal mechanisms for many

atmospheric pollutants (Levy, 1971). Fully characterizing the four-dimensional (latitude, longitude, altitude, and temporal) distribution of tropospheric ozone is critical to our understanding of these issues. However, providing that characterization from the limited observational record is a daunting prospect. In this paper we focus on only a small part of this full distribution but provide that characterization in as quantitatively accurate and simple form as possible. We limit ourselves to (1) northern midlatitudes at altitudes from the marine boundary layer (MBL) to the mid-free troposphere, (2) measurement locations most nearly representative of baseline conditions, and (3) time periods longer than 1 month. Baseline observations are defined here as measurements in air without recent local anthropogenic or continental influence (e.g., see discussion in chapter 1 of HTAP, 2010).

Anthropogenic sources of ozone precursors are concentrated in the continental boundary layer of northern midlatitudes. Thus, it is expected that anthropogenic influences on the tropospheric ozone budget are most clearly evident within this region; a major impetus for this work is to characterize the long-term changes that may have been caused by changes in these anthropogenic influences. However, the intense anthropogenic sources of ozone precursors lead to spatial and temporal variability of ozone on a wide spectrum of scales. Selection of baseline observations minimizes this variability. Nevertheless, transport of air parcels from the continental source regions to the more remote troposphere and variability in natural ozone sources and atmospheric transport cause significant spatial and temporal variability in observed baseline ozone concentrations. In this work we investigate the longer-term temporal variability of ozone in the northern midlatitude regions most remote from the anthropogenic sources. These regions are at or near the downwind (eastern) coasts of the Atlantic and Pacific Oceans and farther downwind from the coasts in the free troposphere over Europe and North America.

Bowdalo et al. (2016) suggest that the troposphere exhibits three distinct scaling regimes of ozone variability. At high frequencies the “weather” regime is driven by meteorological processes with frequencies up to those of planetary-scale weather systems, that is, periods shorter than 10 days. A second “macroweather” regime at lower frequencies with ~10-day to ~10-year periods is driven by the average of the largest planetary-scale weather systems. A third “climate” regime begins between 10 and 100 years and is caused by low-frequency interactions such as solar, volcanic, or anthropogenic forcings. In this work we consider the longest available ozone records (as long as 30 to 40 years) but work with monthly average ozone concentrations. Thus, we investigate the macroweather regime and a higher frequency fraction of the climate regime. By considering monthly mean data we avoid most of the influence from higher frequency variability, although interannual variability of lower frequency weather regime phenomena contributes “noise” to the monthly averages and thereby affects the precision of our analyses.

Global models suggest that the average lifetime of ozone in the troposphere is of the order of 22 days (Stevenson et al., 2006; Young et al., 2013). At northern midlatitudes, where prevailing westerly winds dominate, times for transport around the Earth (e.g., Trickl et al., 2011) are comparable to that estimated lifetime. Consequently, an ozone increase or decrease at one location that persists for a month or longer will necessarily cause a parallel change downwind as ozone rich or poor air is transported zonally. Thus, we expect the temporal variability of ozone on seasonal to decadal time scales to exhibit significant similarity throughout all longitudes at northern midlatitudes. At the same time, these prevailing winds have significant directional variability plus air-mass lifting and subsidence on a variety of spatial and temporal scales, which we expect to cause significant variability about an average, purely zonal uniformity. However, a recent study (Gaudel et al., 2018) did not find this expected zonal similarity of mean concentrations, instead concluding that variability in long-term ozone changes between different data sets precluded the possibility of defining an overall ozone trend over either midlatitude North America or Europe. One goal of this paper is to resolve this inconsistency.

The focus of this paper is to compare and contrast the long-term changes and seasonal cycles of ozone at northern midlatitudes in order to quantify the expected similarity and superimposed variability. To this end, we analyze the longest, highest quality data sets that can provide a characterization of the macroweather and climate regimes of the ozone distribution in the northern midlatitude band. Section 2 gives details of the data sets and the analysis approach and derives the results. Central to the analysis approach is the utilization of a method designed to quantify nonlinear long-term changes, since it has been established that trends of ozone (i.e., the slope of the long-term change) at northern midlatitudes systematically slowed

Figure 1. Maps of surface and profile measurement sites in North America and Western Europe where the ozone data records considered in this work were collected.

since the end of the 20th century (e.g., Derwent et al., 2007; Logan et al., 2012; Parrish et al., 2012). Analysis approaches that explicitly or implicitly assume a constant trend (e.g., those discussed in section 3 of Lefohn et al., 2018) cannot quantify this nonlinear behavior. Section 3 describes the results, and section 4 discusses the significance of the results and presents conclusions.

2. Data, Methods, and Results

2.1. Data Sets Analyzed

To investigate the degree of zonal similarity of ozone at northern midlatitudes, we first select eight data sets for analysis—four European and four North American, a marine boundary layer (MBL) site, a higher elevation site, and two data sets with vertically resolved measurements on each continent—that meet several criteria: (1) baseline representative data, that is, as near the continental west coasts as possible, (2) measurements over the longest possible time period, and (3) provide data from the surface through the lower free troposphere. Importantly, the choice of data sets is made at the outset and not changed during the analysis. Other data sets that have been discussed in the literature could possibly have been chosen, particularly rural surface sites in western North America; comparable analysis of results from one of these sites is discussed in Text S1 in the supporting information. The selected data records include those from surface sites (map in Figure 1) in the MBL (Mace Head, Ireland, and several Pacific MBL sites on the U.S. west coast, predominantly Trinidad Head, California) and higher elevation, more inland sites (European alpine sites in the Alps and Lassen Volcanic National Park in California), ozone sonde records (a combined record from three sites in Europe and the North American records from Trinidad Head, California, and Boulder, Colorado), and the extensive ozone profiles recorded over Frankfurt, Germany, during the MOZAIC commercial aircraft measurement program. For contrast with the eight baseline ozone data sets, long-term ozone measurements from interior continental surface sites in Asia (Mt. Waliguan) and North America (Whiteface Mtn.) are also examined. These data sets have been discussed in previous publications; only brief summaries are given below, along with references to more extensive documentation. Table 1 summarizes the sites and time periods of the data considered, with footnotes indicating the individual data records that are combined into single, more statistically robust records. Figure 2 shows two example time series of monthly mean data from the two European surface sites; seasonal cycles and long-term changes are apparent in each. Also, apparent is a significant interannual variability about both the average seasonal cycles and long-term changes. Throughout this paper, ozone concentrations are quantified as mixing ratios, with units of 10^{-9} -mole O_3 per mole air, denoted as ppb.

The ozone measurements were performed with different measurement techniques by different researchers, but we believe that they are directly comparable. The surface ozone measurements were made using the UV-absorption method, which is the recommended technique for long-term observations (WMO, 2013); Parrish et al. (2009, 2012) discuss the quality control of these data. Appendix A of Parrish et al. (2004) compares sonde measurements at the Trinidad Head site with near-simultaneous measurements from research

Table 1
Long-Term, Ozone Data Sets Investigated in This Work

Monitoring sites	Latitude/longitude	Elevation (km)	Dates
Surface sites			
Mace Head, Ireland	53°10'N/9°30'W	0.02	1987–2017
Zugspitze, Germany ^a	47°25'N/10°59'E	2.7, 3.0	1978–2017
Sonnblick, Austria ^a	47°3'N/12°57'E	3.1	1990–2017
Jungfraujoch, Switzerland ^a	46°33'N/7°59'E	3.6	1990–2018
Olympic N.P., Washington ^b	48°7'N/123°26'W	0.13	1991–2005
Redwood N.P., California ^b	41°34'N/124°5'W	0.24	1987–1995
Trinidad Head, California ^b	41°3'N/124°9'W	0.11	2002–2017
Point Reyes N.S., California ^b	38°7'N/122°55'W	0.08	1987–1992
Lassen Volcanic N.P., California	40°32'N/121°35'W	1.76	1987–2017
Sonde sites			
Hohenpeissenberg, Germany ^c	47°48'N/11°1'E	0.98	1998–2017
Payerne, Switzerland ^c	46°49'N/6°57'E	0.49	1998–2017
Uccle, Belgium ^c	50°48'N/4°21'E	0.10	1998–2017
Trinidad Head, California	41°3'N/124°9'W	0.11	1997–2018
Boulder, Colorado	39°57'N/105°12'W	1.74	1992–2018
Aircraft profiles			
Frankfurt, Germany	50°2'N/8°34'E	0.11	1994–2014
Interior continental sites			
Mt. Waliguan, China	36°17'N/100°54'E	3.8	1994–2016
Whiteface Mtn., New York	44°22'N/73°54'W	1.5	1980–2015

Note. All are considered baseline representative sites except the final two, which are considered representative of continental regions.

^aData sets from Zugspitze, Jungfraujoch, and Sonnblick are combined as European Alpine sites in the analyses. ^bData sets from Olympic N.P., Redwood N.P., Trinidad Head, and Point Reyes N.S. are combined as U.S. Pacific MBL sites in the analyses. ^cData sets from Hohenpeissenberg, Payerne, and Uccle are combined as European sondes in the analyses.

Figure 2. Time series of monthly and annual (orange symbols) mean ozone mixing ratios from two example data sets. The solid curves give the nonlinear, least-squares regression fits of a quadratic polynomial (i.e., the first three terms of Equation 1) to the monthly data, and the vertical dashed line indicates the origin of the time scale for those fits.

aircraft profiles performed directly over the sonde launch site. Excellent agreement was found with the sondes averaging $1.6 \pm 2.4\%$ higher than the aircraft data. Logan et al. (2012) show that the European alpine, sonde, and MOZAIC data sets are consistent over the 1998–2008 period.

During the process of calculating monthly mean data for the sonde and aircraft data sets, measured ozone mixing ratios larger than 150 ppb are excluded. Such high concentrations are taken to represent sporadic stratospheric intrusions and are excluded from the analysis in an effort to derive monthly means characteristic of the troposphere. Very few data are excluded (less than $\sim 1\%$ or 2%) at any altitude interval.

2.1.1. Mace Head

Derwent et al. (2018) present a reanalysis of ozone measurements over a 30-year period from 1987 to 2017 at Mace Head, Ireland. Based on meteorological analyses and a Lagrangian dispersion model, they derived monthly mean baseline ozone mixing ratios; we analyze this data set here. The time series of monthly means is plotted in Figures 2 and S1; annual means derived from the 12 monthly means for complete years of data are included in the latter figure.

2.1.2. Pacific Marine Boundary Layer

Parrish et al. (2012, 2017) discuss a time series of seasonal mean ozone mixing ratios in the Pacific MBL at the U.S. west coast derived from measurements at the four coastal sites listed in Table 1. The majority of these data were collected at the Trinidad Head, California site, beginning in 2002. Inclusion of measurements from three other coastal sites (Parrish et al., 2009) allowed the record of continuous seasonal mean data to be extended back to 1987. Isolation of baseline conditions was achieved by

including measurement data only from periods of high onshore winds, effectively eliminating local continental influences (Parrish et al., 2009). In this work we analyze monthly mean data. At each site, hourly data that fell in the selected wind window described by Parrish et al. (2009) were averaged for each month in November 1987 to March 2017 period, although there are significant numbers of missing months, particularly during summers 1995–2001. For any month with means available from two or more sites, those means were in turn averaged to give the data considered here. The time series of the monthly means is plotted in Figure S2, which also includes annual means for complete years of data.

2.1.3. European Alpine Sites

Parrish et al. (2014) describe a data set that combines monthly mean data from three sites (Zugspitze, Sonnblick, and Jungfraujoch) in the European Alps extending from 1978 to 2011. These same data are analyzed here, with overall monthly averages calculated from the individual site means utilizing all available monthly means. This record is extended through 2017 using all monthly mean data available from these same three sites downloaded from the Tropospheric Ozone Assessment Report (TOAR) data archive. One complication arose from the termination of measurements at the original Zugspitze site in 2011; later years are taken from the Schneefernerhaus GAW data set collected at a different Zugspitze site at 300-m lower elevation. Comparison of data from the 2001–2011 period shows that data from the latter site averaged 97.4% of those from the original site; 2012 and later data are corrected for this difference. The site locations and data records are summarized in Table 1. Logan et al. (2012) and Parrish et al. (2012) considered these same data sets but with data extending only through 2009 and 2010, respectively. As in Logan et al. (2012) and Parrish et al. (2012, 2014), all data from all times of day are included in the analysis without any filtering to isolate baseline conditions. This time series is included in Figures 2 and S1, along with annual means for complete years of data in the latter figure. Many publications have discussed continental influences at these sites (e.g., Yuan et al., 2019, and references therein). However, the relationship between ozone and radon concentrations at the Jungfraujoch site presented by Chambers et al. (2016) demonstrates that these influences do not significantly bias observed ozone concentrations.

2.1.4. Lassen Volcanic NP

Lassen Volcanic National Park in California is the only elevated site in western North America that receives relatively undisturbed air inflow from the Pacific Ocean and where ozone measurements have been made over decadal time scales. Measurements were begun there in 1988. This site lies approximately 240-km inland from the Pacific coast, so continental effects do influence the data. Jaffe et al. (2003) first analyzed the long-term, seasonal average trends in this data set over the 1988 to 2002 period. They showed that filtering the data to isolate marine air, based on either back trajectory air parcel calculations or wind sector filtering, yielded trends not statistically different from the trends including all hourly data. Parrish et al. (2012) extended this time series through 2010 based on seasonal means of all hourly data without filtering, and here we further extend this record in the same manner through April 2017. The time series of monthly means is included in Figure S2, along with annual means for complete years of data.

2.1.5. MOZAIC Data

The Measurement of Ozone and water vapor by Airbus in-service airCRAFT (MOZAIC) program, now continuing as the In-service Aircraft for a Global Observing System (IAGOS) program (Petzold et al., 2015, and references therein), has conducted ozone measurements from commercial aircraft beginning in 1994, with the longest and densest set of profiles collected over the Frankfurt Airport (Petetin et al., 2016). The data used in this work are available from the IAGOS data center (<http://www.iagos.org>, last accessed 14 October 2019). A recent analysis (Petetin et al., 2018) has shown that the MOZAIC observations provide a good representation of lower troposphere ozone concentrations. Here we consider all of the Frankfurt profiles from the beginning of the program (August 1994) through August 2014, the period of reasonably continuous coverage. For several months after that time the coverage became less dense, with fewer profiles measured each month. Data from all profiles within a given month are averaged into 1-km altitude intervals. The time series of the monthly means for the 3- to 4-km altitude interval is included in Figure S3, along with annual means for years that had all 12 monthly means.

2.1.6. European Sondes

Logan et al. (2012) compare ozone measurements from sondes launched from six European sites with data from the European alpine sites and MOZAIC data from profiles over four European airports. Here we analyze the data from the three stations (Hohenpeißenberg, Payerne, and Uccle) that on average launched multiple sonde per week. The sonde data from each sonde launch are averaged into 1-km altitude intervals.

Monthly means are then calculated by averaging these interval means for all sonde launches from any of the sites. This procedure ensures that each sonde launch is weighted equally in the final monthly means. The Uccle sondes report data during the rapid sonde descent after balloon burst, as well as during the controlled ascent; only the ascent data are included in the analysis. These three sonde sites have conducted measurements since the end of the 1960s. However, biases have been identified in the data before 1998 (Logan et al., 2012; Staufer et al., 2014); consequently, we consider the 1998–2017 time period, which includes 2,210, 3,079, and 2,849 sondes from Hohenpeißenberg, Payerne, and Uccle, respectively. The time series of the monthly means for the 3- to 4-km altitude interval is included in Figure S3, along with annual means for years with data for all 12 monthly means.

2.1.7. Trinidad Head and Boulder Sondes

The Global Monitoring Division of NOAA/ESRL has launched ozone sondes (Sterling et al., 2018) from Boulder, Colorado, since 1967 and from Trinidad Head, California, since 1997, generally on a weekly basis in recent decades, although there are some approximately month-long periods with near-daily launches during intensive field campaigns. Here, we consider the 1,364 sondes launched from 1992 through 2017 at Boulder and 1,138 sondes launched from August 1997 through February 2018 at Trinidad Head. The schedule of sonde launches was sporadic in earlier years at Boulder, so data before 1992 are not included in the analysis. The data from all sondes launched from a site within a given month are averaged into 100-m altitude intervals. This ensures that months with many sonde launches are not weighted more heavily than months with fewer sonde launches. We work with these monthly mean data, generally averaged to 1-km altitude intervals. The time series of the monthly means for the 3- to 4-km altitude interval is included in Figure S4, along with annual means for years that had means for all 12 months.

2.1.8. Interior Continental Sites

Two relatively high elevation sites at interior locations in Asia and North America provide contrasts with the baseline ozone data sets. These two sites were investigated by Gaudel et al. (2018). Mt. Waliguan, located in Qinghai Province, China, is included in the WMO/GAW global baseline network and is one of the few global stations located far from oceans. This site is usually impacted by mixed continental air masses from the lower and middle troposphere (Xu et al., 2016, 2018). Monthly mean surface ozone mixing ratio data from 1994–2013 have been analyzed by Xu et al. (2016); this data set, updated through 2016, was provided to us by those authors. The Whiteface Mtn. summit site is a routine monitoring site in the U.S. EPA network. Given its lower elevation (1.5 km), this site is likely more influenced by regional emissions than Mt. Waliguan (3.8-km elevation). Monthly mean data from Whiteface Mtn. were downloaded from the TOAR website (Schultz et al., 2017, <https://join.fz-juelich.de/access/db/>, last accessed 2 September 2019); this website also archives the Mt. Waliguan data.

2.2. Mathematical Description of Ozone Long-Term Changes and Seasonal Cycles

To quantify long-term changes and seasonal cycles of monthly mean ozone data, we adopt the general approach of simultaneously fitting a power series expansion to the long-term change and a Fourier series expansion to the seasonal cycle. The power series provides a method to quantify any continuous, time-varying function without a priori knowledge of the underlying mathematical functional form, while the Fourier series provides a method to quantify any temporally repeating function, such as a seasonal cycle. Parrish et al. (2019) describe this approach in detail. Least-squares fits of Equation 1,

$$[\text{O}_3] = a + bt + ct^2 + A_1 \sin(\chi + \phi_1) + A_2 \sin(2\chi + \phi_2) + \text{residuals}, \quad (1)$$

to the data sets considered in this work provide the required fit of these two series expansions.

The first three terms of Equation 1 are a quadratic polynomial, which constitutes the first three terms of the power series. The three parameters (a , b , and c) are the coefficients that quantify the long-term change of mean ozone mixing ratios. Additional terms of the power series (i.e., $dt^3 + ct^4 + \dots$) would be included in the fit to any data set that statistically justified such inclusion; however, none of the fits to the data sets examined in this work require inclusion of a term of order higher than the quadratic term. Examples of fits of these first three terms to monthly mean data from two sites are illustrated in Figure 2, and the fits to all data sets considered are included in Figures S1–S4. Further discussion of the advantages of using such power series fits is given in Text S1.

The fourth and fifth terms of Equation 1 represent the first two terms of the Fourier series: the fundamental harmonic (i.e., a single sine cycle per year) and the second harmonic (i.e., two sine cycles per year). The two terms have four parameters that quantify the seasonal cycle—the amplitudes (A_1 and A_2) and phases (ϕ_1 and ϕ_2)—of the fundamental and second harmonics. In the fits to the data sets investigated in this work, only one or two harmonic terms are generally statistically justified; higher order harmonics could be included if required.

The time origin for the quadratic polynomial is chosen as the beginning of the year 2000 (i.e., t in Equation 1 equals year 2000) so that the origin is well within the time span of the data series considered; this choice allows a precise determination of the coefficients. Given this choice, the a coefficient, with units ppb O_3 , is the intercept of the fitted curve at the origin; we discuss the derived values of a coefficient to provide a comparison of the absolute ozone mixing ratios between data sets in the year 2000. The b coefficient, with units ppb O_3 year⁻¹, is the slope of the fitted curve, also at the origin; it quantifies the time rate of change of ozone at the beginning of the year 2000. Finally, the c coefficient (with units ppb O_3 year⁻²) is equal to one half of the (constant) time rate of change of the slope of the fitted curve, that is, the acceleration or deceleration of the ozone trend. This third term is important for fully quantifying ozone trends with rates that vary over the data record, that is, nonlinear time dependence. In this work, the statistically significant values of c are negative, with the fitted curve increasing early in the data record, reaching a maximum, and then decreasing at later times. Equation 2 gives the year of the maximum of the fit:

$$\text{year}_{\max} = -b/2c + 2000. \quad (2)$$

The confidence limit for $\text{year}_{\max}$ is obtained from standard propagation of error techniques from the confidence limits of the b and c parameters. Rather than discussing the derived values of the b and c parameters to compare the long-term changes, we will instead discuss the equivalent parameter set: c and $\text{year}_{\max}$ derived from Equation 2. This latter parameter set is selected because it has a more direct physical interpretation. It should be noted that the choice of the year 2000 as the time origin does not affect the shape of the derived fit to the long-term ozone changes and thus does not affect any implications or conclusions derived from that fit.

The independent seasonal cycle variable, χ , spans 1 year's time period in radians from 0 to 2π in the two harmonic terms of Equation 1. The seasonal cycle derived from monthly means is indistinguishable from those derived from higher frequency data, but monthly means provide no sensitivity to higher frequency variability such as synoptic and diurnal variations. In effect, working with monthly means imposes a low-pass filter on the analysis, but this filter does not affect quantification of the seasonal cycle.

The harmonic terms in Equation 1 are orthogonal functions, which implies that the information in the data set that defines that one harmonic is independent of the information defining any other. Consequently, the derived regression parameters are independent of whether the regression procedure is based on fits to Equation 1 with two harmonic terms or to an analogous equation with one, three, or more harmonic terms. There is ambiguity in how the parameters of a harmonic term are defined; the convention adopted here is to select positive amplitudes and phase angles in the range of $-\pi$ to $+\pi$.

2.3. Regression Fits to Data Sets

Quantification of the long-term change and seasonal cycle of baseline ozone in each data set is provided by a nonlinear least-squares regression fit of Equation 1 to the monthly mean time series. This fit comprises a three-step process. First, the first three terms of Equation 1 are fit to the time series to give an initial quantification of the long-term change. Second, the second and third terms are subtracted from the original time series in order to detrend the monthly data. A Fourier transform of the remainders (i.e., the constant a term, the seasonal cycle, and other residuals) indicates the number of statistically significant harmonic terms required to quantify the mean seasonal cycle. The final step of the analysis is a simultaneous fit of all terms of Equation 1 to the original time series of monthly means in each data set; this step gives nearly identical results as the first two steps but with more precise determinations of all seven parameters in Equation 1. The derived parameter values are included in Table 2 and provide the basis for the discussion in the following sections.

The first three terms quantify the long-term changes, as illustrated in Figures 2 and S1–S4 with annotations in the latter four figures giving the derived coefficient values. The parameters derived for Mace Head are

Table 2

Parameter Values of Fits of Long-Term Change and Seasonal Cycle at Baseline Sites and Interior Continental Sites (Last Two Rows)

Data set	a (ppb)	b (ppb year ⁻¹)	c ($\times 10^{-3}$) (ppb year ⁻²)	year _{max} ^d	A_1 (ppb)	ϕ_1 (rad)	A_2 ^e (ppb)	ϕ_2 ^f (rad)	Number of data	RMSD (ppb)
Mace Head	39.8 ± 0.6	0.35 ± 0.06	-20 ± 6	2008.8 ± 3.2	5.7 ± 0.6	0.52 ± 0.10	3.1 ± 0.6	-2.37 ± 0.10	361	2.9
Pacific MBL	32.9 ± 1.1	0.14 ± 0.10	-25 ± 11	2002.8 ± 2.2	5.6 ± 1.0	0.48 ± 0.18	3.5 ± 1.0	-2.31 ± 0.28	328	3.3
Lassen NP	41.0 ± 0.7	0.26 ± 0.07	-24 ± 8	2005.4 ± 2.2	3.7 ± 0.7	-1.19 ± 0.19	2.2 ± 0.7	-0.17 ± 0.32	355	3.4
European alpine	51.5 ± 0.9	0.17 ± 0.05	-19 ± 5	2004.7 ± 1.9	8.6 ± 0.8	-1.24 ± 0.10	(0.4 ± 0.8)	-	480	3.3
European sondes ^a	52.8 ± 1.5	0.01 ± 0.25	-3 ± 15	2001 ± 40	7.7 ± 0.6	-1.24 ± 0.08	(0.6 ± 0.6)	-	240	2.4
MOZAIC ^a	50.2 ± 0.8	0.22 ± 0.22	-14 ± 20	2007.5 ± 13	7.8 ± 0.9	-1.24 ± 0.11	(0.8 ± 0.9)	-	241	2.8
Trinidad Head sondes ^a	53.5 ± 1.2	-0.01 ± 0.35	+5 ± 21	-	6.2 ± 0.9	-1.17 ± 0.15	(0.9 ± 0.9)	-	246	5.3
Boulder sondes ^a	56.1 ± 0.6	0.15 ± 0.10	-24 ± 9	2003.1 ± 2.5	8.4 ± 0.6	-1.33 ± 0.07	(0.7 ± 0.6)	-	312	3.9
All baseline data sets ^b	-	0.21 ± 0.02	-18 ± 2	2006.0 ± 0.7	-	-	-	-	2,563	4.0
2-year means ^c	-	0.20 ± 0.06	-18 ± 6	2005.7 ± 2.5	-	-	-	-	20	1.4
Mt. Waliguan	49.5 ± 0.4	0.19 ± 0.05	+3 ± 7	-	9.3 ± 0.4	-1.33 ± 0.05	1.4 ± 0.4	+1.68 ± 0.32	239	2.1
Whiteface Mtn.	41.4 ± 1.3	-0.19 ± 0.09	-23 ± 9	1995.8 ± 2.5	7.9 ± 1.2	-1.14 ± 0.15	1.3 ± 1.2	-1.78 ± 0.94	421	3.8

Note. Highlighted rows are fits to data from all baseline sites. Of the baseline sites, the first two rows are MBL sites, the fourth through eighth rows represent the free troposphere, and the third row (Lassen NP) is a continental boundary site.

^aResults for sonde and MOZAIC data sets are for the 3- to 4-km altitude means. ^bResults for normalized, deseasonalized monthly means from all data sets illustrated in Figure 9. ^cResults for 2-year means of normalized, deseasonalized monthly means from all data sets illustrated in Figure 9. ^dResults for year_{max} can be derived only if the value derived for c is negative. ^eResults for A_2 in parentheses are judged to be not statistically significantly different from 0. ^fResults for ϕ_2 are given only if the value derived for A_2 is statistically significantly different from 0.

identical to those given by Parrish et al. (2019), who analyzed this same data set, but differ slightly (but well within the respective 95% confidence limits) from those derived by Derwent et al. (2018), who fit the same functional form to annual means. The results of the Mace Head seasonal cycle analysis are consistent with that reported earlier (Parrish et al., 2016, 2019).

Fourier transforms of two surface data sets are illustrated in Figure 3, and transforms for all data sets are included in Figures S5 and S6. In these figures, the magnitudes of the contributions to the seasonal cycle are plotted as a function of frequency. Since we analyze monthly mean data, the highest frequency whose contribution can be quantified is 6 year⁻¹, that is, a term with six sine cycles per year. In general, only the fundamental harmonic (frequency of 1 year⁻¹) and the second harmonic (frequency of 2 year⁻¹) make significant contributions to the seasonal cycles in the data sets investigated here; this is the rationale for including only these two harmonic terms in Equation 1. In addition, the spectra have a strong (i.e., off-scale in the

Fourier transform figures) contribution at zero frequency that quantifies the annual mean concentration. Close examination of the spectra indicates that the third harmonic (frequency of 3 year⁻¹) makes a statistically significant contribution in some spectra (e.g., the European alpine sites in Figure 3) but the magnitudes of its contribution are small; this third harmonic contribution is not investigated further.

The quantification of the seasonal cycle provided by the fundamental and second harmonics (i.e., the fourth and fifth terms of Equation 1) is illustrated in Figure 4 for two example data sets. The time series and Fourier transform spectra of these same data sets are shown in Figures 2 and 3. Figures S7–S10 present additional example seasonal cycle fits and include annotations giving the respective amplitudes and phases (with confidence limits) of the fundamental and second harmonic terms. Importantly, the two or four parameters (i.e., the amplitude and the phase of either the one or two statistically significant harmonic terms) derived from the seasonal cycle fit represent nearly all of the statistically significant information regarding the average seasonal cycle that is available from the observations in the data set.

Figure 3. Results of Fourier transform of detrended, monthly mean data from the Mace head and European alpine data sets illustrated in Figure 2. In each spectrum, there is a point off scale at zero frequency, which corresponds to the annual mean ozone concentration.

Figure 4. Seasonal cycles of the detrended monthly mean data from the Mace Head and European alpine data sets illustrated in Figures 2 and 3. The upper black curves give the sums of the derived values of the a parameter and the fits of the fundamental term of Equation 1 to the respective data sets. The data points about the lower x-axes are the residuals between the detrended data and the fundamental fits, with the corresponding black curves giving the fits of the second harmonic term of Equation 1 to the respective residuals. The orange curves show the sum of a and the two harmonic terms for each data set.

For all data sets, fits are also derived for data subsets—individual seasonal fits for the four surface sites and individual means for 1-km altitude intervals for the sonde and MOZAIC data sets. The Trinidad Head sondes provide the only data set that includes above-surface measurements at low altitudes at a baseline representative site; two smaller intervals at low altitudes (0.2 to 0.5 and 0.5 to 1 km) are analyzed for this data set.

2.4. Confidence Limits and Interpretation of Statistical Significance

For all the regressions presented in this work, confidence limits for the fitted parameters are derived during the fitting process under the assumption that each monthly mean is an independent result, with no autocorrelation between monthly means. This assumption is checked through an autocorrelation analysis; when significant autocorrelation is found, the confidence limits are increased in accord with the indicated number of degrees of freedom in the data, following the procedure suggested by Leith (1973). Parrish et al. (2019) give more details of this process. In these results, each confidence limit requires an increase by a factor between 1 and 2, with an average of 1.4. However, decadal climate variability, such as the El Niño/Southern Oscillation (ENSO) influence discussed by Lin et al. (2014), can cause autocorrelation on longer time scales. We have no analysis approach that allows quantification of such autocorrelation. Consequently, the confidence limits in Table 2 for fits to individual data sets must be considered lower limits, and the statistical significance of apparent differences in results among different data sets may be overestimated. This issue is considered in reaching the conclusions presented in this paper.

Recent literature (e.g., Amrhein et al., 2019; Hurlbert et al., 2019) emphasizes the importance of not using statistical significance in a dichotomous manner, for example, to decide whether the results of two analyses either

Figure 5. Vertical profiles of annual mean ozone mixing ratios at the start of year 2000 as discussed in text. Error bars indicate 95% confidence limits of the derived values. The gray dashed line indicates the nominal top of the MBL at 1-km altitude.

Figure 6. Results from harmonic analysis of seasonal cycle of baseline ozone for (a) the fundamental terms, (b) the second harmonic terms, and (c) the average seasonal cycle (i.e., the sum of the two harmonic terms plus the value of the parameter a). The sonde and MOZAIC results are for the 3- to 4-km altitude interval to approximately correspond to the elevations of the European alpine sites. European data are in blue, green, or violet, and north American data are in orange or brown; dashed curves indicate MBL data. Error bars indicate 95% confidence limits for the magnitude and time of the peak of each fundamental term and second harmonic term.

agree or disagree. It is recommended to simply present p values without label or category. In this work we estimate 95% confidence limits for all results, and we use these confidence limits as the basis for describing a difference between two results or two numbers as “statistically significant” if that difference is outside the propagated confidence limits. We use this statistical significance to guide two decisions central to the analysis. First, the fitting of the power series and the Fourier series to observed time series requires a decision regarding the number of terms to retain in each series (i.e., the number of terms retained in Equation 1); we include those terms whose coefficients are “statistically significant” (i.e., if the confidence limit of the coefficient does not include 0). Including an optimum number of terms in each series is important to maximize the accuracy and precision of the fit, without overfitting the data, since such overfitting can potentially add noise to the fit residuals. Second, if the coefficients derived in the fitting process for two or more time series do not differ by a “statistically significant” amount (i.e., if the confidence limits of the coefficient differences include 0), then we utilize a single regression fit to multiple time series in order to improve the precision of the derived coefficients (being cognizant that combining data sets likely introduces additional autocorrelation); such a fit to multiple time series is discussed in section 3.3. It is important to have an objective basis for these decisions, and “statistically significant” differences as defined here provide that basis. Throughout the analysis, we evaluate the uncertainty of these decisions; in this work this emphasis is particularly important because of the inherent uncertainty in accurately deriving confidence limits in the presence of unquantified autocorrelation in the data sets. To conform as closely as possible to the above-referenced admonitions regarding the use of statistical significance, we present the confidence limits for the results, which allows an estimation of the p values if desired. Importantly, we do not base our final conclusions on an arbitrary dichotomous interpretation of statistical significance.

3. Results

The following sections describe the results of the analysis, with a particular emphasis on exploring the similarity in seasonal cycles and long-term temporal changes.

3.1. Annual Average Baseline Ozone Vertical Profiles

The derived a parameter values from the fits of Equation 1 (Table 2) represent interpolations to the beginning of year 2000 of the fit to the smoothly varying, underlying long-term changes for each data set. These results allow an objective comparison of annual average absolute ozone mixing ratios from data sets that span different time periods, as in the present study. This comparison (Figure 5) illustrates several important features.

The average baseline ozone concentrations through the depth of the troposphere are similar over the western regions of Europe and North America. Over the 3- to 9-km altitude range the four data sets average 57.5 ppb with a standard deviation of 1.7 ppb. From the surface to 9 km the means of all data sets fall in ranges that span no more than 8.2 ppb in each 1-km altitude interval. The only significant difference is the European sonde data lying as much as 11% higher than the other three free troposphere data sets, with the difference increasing at higher altitude. This difference may arise from instrumental, rather than from actual atmospheric, differences; Tarasick et al. (2019) report that sonde data are $5 \pm 1\%$ higher in the lower troposphere and $8 \pm 1\%$ higher in the upper troposphere compared to MOZAIC data, which they suggest can

Figure 7. Vertical profiles of the amplitude and phase of the fundamental of the seasonal cycles determined from all data sets. The phases are simultaneously plotted as radians (top abscissa) and as the date of the peak of the maximum (bottom abscissa). Colors differentiate between European and North American results. The gray dashed line denotes the nominal top of the MBL at 1-km altitude.

the only statistically significant harmonic contribution; a single sine function with a 1-year period captures the large majority of the statistically significant variability associated with the average seasonal cycle. In contrast, and consistent with previous work (Derwent et al., 2016; Parrish et al., 2016), both the fundamental and the second harmonics are required to accurately describe the average seasonal cycle in the MBL (e.g., the Mace Head data in Figure 4). Faster photolysis loss of ozone (photolytic dissociation of ozone to form $O(^1D)$, which then reacts with water) in the MBL is believed to be the physical mechanism primarily responsible for the seasonal cycle difference between the boundary layer and the free troposphere. The dominant source of ozone to the MBL is entrainment from the free troposphere, so a similar seasonal cycle might be expected. However, the rapid photolytic loss within the MBL shifts the phase of the fundamental toward the winter and drives the second harmonic contribution, which arises (with a magnitude of opposite sign) from the second harmonic of the rate of ozone photolysis (Parrish et al., 2016). Consequently, the second harmonic term is statistically significant only in the higher humidity environment of the MBL (Mace Head and the Pacific MBL surface sites illustrated in Figure S8 and the lower altitude intervals from the Trinidad Head sondes, which also are within the MBL). An exception to this general situation is the Lassen NP data set (Figure S8), where there are significant contributions from the first three harmonic terms (Figure S5); the physical significance (if any) of each of these three terms is not clear. As noted by Bowdalo

be considered a reference data set. However, Tarasick et al. (2019) do not compare coincident, colocated measurements as did an earlier comparison (Tanimoto et al., 2015) that found somewhat smaller differences.

Despite this similarity, the vertical gradient in average ozone mixing ratios from 3 to 9 km over western North America (1.2 ppb km^{-1} average for the Trinidad Head and Boulder sondes) is significantly smaller than over Western Europe (2.7 ppb km^{-1} average for the European sondes and the MOZAIC data). Within the MBL the surface Mace Head ozone mixing ratios in the Eastern Atlantic are larger than those in the Eastern Pacific MBL by 7 ppb. This difference has been discussed previously (Derwent et al., 2016; Parrish et al., 2009). However, in the lower free troposphere this difference is absent, which implies that the ozone vertical gradient from the MBL to the lower free troposphere is stronger over the U.S. Pacific coast compared to over Mace Head.

The annual mean ozone mixing ratio at Lassen NP (41 ppb) falls below the value at the same altitude (47 ppb) in the vertical profile derived from the Trinidad Head ozone sondes. Several processes likely contribute to this difference. As air moves inland from the marine environment to the Lassen Volcanic NP site, vertical mixing (driven by orographic flows associated with the coastal mountain ranges to the west and the Cascade Range to the east and convective transport within the continental boundary layer) mixes air from the MBL and the free troposphere through the lower 2 to 3 km of the troposphere. The annual mean mixing ratio at Lassen is similar to the average over the lower 3 km measured by the Trinidad Head sondes (44 ppb), so vertical mixing alone may account for the departure of the Lassen value from the Trinidad Head sonde profile. However, continental influences (surface deposition of ozone, particularly to vegetation, and production or loss of ozone from reaction of natural or anthropogenic precursor emissions) may affect the Lassen measurements. Any interpretation of absolute ozone mixing ratios at the Lassen NP site must consider these influences.

3.2. Seasonal Cycles of Baseline Ozone

The seasonal cycle differs markedly between the MBL and the free troposphere as illustrated by the two example data sets in Figure 4. In the free troposphere (i.e., the European alpine data in Figure 4 and the sonde and MOZAIC data in Figures S9 and S10), the fundamental term is generally

Figure 8. Parameters of fits of Equation 1 to annual mean baseline ozone concentrations, with year_{max} calculated from Equation 2. Error bars indicate $\pm 95\%$ confidence limits. For the MOZIAIC data and Boulder sondes, the fit is to monthly means over the 3- to 9-km altitude range. The small symbols indicate separate seasonal determinations (in the order of MAM, JJA, SON, and DJF) at the surface sites and separate determinations for 1-km altitude intervals (in order of increasing altitude) for the MOZIAIC and sonde data sets.

et al. (2016), independent physical forcings of each harmonic are not necessary; a contribution from any given harmonic can simply result from the harmonics required to mathematically fit the particular seasonal cycle at Lassen NP where, as previously discussed, mixing of MBL with free troposphere air and other continental-based processes may all act together to determine the seasonal cycle. In the following discussion the second harmonic contribution to all data sets is quantified and illustrated in the figures, but if the contribution is not statistically significant, it is not discussed further.

A comparison of the seasonal cycles and the fundamental and second harmonic contributions for seven baseline ozone data sets is shown in Figure 6; strong zonal similarity is apparent, despite large differences between the MBL and the free troposphere (see parameter values in Table 2). Within the MBL there are no statistically significant differences between the eastern Atlantic and the eastern Pacific in either the amplitude or the phase of fundamental (Figure 6a) or the second harmonic (Figure 6b). The harmonics derived from the lowest 0.2- to 0.5-km interval of the Trinidad Head sondes (not shown) agree similarly. Above the MBL, there is similar agreement among the 3- to 4-km altitude intervals of the MOZIAIC and sonde data and the alpine surface site data. The second harmonic amplitude is not statistically significant in any of these data sets, and the amplitudes and phases of the fundamental (Figure 6a) generally agree within their statistical uncertainties; the one exception is the amplitude of the fundamental derived from the Trinidad Head sonde data, which is 25–30% smaller than those derived from the other four data sets. Figure 6c compares the overall seasonal cycles, which again differ between the MBL and the free troposphere but have similar shapes within these two regimes of the troposphere (apart from the offsets associated with differences in the a parameter values discussed in section 3.1).

With increasing altitude (Figure 7) the amplitude of the fundamental decreases to a minimum near the top of the MBL and then increases to even larger values in the free troposphere. In contrast, the phase of the fundamental changes abruptly at the top of the MBL but then remains nearly constant at higher altitudes. In the free troposphere the maximum

of the fundamental is in mid-June, but the maximum moves to earlier in the month with increasing altitude over North America, approaching late May above 8 km—a shift that is not apparent over Europe. In the free troposphere, the influence of the second harmonic is small, so the peak of the seasonal cycle (Figure 6c) coincides closely with that of the fundamental harmonic. In the MBL the peak of the fundamental is near the end of February (with a minimum 6 months later in mid-August), but the second harmonic contribution, which is larger than in the free troposphere, shifts the seasonal cycle peak to later in the year (mid-April) and the seasonal minimum to earlier in the year (near the end of July); as a consequence, baseline ozone in the MBL decreases rapidly between the seasonal maximum and minimum but increases more slowly during late summer, winter, and early spring, with some indication of a secondary maximum and minimum during that period.

As expected, the magnitudes of the contributions at frequencies 0, 1, and 2 year^{-1} in the Fourier transform spectra illustrated in Figures S5 and S6 are equal to the magnitudes of the parameter a and the amplitudes of the first and second harmonic terms, respectively, derived from the regression fits of Equation 1 shown in Figures 4 and S7–S10 (the phase angles of the two harmonic terms can also be derived from the Fourier transform analysis, but that analysis is not included here). The regression fits are utilized here to provide quantitative confidence limits for the five parameters, to allow inclusion of all measured monthly means in the regression fit even if there are missing data (the Fourier transform software package that we use, Wavemetrics IGOR Pro, requires complete years of monthly means), and to give clear illustrations of the fits (i.e., Figures 4 and S7–S10).

Figure 9. Time series of monthly mean (colored points) and normalized, deseasonalized monthly mean (gray points) data from all eight data sets. The sonde and MOZAIC data sets are 3- to 9-km means. The symbols with error bars are 2-year means with standard deviations of the gray points. The solid curve is the quadratic polynomial fit to the 2-year means.

3.3. Long-Term Changes of Baseline Ozone

Statistically significant long-term changes can be quantified for the six data sets that span the longest time periods. The resulting values of year_{max} and the c parameter are similar (Figure 8 and Table 2). All derived year_{max} occurred between 2002 and 2010, although there are some differences that appear to be statistically significant, for example, year_{max} of the Mace Head and Pacific MBL data sets. However, as discussed earlier, tabulated 95% confidence limits do not account for some sources of systematic uncertainty, so the derived confidence limits are lower limits for the actual uncertainty. Thus, the year_{max} values may well be equal within statistical uncertainties for all data sets. On balance, the upper panel of Figure 8 indicates that northern midlatitude baseline ozone increased in the years before 2000, reached a maximum on average in ~ 2005 , and has since decreased. The lower panel of Figure 8 indicates no statistically significant differences in the c parameter values (which indicate the time rate of change of the trend) between data sets. The small symbols in Figure 8 indicate the results for individual seasons (for the four surface data sets) and different altitude intervals (for the MOZAIC and Boulder sonde data sets). There are no statistically significant differences in the parameters derived from either the seasonal or the altitude subsets of the data, suggesting the absence of longitudinal, seasonal, or altitude differences in the long-term baseline ozone changes within the lower 9 km of the northern midlatitude troposphere.

Given the similarity of the long-term changes in these northern midlatitude data sets, it is useful to combine these data sets and then remove the variance associated with spatial variability of the annual means and the seasonal cycles. The combined data set includes 2,563 total monthly means (plotted as colored symbols in Figure 9). The total variance of this data set is 140 ppb^2 . To remove the spatial (i.e., longitude,

elevation, and altitude) differences illustrated in Figure 5, the data are normalized by subtracting the a parameter value (i.e., the first term of Equation 1 as given in Table 2) derived for each individual data set; the resulting normalized data set is plotted in Figure S11. This spatial normalization removes the majority of the overall variance, leaving 50 ppb^2 . To remove the seasonal cycles from the normalized data set, the fourth and fifth terms of Equation 1 (calculated from the parameter values given in Table 2) are subtracted from each individual data set; this process gives deseasonalized, normalized data plotted as gray symbols in Figure 9.

The variance remaining in the deseasonalized, normalized data set is 18.5 ppb^2 . To reduce this variance further, 2-year averages of the deseasonalized, normalized data are plotted with their standard deviations in Figure 9. The 2-year averaging period is chosen to be as long as possible to minimize the variance associated with random variability, while still providing adequate temporal resolution to quantify long-term changes. The variance of these means (16.9 ppb^2) is not much reduced from the 18.5 ppb^2 variance of the monthly means, indicating that long-term changes dominate the variance of these 2-year means; thus, they provide a robust basis for quantifying the average long-term changes in baseline ozone.

A quadratic polynomial fit to the 2-year means (solid curve in Figure 9) yields parameters with high statistical precision and significance (Table 2): $\text{year}_{\text{max}} = 2005.7 \pm 2.5$ and $c = -0.018 \pm 0.006 \text{ ppb year}^{-2}$. The magnitudes of these results agree with the fits to the individual gray points plotted in Figure 9 and are generally consistent with the parameters derived from all of the individual data sets (Table 2). The root-mean-square deviation (RMSD) of the 2-year means about the fit is 1.42 ppb corresponding to a variance of 1.7 ppb^2 , which indicates that the quadratic fit captures 90% of the variance of the 2-year means.

Other fits to the long-term changes are possible. A linear fit to the 2-year means (dashed line in Figure 10) gives a significant positive slope of $+0.27 \pm 0.11 \text{ ppb year}^{-1}$, which quantifies the average baseline ozone

Figure 10. Time series of normalized, deseasonalized monthly mean data (gray points) from all eight data sets and 2-year means with standard deviations, as shown in Figure 9. The solid curve and dashed line (blue traces) are quadratic polynomial and linear regression fits, respectively, to the 2-year means. Linear fits to the means before and after 2000 are shown by the violet lines.

increase over the 40-year (1978–2017) record spanned by these data sets. The $r^2 = 0.62$ value indicates that the linear fit captures 62% of the variance of the means, compared to the 90% captured by the quadratic fit. This difference is reflected in a larger RMSD = 2.6 ppb of the means about the linear fit compared to 1.42 ppb for the quadratic fit. These differences indicate the significant nonlinear character of the long-term baseline ozone changes that are quantified by the quadratic polynomial fit. This nonlinear character can also be examined through two separate linear fits (Figure 10), which give a positive trend larger ($+0.60 \pm 0.23$ ppb year $^{-1}$) than the 40-year average trend before 2000 and a negative trend (-0.09 ± 0.08 ppb year $^{-1}$) after 2000. These two linear fits give an overall RMSD = 1.44 ppb, comparable to that of the quadratic fit (RMSD = 1.42 ppb).

3.4. Interior Continental Sites

The analysis in the preceding sections treats data sets representative of northern midlatitude baseline ozone. Data from interior continental sites provide contrasts that inform us regarding how continental influences affect long-term changes and seasonal cycles of ozone at regional scales, at least in areas outside of directly impacted urban areas. Here we examine long-term measurement records from two sites: Mt. Waliguan in central Asia and Whiteface Mtn. in eastern North America. These sites were identified as two of eight mountaintop sites in the Northern Hemisphere providing ozone observations largely representative of the lower free troposphere (Gaudel et al., 2018). The time series of monthly mean ozone from these sites is shown in Figure S12 in the same format as Figure 3. At the Asian site, ozone increased over the entire 23-year (1994–2016) data record, while over eastern North America ozone increased early in the record (1980 to the mid-1990s), followed by a decrease over the last two decades (mid-1990s to 2015).

The quantitative analysis of these two data sets proceeds in the same manner as for the baseline data sets; Figures S13–S16 present the results in generally the same format as earlier figures. The Fourier transform (Figure S13) shows that the seasonal cycle at each site is dominated by the fundamental, with small contributions from the second harmonic. The fits to the seasonal cycles (Figure S14) indicate that the fundamentals have similar amplitudes and phases (see Table 2) at the two sites, with maxima occurring in early to mid-June. The second harmonics have similar amplitudes but nearly opposite phases; the second harmonic contribution shifts the Whiteface Mtn. seasonal cycle peak to earlier in the year (May) while primarily reinforcing the Mt. Waliguan fundamental maximum to give a somewhat stronger mid-June seasonal peak. We cannot provide a firmly established cause of the different character of the second harmonics between these two sites. The seasonal cycle parameters derived for these two sites are generally similar to those derived for the baseline sites. Figure S15 shows that the altitude dependence of the fundamental amplitudes and phases agrees well at the European baseline and regional continental sites; the different behavior observed at the North American west coast (Trinidad Head sondes below ~2 km and Lassen NP) may reflect the transition from the marine to continental environment, a regime not represented in any of the other data sets. Figure S16 shows that the altitude dependence of the annual average ozone mixing ratios is within a few ppb of those found from the baseline data sets.

The comparison between these sites and the baseline sites demonstrates how continental influences can modify temporal ozone changes at regional scales. The continued increase in concentrations at the Asian site and the earlier end to the increase at the North American site demonstrate the influence of the contrasting anthropogenic emission trends over the different continents. Transport of air masses from continental source regions and mixing into the background troposphere determine the temporal trends of ozone concentrations over these sites and influence the baseline ozone concentration distribution farther

downwind. The differences between the interior continental sites and the baseline sites emphasize the importance of careful selection of the sites chosen for characterization of baseline ozone concentrations.

4. Discussion and Conclusions

Regression fits of Equation 1 to monthly mean ozone mixing ratios have quantified the average long-term changes and seasonal cycles of baseline ozone concentrations at northern midlatitudes. A small set of parameter values provides this quantification for each data set: a total of five values in the free troposphere and seven in the MBL (Table 2). The fits capture the large majority of the variance in the monthly means and provide the basis for investigating the degree of similarity in the temporal and spatial distribution of baseline ozone. The a parameter (i.e., annual average ozone mixing ratio in the year 2000) has a positive vertical gradient (Figure 5) that is strongest from the surface through the MBL; there is marked similarity (with some notable differences, particularly in the MBL) between the North American and European west coasts. Despite this similarity, the spatial variability of the annual average ozone mixing ratios accounts for nearly two thirds (65%) of the variance in the 2,563 total monthly means in the eight data sets. The seasonal cycle is quantified by the fundamental harmonic in the free troposphere (i.e., a sine function defined by its amplitude and phase) and two harmonics (the fundamental plus the second harmonic) in the MBL. Within both of these tropospheric layers, the seasonal cycle (Figures 6 and 7) exhibits little statistically significant difference (see parameter values in Table 2). The seasonal cycle accounts for nearly two thirds of the variance remaining after removing the spatial variance. After the seasonal variance is removed, only 13% of the total variance remains (i.e., 18.5 ppb^2), indicating that the spatial variability and zonally similar seasonal cycles dominate the variance of monthly mean baseline ozone at northern midlatitudes. The northern midlatitude zonal similarity found in this work is consistent with a recent analysis of the ozone observations from the remote troposphere collected during the global HIPPO and ATom airborne field missions (Bourgeois et al., 2020). This study found that the ozone distribution was similar in the extra tropics over the Atlantic and Pacific Oceans in both the Southern and Northern Hemispheres. Consistent with the hypothesis guiding this work, Bourgeois et al. (2020) attributed the similarity to the zonal circulation of baseline ozone.

The long-term change of baseline ozone is quantified by a fit of the second and third terms of Equation 1 and 2-year means of the normalized, deseasonalized monthly mean data from all sites (Figure 9), which gives values for the b and c parameters and year_{max} . This fit indicates that average baseline ozone concentrations at northern midlatitudes increased through the 1980s and 1990s, reached a maximum in $\text{year}_{\text{max}} = 2005.7 \pm 2.5$, and have since decreased. The parameter values from this overall fit are similar to the those derived from fits to the separate data sets (Figure 8 and Table 2). The RMSD of the 2-year means about the fit corresponds to a remaining variance of 1.7 ppb^2 (1.2% of the variance of the original monthly means), which indicates that the common long-term change in average baseline ozone concentrations described by the quadratic fit captures 90% of the variance of the 2-year means. Linear fits over two separate time intervals (Figure 10) also indicate that baseline ozone reached a maximum and has since decreased. However, the discontinuous first derivative implied by two straight line segments is not physically realistic, since it would imply an effectively instantaneous change in ozone sources, sinks, or transport throughout northern midlatitudes.

The zonal similarity found in this analysis suggests a simple conceptual picture to describe northern midlatitude ozone—a circulating river of air traverses all longitudes while receiving injections of ozone and photochemical precursors from all sources (including European, Asian, North American, and natural) and losing ozone to physical and chemical processes. The long lifetime of ozone compared to the circum-global transport time allows mixing of the influence of all sources and sinks so that a zonally similar, average ozone concentration is established on a time scale of weeks to months. However, as that river of air circulates, injection of ozone from sources is sporadic, loss of ozone occurs on varying time scales and at varying spatial locations, and air parcels are entrained from and exported to higher and lower latitudes, all of which results in local and regional, quasi-chaotic ozone variability superimposed on the average seasonal cycles and long-term change. The variance of the monthly data points about the quadratic fit to the 2-year means in Figure 10 is 13.6 ppb^2 . Thus, the zonal average long-term trend accounts for 27% of the variance (18.5 ppb^2) of the normalized, deseasonalized monthly mean data, with the remainder attributed to other

factors that contribute to ozone variability. A multitude of such factors can be suggested or identified from the literature; some of the more prominent include ozone measurement errors, systematic differences in the long-term trends and seasonal cycles between the eight data sets considered in this work, systematic decadal shifts in the seasonal cycle (e.g., Parrish et al., 2013), decadal climate variability (e.g., Lin et al., 2014), incomplete mixing of air masses from different continental regions into the circulating zonal air flow (e.g., the air masses from the interior continental boundary layer that are discussed in section 3.4 and the downwind influence of Asian emissions as suggested by Lin et al., 2017), and sporadic events such as wildfires (Lin et al., 2017) and heatwaves and drought (Lin et al., 2020). Importantly, averaging the monthly means over 2-year periods greatly reduces this unexplained, chaotic variance by 87% (13.6 to 1.7 ppb²), as discussed above.

The quadratic fit illustrated in Figures 9 and 10 suggests that baseline ozone concentrations have been decreasing at an accelerating rate since a maximum occurred in 2005.7 ± 2.5 . Polynomial fits with additional terms indicate that no higher order terms make statistically significant contributions to the quantification of the long-term changes. However, a fit to a polynomial with the addition of a cubic term gives a coefficient of 0.0002 ± 0.0006 ppb year⁻³ for that term; this positive cubic coefficient indicates that the acceleration of the decrease is likely (~75% probability) slowing. It is important to note that extrapolation of any polynomial fit outside of the range of available data is unreliable, as the polynomial diverges at positive and negative times. Without a firm understanding of the causes of the observed long-term changes, future baseline ozone changes cannot be predicted, at least by extrapolation of the fits derived in this work.

Earlier studies documented a decades long increase of baseline tropospheric ozone at northern midlatitudes that reached a maximum, followed by relatively constant or decreasing concentrations. Derwent et al. (2007) analyzed ozone mixing at Mace Head Ireland and found that ozone concentrations rose steadily during the 1980s and 1990s but showed evidence of decline and stabilization during the 2000s. A revised and updated analysis with 10 additional years of data (Derwent et al., 2018) confirmed that this rate of increase slowed to the extent that levels remained relatively constant through the 2000s and started to decline in 2010s. Logan et al. (2012) constructed a mean time series using data from the same three European alpine sites considered in this study and concluded that ozone increased by 6.5 to 10 ppb in the 1978–1989 period and 2.5 to 4.5 ppb in the 1990s. Based on these surface measurements plus sonde and MOZAIC data sets, they further concluded that ozone slowly decreased after 1998, with an annual mean trend of approximately -0.15 ppb year⁻¹ at ~3 km. As part of the work of the Task Force on Hemispheric Transport of Air Pollution (HTAP), Parrish et al. (2012, 2014) analyzed a wider range of 11 baseline representative ozone data sets in Europe, North America, and Asia that spanned six decades (1950 to 2010). They concluded that baseline ozone increased by a factor of ~2 from 1950 to 2000, but that rate slowed at all sites during the 2000s and began decreasing over Europe. A recent reassessment of historical European rural surface ozone observations concluded that there was no evidence of a change between the late 19th century and the 1970s, followed by an increase of 12 to 16 ppb afterward (Tarasick et al., 2019). That increase is consistent with the total increase shown over the 1978 to 2006 period in Figures 9 and 10. Petetin et al. (2016) investigated annual trends above Frankfurt using the MOZAIC aircraft measurements; they found no significant changes over the 1994–2012 period, except in winter with a slightly significant increase. Since the period covered in their analysis is approximately centered on the year of the baseline ozone maximum found in the present work, the lack of a significant trend is consistent with the present findings. More recently, Parrish et al. (2017) examined three baseline data sets at the west coast of North America and found that ozone increased prior to 2000 but that rate of increase slowed and reversed in all seasons in later years. The results of the present study are in quantitative accord with the results of these earlier published studies, but it should be noted that many of the same data sets are considered in all of the studies.

Despite the agreement between these earlier studies and the present results, a recent study reached contrasting conclusions. Gaudel et al. (2018) provided a global analysis (not just northern midlatitudes as in the present work and in the studies discussed above), focused on the period from the mid-1970s through ~2015, and considered results reported from all measurement techniques. At northern midlatitudes they derived ozone trends that varied both spatially and seasonally over North America and Europe, precluding any generalized statement regarding zonal ozone trends. However, Gaudel et al. (2018) did not limit their analysis to baseline representative data sets (e.g., they included the Mt. Waliguan and Whiteface Mtn. data

shown in Figure S12 and discussed in section 3.4), included records of considerably shorter temporal coverage, and most importantly, their analysis approach did not attempt to quantify the changing slopes of long-term ozone changes that have occurred over recent decades. The present analysis and the results of earlier studies (Derwent et al., 2007, 2018; Logan et al., 2012; Parrish et al., 2012, 2004, 2017) demonstrate that the long-term change of baseline ozone at northern midlatitudes is strongly nonlinear, so accurate quantification requires analysis techniques capable of quantifying nonlinear changes. The analysis utilized in this study is based on a fit to a power series that can quantify nonlinear changes (see discussion of Equation 1 in section 2.3). Text S1 further discusses the importance of utilizing nonlinear analysis and compares linear and nonlinear analysis approaches for three example ozone time series. These differences in analysis approach account for the different conclusions between those of Gaudel et al. (2018) and the present work.

The causes of the long-term zonal baseline ozone change have not been firmly established. Simulations of historical baseline ozone concentration changes do not agree well between models (e.g., figure 9 of Turnock et al., 2020) or with observational-based analysis (e.g., Parrish et al., 2014). There is qualitative agreement between observed ozone changes and estimated changes in ozone precursor emissions, which are believed to have increased through the 20th century, followed by more recent decreases, but it has not been possible to make direct quantitative connections (Logan et al., 2012; Parrish et al., 2014). There is also analysis suggesting that stratosphere-to-troposphere transport may have changed over the time period (Trickl et al., 2020). Some recent studies have suggested significant contributions from particular factors over specific regions (e.g., increasing baseline ozone over western North America in spring from increasing Asian precursor emissions, Lin et al., 2017, and vegetation feedbacks during drought over Europe, Lin et al., 2020), but a quantitative explanation of the zonally similar long-term change quantified here is not yet available.

Some shortcomings have been identified in past global model ozone simulations through model-measurement comparisons. For example, model results were consistently biased, usually high in the Northern Hemisphere and low in the Southern Hemisphere (Young et al., 2018). Some example simulations underestimated the 1950 to 2000 increase of northern midlatitude baseline ozone by a factor of ~ 2 (Parrish et al., 2014; Staehelin et al., 2017). The ozone seasonal cycle in the MBL and into the free troposphere was poorly reproduced in many respects, including failure to reproduce the abrupt changes at the top of the MBL shown in Figure 7. Models also failed to reproduce the interhemispheric differences in annual average ozone between Mace Head and the U.S. MBL sites (Derwent et al., 2016, 2018; Parrish et al., 2016, and Figure 5). When model results fail to reproduce observations, the nature of the disagreement may be able to guide future model development. The zonal similarities in long-term changes and seasonal cycles quantified in this work give additional comparison opportunities that may provide such guidance. An example inconsistency that could be particularly illuminating to investigate is between model simulations indicating baseline ozone concentrations over western North America continued to increase in spring until at least 2014 (Lin et al., 2017) while observations indicate that the increase ended in the mid-2000s (Parrish et al., 2017, and this work).

Decreasing baseline ozone concentrations at northern midlatitudes is encouraging from the perspective of the contributions that baseline ozone makes to urban and regional air pollution. It has been recognized that increasing baseline ozone concentrations makes the achievement of ozone air quality goals more difficult in the United States (Jacob et al., 1999) and Europe (Bach et al., 2014). Similarly, the presently decreasing baseline ozone concentrations now ease the achievement of ozone air quality goals in northern midlatitude regions. The greatest potential for further decreasing baseline ozone concentrations lies in reducing emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOC) on a hemispheric scale (Bach et al., 2014); the baseline ozone decrease quantified in this work may indicate the success of this approach, as the total global annual NO_x emissions stopped increasing in about 2013 (Huang et al., 2017).

A final implication of this work is that observational quantification of long-term baseline ozone changes at latitudes dominated by zonal flow, such as the northern midlatitudes discussed in this work, may be less difficult than generally recognized. Only a limited number of long-term measurement sites may be required in midlatitude regions to accurately quantify the temporal and spatial variability of the zonal baseline ozone distribution.

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