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Recent tropospheric ozone changes – A pattern dominated by slow or no growth

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HIGHLIGHTS

- O_3 at mid-latitudes of the N.H. is flat or declining in the last 10–15 years.
- O_3 in S.H. subtropics and mid-latitudes increased earlier but has leveled off.
- 15-year moving trends reveal changes in both high and low O3 concentrations.
- Precursor (NO_x) reductions in Europe and N.A. likely contribute to O_3 decline.

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ABSTRACT

Longer-term (i.e., 20–40 years) tropospheric ozone (O_3) time series obtained from surface and ozonesonde observations have been analyzed to assess possible changes with time through 2010. The time series have been selected to reflect relatively broad geographic regions and where possible minimize local scale influences, generally avoiding sites close to larger urban areas. Several approaches have been used to describe the changes with time, including application of a time series model, running 15-year trends, and changes in the distribution by month in the O_3 mixing ratio. Changes have been investigated utilizing monthly averages, as well as exposure metrics that focus on specific parts of the distribution of hourly average concentrations (e.g., low-, mid-, and high-level concentration ranges). Many of the longer time series (~30 years) in mid-latitudes of the Northern Hemisphere, including those in Japan, show a pattern of significant increase in the earlier portion of the record, with a flattening over the last 10–15 years. It is uncertain if the flattening of the O_3 change over Japan reflects the impact of O_3 transported from continental East Asia in light of reported O_3 increases in China. In the Canadian Arctic, declines from the beginning of the ozonesonde record in 1980 have mostly rebounded with little overall change over the period of record. The limited data in the tropical Pacific suggest very little change over the entire record. In the southern hemisphere subtropics and mid-latitudes, the significant increase observed in the early part of the record has leveled off in the most recent decade. At the South Pole, a decline observed during the first half of the 35-year record has reversed, and O_3 has recovered to levels similar to the beginning of the record. Our understanding of the causes of the longer-term changes is limited, although it appears that in the mid-latitudes of the northern hemisphere, controls on O_3 precursors have likely been a factor in the leveling off or decline from earlier O_3 increases.

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1. Introduction

Recently, particular attention has focused on tropospheric ozone (O_3) as a climate forcing constituent (Shindell et al., 2012) and as an impediment to attainment of air quality standards (McDonald-Buller et al., 2011). In addition tropospheric O_3 plays a key role in the oxidative chemistry of the atmosphere through its participation in the production of the hydroxyl radical (Levy, 1971). A recent report (HTAP, 2010) has reemphasized the importance of the long-range transport of pollution-produced O_3 to the hemispheric O_3 background concentration. Two workshops (Logan et al., 2010; Schultz et al., 2011) have emphasized the need for a more systematic assessment of tropospheric O_3 changes. Several publications have presented results on O_3 changes in Europe and mid-latitudes of the Northern Hemisphere (N.H.) (Logan et al., 2012; Parrish et al., 2012) as well as broader regional changes (Oltmans et al., 1998, 2006; Vingarzan, 2004). Oltmans et al. (2006) noted that continental Europe and Japan showed significant increases in the 1970s and 1980s but that tropospheric O_3 amounts appeared to have leveled off or in some cases declined in the more recent decades. Logan et al. (2012) described the decrease in O_3 over Europe since 1998, with the largest decrease during the summertime. Using Zugspitze data for 1978–1989 and the mean time series from three Alpine stations since 1990, Logan et al. (2012) found that the O_3 increased substantially in 1978–1989 (i.e., 6.5–10 ppb but began to exhibit a reduced rate of increase in the 1990s (i.e., 2.5–4.5 ppb) with decreases in the 2000s (i.e., 4 ppb) in summer with no significant changes in other seasons. Overall in summer no trend was noted for the 1990–2009 period.

This work updates through 2010 the temporal trends at background O_3 monitoring sites around the world in both the Northern and Southern Hemispheres. Background O_3 is defined differently by various researchers (McDonald-Buller et al., 2011). Zhang et al. (2011), using a model, estimated background by eliminating precursor sources in North America. Here it is used in a more general way to describe conditions where local or identifiable regional sources are not prominent or have been excluded. An example is the use of downslope (nighttime) observations at Izana and Mauna Loa as representative of free tropospheric O_3 at the altitude of the station. In addition, characteristic trends are investigated at sites that are not necessarily considered to be background O_3 monitoring sites (e.g., Whiteface Mountain, New York and several US National Park locations) but are in key locations that have particularly long, continuous records. A number of representative ozonesonde locations that have long records provide key information on tropospheric O_3 changes above the boundary layer. These sites extend the time period of tropospheric O_3 observations and provide information on the representativeness of the surface trends for lower tropospheric O_3 changes in general. The earliest ozonesonde records date from the late 1960s or early 1970s, while a number of other sites begin in the 1980s. In addition to length of record, the ozonesonde locations have been chosen for broad representativeness of a region. As with surface locations, a selection of sites is chosen rather than a comprehensive analysis of every available location. This work represents an extension and update of earlier studies (Oltmans et al., 1998, 2006) that also focused on providing a broad geographic perspective on O_3 changes.

Information on the pattern of changes is provided by the distribution of hourly average concentrations as higher hourly average O_3 concentrations are reduced as a result of lowering NO_x emissions. Lefohn et al. (1998) noted that as O_3 levels improved (i.e., the environment experienced lower O_3 exposures) due to reduced emissions, reductions in the number of high hourly average concentrations, as well in the number of low hourly average

Table 1
Location of surface and ozonesonde stations.

Station	Lat.	Lon.	Elev (m)	Period	Type
Resolute, NWT, Canada	74.7N	95.0W	64	1981–2010	Ozonesonde
Barrow, Alaska, USA	71.1N	156.6W	11	1973–2010	Surface
Denali NP, Alaska, USA	63.7N	149.0W	661	1987–2010	Surface
Churchill, Manitoba, Canada	58.8N	94.1W	35	1981–2010	Ozonesonde
Edmonton, Alberta, Canada	53.6N	114.1W	766	1981–2010	Ozonesonde
Goose, Newfndlnd, Canada	53.3N	60.3W	44	1979–2010	Ozonesonde
Mace Head, Ireland	53.2N	9.54W	25	1988–2010	Surface
Glacier NP, Montana, USA	48.5N	114.0W	976	1989–2010	Surface
Hohenpeissenberg, Germany	47.8N	11.0E	975	1966–2010	Ozonesonde
Zugspitze, Germany	47.4N	11.0E	2962	1978–2010	Surface
Whiteface Mtn., NY, USA	44.4N	73.9W	1484	1973–2010	Surface
Sapporo, Japan	43.1N	141.3E	19	1967–2010	Ozonesonde
Lassen NP, Calif., USA	40.5N	121.6W	1756	1987–2010	Surface
Boulder, Colorado, USA	40.0N	105.0W	1745	1985–2010	Ozonesonde
Rocky Mtn., NP, CO, USA	40.3N	105.6W	2743	1989–2010	Surface
Pinedale, Wyoming, USA	42.9N	109.8W	2388	1989–2010	Surface
Ryori, Japan	39.0N	141.8E	260	1991–2010	Surface
Wallops Isl., Virginia, USA	37.9N	75.5E	13	1971–2010	Ozonesonde
Tsukuba (Tateno), Japan	36.1N	140.1E	31	1968–2010	Ozonesonde
Tudor Hill, Bermuda	32.3N	64.9W	30	1988–2010	Surface
Izaña, Tenerife, Spain	28.3N	16.5W	2800	1988–2010	Surface
Naha, Japan	26.2N	127.7E	27	1989–2010	Ozonesonde
Minamitorishima, Japan	24.3N	154.0E	8	1994–2010	Surface
Hilo, Hawaii, USA	19.7N	155.1W	11	1982–2010	Ozonesonde
Mauna Loa, Hawaii, USA	19.5N	155.6W	3397	1973–2010	Surface
Matatula Pt., Am. Samoa	14.3S	170.6W	82	1976–2010	Surface
Pago Pago, American Samoa	14.5S	170.5W	10	1995–2010	Ozonesonde
Cape Point, South Africa	34.4S	18.5E	230	1983–2010	Surface
Cape Grim, Australia	40.7S	144.7E	104	1982–2010	Surface
Baring Head, New Zealand	41.4S	174.9E	85	1991–2010	Surface
Lauder, New Zealand	45.0S	169.7E	370	1986–2010	Ozonesonde
Syowa, Antarctica	69.0S	39.6E	21	1966–2010	Ozonesonde
South Pole, Antarctica	90.0S	–	2840	1975–2010	Surface
				1986–2010	Ozonesonde

concentrations occurred. The reduction in the number of low hourly average O_3 concentrations was associated with lack of NO_x scavenging (US EPA, 1996). Lefohn et al. (1998) noted that as the site air quality improved, the distribution of the hourly average concentrations appeared to move from both the high end as well as the low end of the distribution toward the center (i.e., 30–60 ppb). In our analysis of the O_3 time series, we use a number of techniques, some of which were employed in previous research efforts (Oltmans et al., 2006; Lefohn et al., 2008; Oltmans et al., 2008; Lefohn et al., 2010). Using the monthly average concentrations, a linear regression that simultaneously estimates contributions for seasonality and various types of temporal trend is used. An autoregressive time series model (Harris et al., 2001) is applied to each site evaluating the changes in monthly average concentrations to estimate O_3 temporal trends at individual sites. In addition, changes in the peak, mid-level (50–99 ppb), and low hourly average O_3 values (<50 ppb) were investigated using two exposure metrics and the quantification of the monthly changes in the distribution of hourly average concentrations. We have characterized the trends in the distribution of the hourly average mixing ratios in intervals to better understand the changes in interval frequency over time. With a lifetime of 10–30 days, the local tropospheric O_3 signal will include a hemispheric component. Superimposed on this signal will be distinct regional characteristics resulting from O_3 precursor emissions and variations in long-range transport (including stratospheric exchange). The analysis presented in this study characterizes O_3 changes within various geographic regions as a way of organizing the presentation of the changes. The characterization of changes in the frequency of high-, mid-, and low-level hourly average concentrations over time provides investigators with quantitative information for assessing possible physical processes associated with observed changes.

2. Tropospheric ozone time series

2.1. Data sets

The O_3 time series sites considered here are listed in Table 1 with relevant information on the location, altitude, and length of the record. The data have been gleaned from a number of sources, including the World Data Centre for Greenhouse Gases (WDCGG), the World Ozone and Ultraviolet Radiation Data Centre (WOUDC), and the US EPA Air Quality System (AQS) data base. A number of the data sets have been updated through 2010 by authors participating in this study. Data quality control has been carried out by the institution responsible for managing the measurement program at the individual locations. A number of the surface and ozonesonde sites are World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) locations and follow measurement procedures consistent with their recommendations (Smit et al., 2007; Galbally and Schultz, submitted for publication). However, detailed methodological records, including a history of changes, are not widely available. The national air quality data measurements follow procedures established by national agencies, such as the US EPA. The uniformity of the procedures and the homogeneity of the time series are not, however, assured over the multi-decade series considered here. For many of the time series used in this study, the participating authors have provided additional information on the time series characteristics so that these data are at a quality level deemed appropriate for the analysis carried out here.

2.2. Analysis approaches

Ozone changes are considered over several time periods to assess the way such changes have evolved over time and to place the most recent time period (15–20 years) in perspective. The longest ozonesonde records considered here go back at least 40 years, while several of the surface records are over 35 years in length. For the three long ozonesonde records (Hohenpeissenberg, Wallops Island, and Tsukuba), the record is analyzed over 40 years. For the surface O_3 series with records between 32 and 35 years, the entire record has been used. Where the time series are at least 30 years in length, trends for periods of 30 and 20 years are considered. The uniform periods of 30 years and 20 years allow comparison of the changes among the sites as well as assessment of recent changes provided by running 15-year trends of the W126 metric (Lefohn and Runeckles, 1987; Lefohn et al., 1988). The W126 index accumulates the weighted hourly average concentration over the entire distribution for a specified period, with the result that the middle and upper portions of the distribution are accentuated (Fig. 1a). An additional exposure metric, the W_Low, has been developed for this analysis to assess changes in the lower mixing ratio range (i.e., <50 ppb) that may be associated with reductions in anthropogenic emissions. Unlike the W126 metric, the W_Low metric places greater weight on the lower portion of the distribution (Fig. 1b). In this analysis, the focus is on whether increasing or decreasing trends are observed in the W_Low index. An increase in the W_Low index implies that the frequency of hourly average concentrations is increasing at the lower hourly average mixing ratios (i.e., <50 ppb), while a decrease in W_Low index implies that the frequency of hourly average concentrations in the low end is decreasing, with the result that the concentrations are shifting from the low to the mid-level range. As a confirmation that the W_Low index is characterizing the shifts properly, the change in the hourly

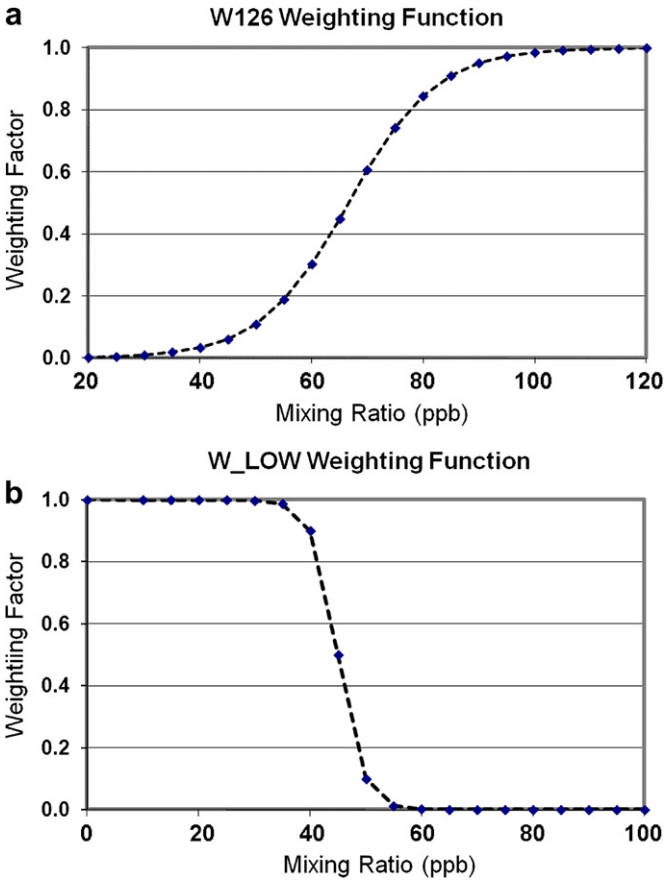

Fig. 1. Form of the weighting function for computing the 24-h (a) W126 and (b) W_Low exposure metrics for each month from the hourly average O_3 mixing ratios.

average mixing ratios using 10 ppb intervals is characterized over the period of record. This information is used to identify statistically significant trends for each month by characterizing the changes in frequency within each of the 10 ppb increments (i.e., bin) of the distribution. For both the W126 and W_Low metrics, the accumulation is performed over a 24-h period.

2.3. Trend computation

Several approaches were used to determine the changes with time in the O_3 time series. These methods have been described in detail in earlier publications (Oltmans et al., 2006; Lefohn et al., 2010) but are briefly summarized here. The data from each location are treated as individual time series because we are looking for a pattern across monitoring sites within a specific region to investigate whether similar patterns of change exist within a region. Therefore, the data from multiple sites are not combined. The time series is not considered to be a continuous series when multiple consecutive years are missing. Varying data capture criteria were used depending on the analysis approach. These are noted below in describing the results from the various analyses.

Using monthly average concentrations, the overall O_3 trend is computed in a two-step process (Harris et al., 2001). Monthly values at sites with a very small diurnal variation, observed at some island and higher-altitude locations, are constructed from daily 24-h averages. For continental boundary layer locations, where urban nighttime loss is significant and in some cases daytime regional enhancements are present, an 8-h daytime average (1100–1800 LST) is used. For Mauna Loa, Hawaii and Izaña (Canary Islands), where a significant mountain wind regime prevails, the nighttime (0000–0800 LST) downslope data are taken as most representative of the troposphere at the altitude of the station. The O_3 profile data are averaged into several layers in the troposphere; Surface-850 hPa, 850–700 hPa, 700–500 hPa, and 500–300 hPa (approximately Sfc-1.5 km, 1.5–3 km, 3–6 km, and 6–9 km).

The first step of the trend calculation uses an auto-regressive model that incorporates explanatory variables and a cubic polynomial fit rather than a straight line for better representation of the long-term variations. The explanatory variables include a seasonal component, 500 hPa and 100 hPa temperatures, QBO and ENSO indices. The model accounts for serial correlation in the O_3 data and minimizes the residual variance of the model fit by regressing to known sources of O_3 variability noted above. The second step determines the O_3 tendency (trend line) and growth rate curves (Harris et al., 2001). A bootstrap method (Harris et al., 2001) produces 100 statistical realizations of the population from which the original data were drawn by combining the tendency curve with randomly selected residuals from the curve according to month (Harris et al., 2001). The growth rate curve is obtained by numerical differentiation of the tendency curve with the 95% confidence limits determined using the standard deviation of the growth rate curves from the 100 bootstrap samples. The average O_3 growth rate, which is the average of the monthly values on the growth rate curve, is a measure of the overall change. Seasonal changes are examined by comparing the decadal seasonal variation for three periods: 2001–2010, 1991–2000 and 1981–1990. For the time series with the longest records that go back into the early 1970s, the segment from the beginning of the record (or 1971 if the record begins earlier than 1971) to 1980 was also considered.

The Theil estimate (Hollander and Wolfe, 1999) was used to estimate the trend slope for the running 15-year trends for the W126, W_Low. The Theil estimate is a non-parametric estimator that is numerically identical to the ordinary least squares (OLS) slope estimate when the OLS model assumptions are satisfied. The Theil estimate is determined as the median of slope estimates calculated as the slope of the line passing through paired points for all point pairs in the data set of interest. To test for statistical significance, Kendall's tau test (Lefohn and Shadwick, 1991; Hollander and Wolfe, 1999) was used to determine significance at the 10% level. Because the tail probability of the distribution can change abruptly from year to year, the significance level of 0.10 was selected to reflect the degree of variability for the Kendall's τ statistic over the range of years in the time series. The W126 and W_Low metrics were adjusted for missing values as follows: (1) the monthly value of each metric was calculated if at least 75% of the hourly data were available for a specific month (a corrected monthly cumulative metric was calculated as the uncorrected monthly cumulative metric divided by the fractional data capture), and (2) if a month with less than 75% data capture had the two adjacent months each having at least 75% data capture (a corrected monthly cumulative metric with less than 75% data capture was calculated as the arithmetic mean of the corrected monthly cumulative metrics for the two adjacent months). There was no restriction on the number of such interpolations during a specific year. If all of the months contained within a year or season had valid

Table 2
Surface ozone trends in %/decade and ppbv/year for three time periods: Full record, 1981–2010, and 1991–2010 (±1 Standard Error).

Station	Full record (first year)-2010			1981–2010		1991–2010	
	1st Year	%/dec	ppb yr^{-1}	%/dec	ppb yr^{-1}	%/dec	ppb yr^{-1}
Barrow	(1973)	3.50 ± 1.04	0.09 ± 0.03	1.28 ± 1.20	0.03 ± 0.03	5.00 ± 2.00	0.13 ± 0.05
Denali NP	(1987)	1.09 ± 1.19	0.04 ± 0.04			4.69 ± 1.49	0.15 ± 0.05
Mace Head	(1988)	2.47 ± 1.18	0.09 ± 0.04			0.33 ± 1.28	0.01 ± 0.05
Glacier NP	(1989)	−2.76 ± 1.19	−0.07 ± 0.05			2.79 ± 1.63	−0.07 ± 0.04
Zugspitze	(1978)	8.10 ± 0.58	0.39 ± 0.03	2.76 ± 0.67	0.14 ± 0.03	0.94 ± 0.82	0.05 ± 0.04
Whiteface	(1973)	2.10 ± 0.84	0.09 ± 0.03	1.80 ± 0.92	0.07 ± 0.04	−5.32 ± 1.43	−0.22 ± 0.06
Lassen	(1987)	4.43 ± 1.16	0.19 ± 0.05			3.01 ± 1.15	0.13 ± 0.05
RMNP	(1987)	4.70 ± 0.93	0.22 ± 0.04			6.69 ± 1.01	0.33 ± 0.05
Pinedale	(1989)	1.87 ± 0.78	0.09 ± 0.04			−0.95 ± 0.86	−0.05 ± 0.04
Ryori	(1991)	5.44 ± 10.9	0.22 ± 0.45			5.44 ± 1.09	0.22 ± 0.45
Izana	(1987)	1.98 ± 0.92	0.09 ± 0.04			3.11 ± 1.05	0.14 ± 0.05
Minamitorishima	(1994)	−10.3 ± 2.54	−0.29 ± 0.07				
Mauna Loa	(1974)	3.79 ± 0.94	0.16 ± 0.04	3.34 ± 1.00	0.14 ± 0.04	7.18 ± 1.69	0.31 ± 0.07
Samoa	(1976)	0.73 ± 1.41	0.01 ± 0.02	3.48 ± 1.81	0.05 ± 0.02	1.20 ± 2.50	0.02 ± 0.34
Cape Point	(1983)	5.70 ± 0.50	0.13 ± 0.01			7.29 ± 0.67	0.17 ± 0.02
Cape Grim	(1982)	2.51 ± 0.55	0.06 ± 0.01			3.44 ± 0.67	0.09 ± 0.02
Baring Head	(1991)	0.51 ± 1.22	0.01 ± 0.03			0.51 ± 1.22	0.01 ± 0.03
South Pole	(1975)	0.18 ± 0.54	0.01 ± 0.02	−0.22 ± 0.74	−0.01 ± 0.21	7.07 ± 0.83	0.20 ± 0.02

Table 3
Ozonesonde layer trends %/decade and ppbv/year for three time periods (±1 Standard Error). Layer 1 = Surface-850 hPa, Layer 2 = 850–700 hPa, Layer 3 = 700–500 hPa, Layer 4 = 500–300 hPa.

Station	Full record (1st year or 1971)–2010			1981–2010		1991–2010	
	1st Year	%/dec	ppb yr^{-1}	%/dec	ppb yr^{-1}	%/dec	ppb yr^{-1}
Resolute	(1981)						
1.		−2.98 ± 1.96	−0.09 ± 0.06	−2.98 ± 1.96	−0.09 ± 0.06	6.69 ± 2.75	0.21 ± 0.08
2.		0.81 ± 1.57	0.03 ± 0.06	0.81 ± 1.57	0.03 ± 0.06	9.62 ± 2.08	0.39 ± 0.09
3.		−0.07 ± 1.35	−0.00 ± 0.07	−0.07 ± 1.35	−0.00 ± 0.07	8.11 ± 1.90	0.40 ± 0.09
4.		0.10 ± 2.64	0.00 ± 0.21	0.10 ± 2.64	0.00 ± 0.21	15.00 ± 4.13	1.17 ± 0.32
Churchill	(1981)						
1.		−5.34 ± 1.18	−0.18 ± 0.04	−5.34 ± 1.18	−0.18 ± 0.04	2.82 ± 1.96	0.09 ± 0.06
2.		−2.83 ± 1.08	−0.12 ± 0.05	−2.83 ± 1.08	−0.12 ± 0.05	2.25 ± 1.85	0.10 ± 0.08
3.		−1.21 ± 1.03	−0.06 ± 0.05	−1.21 ± 1.03	−0.06 ± 0.05	5.96 ± 1.47	0.31 ± 0.08
4.		−0.72 ± 2.14	−0.05 ± 0.15	−0.72 ± 2.14	−0.05 ± 0.15	7.73 ± 2.81	0.55 ± 0.20
Edmonton	(1981)						
1.		−1.63 ± 1.80	−0.05 ± 0.05	−1.63 ± 1.80	−0.05 ± 0.05	0.57 ± 2.57	0.02 ± 0.08
2.		3.04 ± 1.11	0.13 ± 0.05	3.04 ± 1.11	0.13 ± 0.05	7.55 ± 1.50	0.31 ± 0.06
3.		2.65 ± 1.06	0.13 ± 0.05	2.65 ± 1.06	0.13 ± 0.05	9.01 ± 1.28	0.45 ± 0.06
4.		3.44 ± 1.65	0.21 ± 0.10	3.44 ± 1.65	0.21 ± 0.10	11.05 ± 2.11	0.69 ± 0.13
Goose Bay	(1981)						
1.		1.18 ± 1.58	0.04 ± 0.05	1.18 ± 1.58	0.04 ± 0.05	10.17 ± 2.02	0.32 ± 0.06
2.		1.29 ± 1.33	0.05 ± 0.06	1.29 ± 1.33	0.05 ± 0.06	9.66 ± 1/84	0.40 ± 0.08
3.		1.90 ± 1.09	0.10 ± 0.06	1.90 ± 1.09	0.10 ± 0.06	10.01 ± 1.48	0.51 ± 0.08
4.		1.95 ± 2.04	0.14 ± 0.14	1.95 ± 2.04	0.14 ± 0.14	9.63 ± 2/24	0.68 ± 0.16
Hohenpeissenberg	(1971)						
1.		4.41 ± 0.96	0.15 ± 0.03	0.51 ± 1.04	0.02 ± 0.04	1.35 ± 1.53	0.05 ± 0.05
2.		3.63 ± 0.77	0.16 ± 0.03	−1.31 ± 0.85	−0.06 ± 0.04	−2.96 ± 1.13	−0.14 ± 0.05
3.		4.87 ± 0.60	0.26 ± 0.03	−0.29 ± 0.68	−0.02 ± 0.04	−0.20 ± 0.92	−0.01 ± 0.05
4.		5.36 ± 0.77	0.34 ± 0.05	0.53 ± 0.91	0.04 ± 0.06	1.59 ± 1.43	0.10 ± 0.09
Sapporo	(1971)						
1.		11.13 ± 1.57	0.35 ± 0.05	18.77 ± 1.84	0.63 ± 0.06	4.38 ± 2.17	0.15 ± 0.07
2.		5.34 ± 1.14	0.23 ± 0.05	10.69 ± 1.29	0.48 ± 0.06	−0.39 ± 1/38	−0.02 ± 0.06
3.		4.35 ± 0.98	0.23 ± 0.05	7.04 ± 1.11	0.38 ± 0.06	1.20 ± 1.26	0.07 ± 0.07
4.		2.35 ± 1.50	0.16 ± 0.10	1.45 ± 1.49	0.10 ± 0.10	−0.46 ± 2.05	−0.03 ± 0.14
Boulder	(1979)						
2.		−7.02 ± 1.38	−0.35 ± 0.07	−4.79 ± 1.37	−0.24 ± 0.07	3.85 ± 1.69	0.19 ± 0.08
3.		−8.14 ± 1.00	−0.46 ± 0.06	−6.43 ± 0.92	−0.36 ± 0.05	1.12 ± 1.11	0.06 ± 0.06
4.		−11.74 ± 1.59	−0.72 ± 0.10	−6.34 ± 1.44	−0.38 ± 0.09	1.98 ± 2.15	0.12 ± 0.13
Wallops Is	(1971)						
1.		3.51 ± 1.42	0.16 ± 0.06	0.43 ± 1.79	0.02 ± 0.08	5.97 ± 2.35	0.27 ± 0.11
2.		1.55 ± 0.99	0.08 ± 0.05	0.18 ± 1.18	0.01 ± 0.06	6.02 ± 1.37	0.33 ± 0.07
3.		1.55 ± 0.81	0.09 ± 0.05	0.16 ± 1.12	0.01 ± 0.07	4.62 ± 1.24	0.27 ± 0.07
4.		−0.06 ± 1.28	−0.00 ± 0.09	3.05 ± 1.44	0.20 ± 0.10	1.28 ± 2.37	0.09 ± 0.16
Tsukuba	(1971)						
1.		1.75 ± 1.41	0.08 ± 0.07	4.78 ± 2.27	0.23 ± 0.11	2.01 ± 3.13	0.09 ± 0.15
2.		3.28 ± 1.11	0.16 ± 0.06	4.25 ± 1.55	0.21 ± 0.08	1.83 ± 2.30	0.09 ± 0.12
3.		3.00 ± 0.97	0.16 ± 0.05	4.19 ± 1.26	0.23 ± 0.07	3.86 ± 1.77	0.21 ± 0.10
4.		5.35 ± 1.48	0.34 ± 0.10	6.34 ± 2.06	0.41 ± 0.13	8.23 ± 5.37	0.92 ± 0.56
Naha	(1991)						
1.		5.27 ± 2.98	0.17 ± 0.10			5.27 ± 2.98	0.17 ± 0.10
2.		2.46 ± 2.55	0.09 ± 0.10			2.46 ± 2.55	0.09 ± 0.10
3.		4.50 ± 2.23	0.21 ± 0.10			4.50 ± 2.23	0.21 ± 0.10
4.		3.91 ± 1.94	0.22 ± 0.11			3.91 ± 1.94	0.22 ± 0.11
Hilo	(1982)						
1.		−1.46 ± 2.97	−0.38 ± 0.08			9.74 ± 3.65	0.25 ± 0.09
2.		1.03 ± 2.19	0.04 ± 0.08			4.09 ± 2.98	0.15 ± 0.11
3.		2.38 ± 1.65	0.11 ± 0.08			3.06 ± 2.50	0.14 ± 0.12
4.		1.91 ± 1.70	0.09 ± 0.08			1.00 ± 2.70	0.05 ± 0.13
Lauder	(1986)						
1.		6.70 ± 1.17	0.15 ± 0.03			5.11 ± 1.56	0.12 ± 0.04
2.		4.67 ± 1.04	0.14 ± 0.03			3.43 ± 1.14	0.10 ± 0.03
3.		4.46 ± 1.06	0.16 ± 0.04			5.34 ± 1.16	0.20 ± 0.04
4.		1.39 ± 1.36	0.06 ± 0.06			2.58 ± 1.43	0.12 ± 0.07
Syowa	(1971)						
1.		6.83 ± 1.33	0.15 ± 0.03	4.67 ± 1.22	0.10 ± 0.03	1.04 ± 1.55	0.02 ± 0.04
2.		2.33 ± 1.11	0.06 ± 0.03	1.10 ± 1.18	0.03 ± 0.03	2.32 ± 1.38	0.06 ± 0.03
3.		1.94 ± 0.80	0.05 ± 0.02	0.32 ± 1.24	0.01 ± 0.03	4.12 ± 1.46	0.12 ± 0.04
4.		−2.50 ± 1.26	−0.10 ± 0.05	−1.72 ± 1.77	−0.07 ± 0.07	4.50 ± 2.09	0.18 ± 0.08
South Pole	(1986)						
3.		1.93 ± 0.79	0.05 ± 0.02			2.91 ± 0.92	0.08 ± 0.03
4.		3.02 ± 1.72	0.12 ± 0.07			2.29 ± 2.32	0.09 ± 0.09

estimates (by the method described above) of the corrected monthly cumulative metric, the corrected seasonal cumulative metric was calculated as the sum of the corrected monthly cumulative metrics. Otherwise, a valid estimate of the corrected seasonal cumulative metric was not reported. To report a valid trend, the time series for trend calculations had to satisfy the following two further data capture criteria: (1) at least 11 (73%) valid years for 15-year running trend periods and (2) beginning with the last five years of record, at least three of five valid years were required within each 5-year block of years.

The monthly change in the distribution of hourly average concentrations for several monitoring sites was investigated by characterizing the median difference between each 10 ppb increment in absolute frequency except at the South Pole site, where increments of 5 ppb were used. These median differences for each increment (10 or 5 ppb) are plotted as histograms. The Theil estimate was also used to estimate the trend slope. To test for statistical significance, Kendall's tau test (Lefohn and Shadwick, 1991) was used to determine significance at the 10% level for the specified increments.

3. Results

In this section, results from the analysis of the time series in broad geographical regions are considered. In some cases these groupings might be expected to produce similar changes and thus, the consistency of the changes or the geographic scope of the changes can be assessed. The linear trend estimates from the regression model for each location are provided in Table 2 (surface sites) and Table 3 (ozonesondes). Trends are given for three periods; 1971–2010 (or the beginning of the record if after 1971), 1981–2010, and 1991–2010. For the O_3 profile data the trends are given for each layer. Both the percentage change (in %/decade) and the mixing ratio change (ppb yr^{-1}) are shown with plus/minus one standard error. Trend estimates exceeding two standard errors are deemed statistically significant.

3.1. North polar

Polar latitudes of the N.H. (north of 65N) are not usually considered as a likely region for significant local photochemical tropospheric O_3 production, although biomass burning related to boreal fires can have an impact (Stohl et al., 2007; Oltmans et al., 2010). However, transport from the stratosphere or lower latitudes along with the possible influence of rapid climate change are potential sources of longer-term changes. At Barrow, Alaska (71N) the 38-year record shows a modest increase of 3.5 ± 1.0%/decade with most of that occurring in the first and last decade of the record (Fig. 2 and Table 4). However, changes for individual months from one decade to another are smaller than the variations within a decade (Table 4). The largest change appears to have occurred during summer and autumn months between the initial period (1973–1980) and the subsequent decade (1981–1990). During the 30-year period (1981–2010) covered by the Resolute, Nunavut ozonesonde record, there was no significant change at Barrow, which is consistent with the profile measurements at Resolute (Fig. 3), where no significant overall change is present. Over the last two decades, both locations show a positive trend that is not statistically significant, which primarily reflects the lower values in the 1980s to the mid 1990s. The running 15-year trends of the W126 metric for the Barrow site (Fig. 2c) illustrates the statistically significant change in the early years but no further statistically significant trends during the later years. These sites illustrate the decadal variations that influence the trend calculations when considering different time periods even though the records are relatively long (Logan et al., 1999, 2012).

3.2. Mid-latitudes of the N.H

The mid-latitudes of the N.H. are a zone of high population and industrial and transportation activity encompassing Europe, North America, and Asia. Several recent studies have investigated changes in this latitude band (Parrish et al., 2012) or a particular region

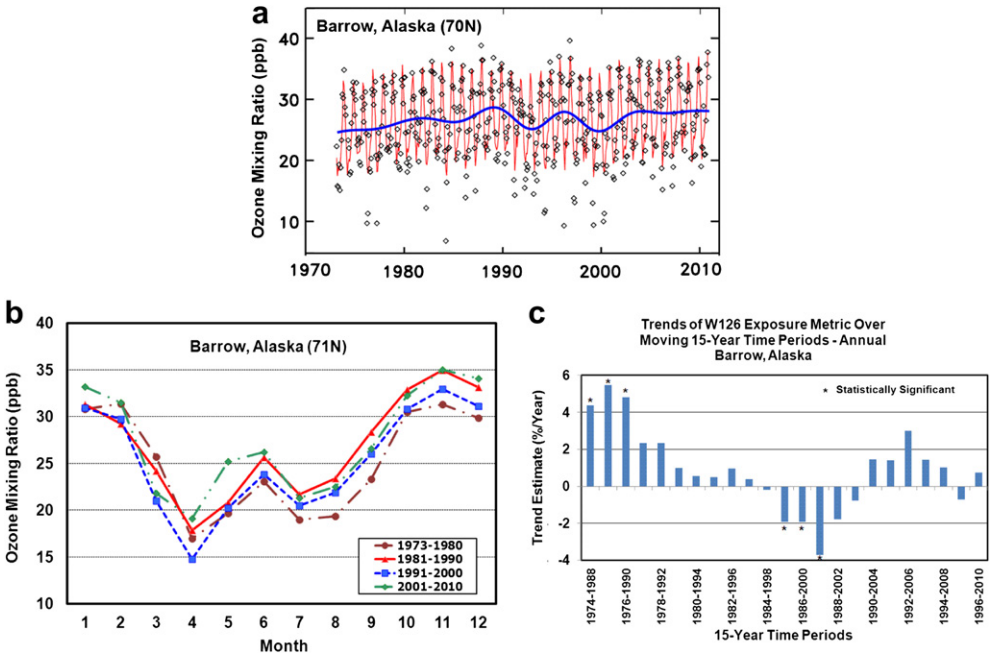

Fig. 2. a) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Barrow, Alaska. b) The seasonal variation at Barrow for 10-year periods. c) Moving 15-year trends at Barrow of the W126 exposure metric. Significant trends are marked with an asterisk.

Table 4
Mean and standard deviation for each month for multiple time periods.

MN	Barrow							
	1973–1980		1981–1990		1991–2000		2001–2010	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	30.87	2.49	31.41	2.95	30.99	2.72	33.13	1.81
2	31.19	2.07	29.37	4.51	29.77	2.52	31.77	1.93
3	25.47	4.56	24.40	3.84	21.25	5.70	21.76	2.67
4	16.96	5.39	17.91	6.23	14.80	5.49	19.15	3.91
5	19.88	4.65	20.86	3.74	20.27	6.79	25.24	4.95
6	23.11	1.81	25.68	2.79	23.37	3.78	26.44	2.17
7	19.10	2.05	21.74	1.60	20.67	2.78	21.35	1.11
8	19.36	1.47	23.34	1.62	21.92	4.09	22.56	1.61
9	23.46	2.50	28.41	2.80	26.10	3.38	26.62	3.32
10	30.19	2.98	32.88	1.77	30.81	2.85	32.31	2.41
11	31.46	2.09	34.98	2.35	32.97	3.37	35.12	1.79
12	29.84	2.47	33.14	1.89	31.09	3.02	34.13	1.48

MN	Zugspitze					
	1981–1990		1991–2000		2001–2010	
	Mean	SD	Mean	SD	Mean	SD
1	36.46	4.78	42.64	3.13	44.52	2.03
2	40.14	5.07	45.83	3.03	46.53	2.29
3	46.42	5.47	49.36	2.37	51.60	1.89
4	53.80	6.56	56.48	3.29	58.02	1.99
5	55.80	6.95	58.13	3.80	57.30	2.18
6	54.14	4.98	58.10	3.76	57.42	3.18
7	54.62	4.11	57.99	5.13	57.11	4.71
8	53.57	4.34	56.18	2.02	54.24	5.52
9	46.41	1.79	48.82	2.93	48.49	3.47
10	40.97	2.21	44.66	2.29	45.21	2.00
11	39.18	2.89	41.93	2.62	42.10	1.53
12	37.28	2.83	41.09	1.84	42.63	1.74

MN	Westman Islands			
	1992–1997		2003–2010	
	Mean	SD	Mean	SD
1	38.40	1.85	41.50	1.86
2	41.32	1.52	43.02	0.98
3	44.50	1.89	46.25	0.72
4	45.34	1.65	47.08	1.59
5	42.60	2.11	43.36	2.85
6	33.40	2.81	36.89	1.59
7	29.42	1.89	30.87	2.15
8	29.20	2.29	32.33	3.57
9	33.04	4.38	35.09	1.41
10	35.72	1.71	37.43	1.11
11	37.72	1.39	38.56	1.56
12	38.25	2.16	40.05	0.71

MN	Bermuda			
	1992–1997		2003–2010	
	Mean	SD	Mean	SD
1	37.34	4.87	43.10	1.52
2	38.93	2.62	47.54	2.69
3	43.73	4.65	50.01	2.51
4	45.78	4.09	50.98	2.66
5	39.50	4.13	43.90	5.09
6	28.25	3.18	32.11	4.12
7	22.79	3.53	24.46	3.12
8	22.66	2.99	27.56	2.78
9	25.17	6.64	28.76	3.54
10	34.73	3.33	36.53	7.21
11	37.47	3.75	39.94	4.22
12	38.10	3.62	41.20	2.99

MN	Mace Head (12–19 LST)					
	1988–1995		1996–2002		2003–2010	
	Mean	SD	Mean	SD	Mean	SD
1	34.25	4.18	34.11	4.94	38.10	2.90

Table 4 (*continued*)

MN	Mace Head (12–19 LST)					
	1988–1995		1996–2002		2003–2010	
	Mean	SD	Mean	SD	Mean	SD
2	36.21	2.93	41.54	3.14	39.25	1.79
3	41.33	3.52	42.57	3.66	45.38	2.10
4	44.25	2.14	45.61	2.32	48.11	1.33
5	45.15	2.25	45.69	1.05	45.13	3.31
6	36.11	2.38	38.37	2.27	38.50	3.04
7	33.11	3.23	31.57	1.80	32.91	2.45
8	32.95	3.54	32.16	1.70	32.17	1.90
9	35.70	2.65	34.89	3.36	35.71	1.51
10	32.97	3.03	36.06	2.89	35.96	0.97
11	31.99	4.01	35.93	5.83	38.27	1.92
12	31.54	5.06	33.14	4.75	35.78	1.39

MN	Izana (00–08 LST)					
	1988–1995		1996–2002		2003–2010	
	Mean	SD	Mean	SD	Mean	SD
1	40.95	2.00	45.23	3.07	43.94	1.45
2	40.99	1.36	46.29	3.91	44.94	2.57
3	44.83	2.18	50.27	2.98	48.26	1.84
4	51.10	4.02	55.29	4.77	54.55	2.37
5	52.69	2.98	55.44	4.35	55.31	4.89
6	52.86	3.59	55.30	3.73	54.82	3.35
7	45.88	3.50	55.73	3.92	50.23	4.37
8	42.00	3.31	48.80	3.17	46.51	5.15
9	40.05	3.11	41.41	3.32	41.62	2.69
10	36.34	2.35	41.23	3.56	39.64	3.60
11	38.19	1.71	41.87	2.28	41.75	2.40
12	38.61	1.56	43.54	2.94	43.56	1.36

MN	Denali NP (12–19 LST)					
	1988–1995		1996–2002		2003–2010	
	Mean	SD	Mean	SD	Mean	SD
1	31.62	2.38	34.79	3.99	33.85	2.61
2	33.89	3.03	37.82	3.32	37.72	3.29
3	37.36	1.67	41.26	5.68	39.04	1.84
4	41.96	1.62	43.84	5.33	45.76	2.45
5	38.74	1.02	42.37	4.96	43.66	2.46
6	30.57	1.42	34.11	2.21	33.36	3.90
7	26.15	2.97	24.40	2.40	25.81	3.74
8	23.44	2.27	22.41	2.77	24.33	4.01
9	26.79	1.66	25.81	2.86	26.69	1.74
10	27.66	2.73	29.11	2.37	27.69	2.79
11	30.19	2.37	31.21	3.70	31.58	2.67
12	32.30	1.43	32.01	5.57	34.64	2.57

MN	Lassen NP (12–19 LST)					
	1988–1995		1996–2002		2003–2010	
	Mean	SD	Mean	SD	Mean	SD
1	35.67	2.55	37.89	2.42	38.60	3.12
2	38.97	2.18	40.19	1.78	41.49	2.08
3	39.44	5.49	40.90	6.40	45.39	3.04
4	42.60	2.64	46.13	3.74	48.18	2.31
5	44.42	3.18	47.94	4.48	48.31	3.94
6	45.23	4.63	49.54	3.15	50.00	5.24
7	49.86	5.98	55.31	2.67	55.36	3.32
8	52.58	3.96	56.01	4.23	53.78	4.91
9	48.56	3.37	49.26	5.89	48.66	3.90
10	40.61	4.06	42.51	4.27	39.51	3.10
11	33.14	4.58	35.30	3.89	34.64	2.07
12	33.83	3.89	36.69	3.47	37.67	1.86

MN	Mauna LOA (00–08 LST)							
	1973–1980		1981–1990		1991–2000		2001–2010	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	36.63	3.46	41.06	3.54	42.08	3.85	43.23	2.43
2	39.57	2.73	41.81	4.49	43.03	3.40	44.15	4.13
3	46.14	4.77	49.45	5.04	49.00	5.24	46.02	6.34
4	48.51	5.06	53.45	5.90	57.48	3.72	53.25	7.08

Table 4 (*continued*)

MN	Mauna LOA (00–08 LST)							
	1973–1980		1981–1990		1991–2000		2001–2010	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
5	45.26	4.94	51.43	5.34	49.61	5.62	48.55	7.33
6	40.39	5.15	41.44	5.24	43.43	4.83	43.02	4.88
7	35.53	4.53	37.72	4.26	38.82	5.31	40.36	4.82
8	33.04	5.79	35.24	2.78	35.32	5.16	39.06	4.08
9	31.27	4.32	32.71	4.02	35.76	7.85	38.95	4.16
10	32.49	3.01	33.89	4.48	35.68	4.81	41.43	4.15
11	34.40	4.89	34.13	3.95	35.17	4.65	40.53	3.67
12	35.47	3.27	39.29	3.31	39.27	5.32	41.66	5.94

within this band (Logan et al., 2012; Cui et al., 2011; Cooper et al., 2010; Parrish et al., 2009; Tanimoto et al., 2009).

3.2.1. *Western Europe*

In Western Europe there are a multiplicity of locations and measurement platforms (aircraft, high-altitude surface, and ozonesondes) that have longer-term tropospheric O_3 records. A number of the measurement locations are in relative proximity to each other providing an opportunity to determine the consistency of the longer-term changes within this region. An extensive analysis of the long-term changes and the consistency of the results has been carried out by Logan et al. (2012). Over the multiple decades considered, different trends were deduced that were not always consistent. Some of these differences were ascribed to possible problems with the data record itself, although it was not always possible to identify the cause of the problem. In this study, the data from Zugspitze, which is the longest Alpine surface O_3 record, have been selected because of their use in previous studies (Oltmans et al., 1998, 2006) and consistency of the record with those of nearby sites (Logan et al., 2012). The ozonesonde measurements at Hohenpeissenberg have used the same type of ozonesonde (Brewer-Mast) and only modest changes in preparation procedures (Attmannspacher and Dütsch, 1978; Claude et al., 1987; WCRP, 1998) procedures over the long period of observations (40 years for this analysis), although differences from other long-term records in Europe have been noted (Logan et al., 2012). The time series of the Hohenpeissenberg ozonesonde monthly mean mixing ratios in the 700–500 hPa (~3–6 km) layer (Fig. 4a) shows increases from the beginning of the record that are seen throughout the troposphere (Fig. 4b) that, however, plateau by the mid-1980s so that the 30-year trend (Fig. 4b) is zero. At Zugspitze, on the other hand, O_3 continues to increase significantly into the late 1980s and plateaus (i.e., flattens) in the early 1990s (Fig. 4c and d), with the result that there is a significant increase over the past 30 years, which differs from the pattern at Hohenpeissenberg. A closer look at the pattern of change for Zugspitze shows that non-significant trends are observed beginning with the 15-year period 1988–2002 until 1993–2007, while significant decreasing trends are observed for the last three 15-year periods (i.e., 1994–2008, 1995–2009, and 1996–2010) (Fig. 4d). Over the period of record, there is an indication that the frequency of the lower hourly average concentrations (20–40 ppb) has shifted upward (i.e., 50–70 ppb) (Fig. 4e). The running 15-year W_Low metric illustrates that the shifting of the frequency of the lower to the mid-level concentrations was statistically significant from the beginning of the record until the 15-year period 1990–2004 (Fig. 4f). For the 15-year periods starting in 1993–2007, the frequency of the mid-level concentrations begins to shift toward the lower concentrations as indicated by an increase in the W_Low values along with the decrease in the higher concentrations indicated by the decrease in the W126 trends. Together these changes suggest that the entire distribution is shifting downward, which could be indicative of a decline in the regional background. The seasonal pattern at Zugspitze shows increases in all months from the decade 1981–1990 to the period 1991–2000 with the largest increases coming during the winter (Fig. 4g). In the most recent decade (2000–2010), the changes in all months have been small in comparison with the previous decade (Fig. 4g and Table 4). This pattern is consistent with what was seen in the changes of the W_Low metric and suggests that earlier increases included a component from the reduction in NO titration, especially during the winter, associated with NO_x reductions in Europe (http://www.eea.europa.eu/data-and-maps/indicators/eea-32-nitrogen-oxides-nox-emissions/eea-32-nitrogen-oxides-nox).

The relatively nearby locations of Hohenpiessenberg and Zugspitze should both sample predominantly free tropospheric air. The somewhat different pattern of change may result from the fact that the ozonesonde measurements at Hohenpeissenberg and the surface measurements at Zugspitze represent different measurement protocols. At Zugspitze, the surface measurements are continuous and include both day and night observations. At Hohenpeissenberg, on the other hand, the ozonesonde profiles provide a snapshot every few days and are made during a fixed time of day. It has also been found that the sonde profile and mountain surface measurements do not always observe the same air mass even at sites in close proximity to each other, and this is more likely to occur during the summer (Brodin et al., 2011). Sampling the Zugspitze time series for only the days when the Hohenpeissenberg sonde measurements were made does not resolve the differences (J. Logan – private communication, 2012).

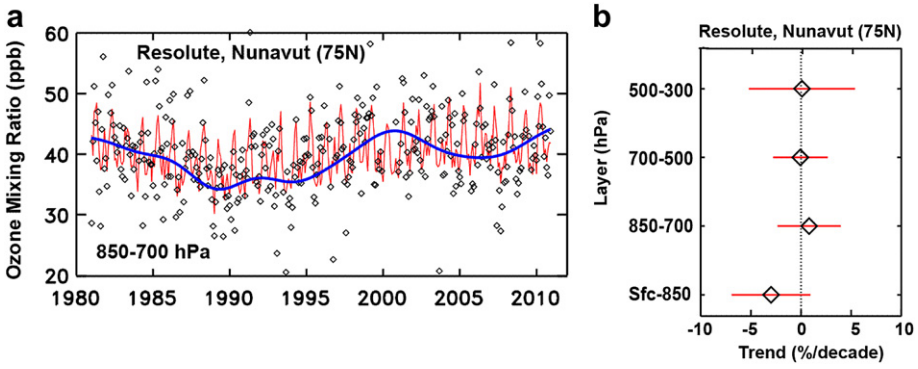

Fig. 3. Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 850–700 hPa (~1.5–3 km) layer from ozonesondes at Resolute, Nunavut. b) Trend with altitude (diamond) of O_3 at Resolute for the period 1981–2010 and ±2 standard errors (horizontal bar). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

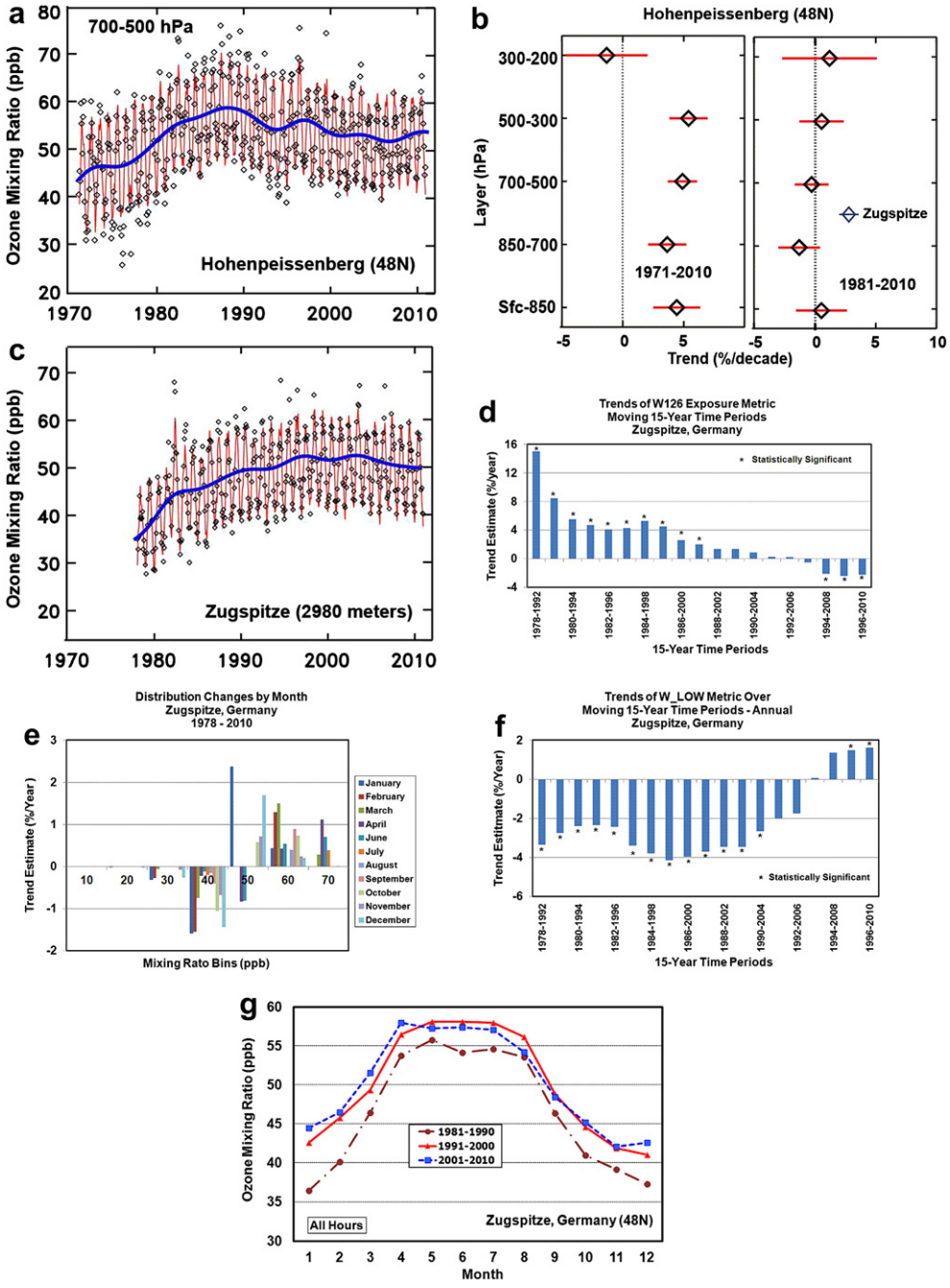

Fig. 4. a) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 700–500 hPa (~3–6 km) layer from ozonesondes at Hohenpeissenberg, Germany. b) Year-round linear trend of the monthly mean O_3 (diamond) and ±2 S.E. (horizontal bar) in layers in the troposphere at Hohenpeissenberg for 1971–2010 and 1981–2010. c) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Zugspitze, Germany. d) Moving 15-year trends at Zugspitze of the W126 exposure metric. Significant trends are marked with an asterisk. e) Change in occurrence of O3 values in 10 ppb bins for months with significant changes. f) Moving 15-year trends at Zugspitze of W_LOW. Significant trends are marked with an asterisk. g) The seasonal variation of surface O_3 at Zugspitze for three periods (1981–1990, 1991–2000, and 2001–2010).

As noted above, there have been modest changes in sonde preparation procedures at Hohenpeissenberg, and there are indications that there have been some minor changes in sonde manufacture over the long period of record (WCRP, 1998). Even so, important tentative conclusions can be drawn from the measurements at these two sites. Over the entire period of record, year-round O_3 mixing ratios have increased significantly (more than 5%/decade) throughout the troposphere since the beginning of ozonesonde measurements in the late 1960s. Similarly, over the entire period of record, the surface measurements that begin in the late 1970s also capture this significant overall increase. Also, though there are differences in details of the pattern of change, over the past two decades O_3 mixing ratios have leveled off or have shown small but statistically significant decreases.

3.2.2. North Atlantic

Two sites in the North Atlantic have continuous measurements with nearly 25 years of observations, while at two other sites the measurements span a similar period but have a significant period without measurements in the middle of the record. The high-altitude site at Izaña in the Canary Islands and the low-elevation site at Mace Head, Ireland both have year-round

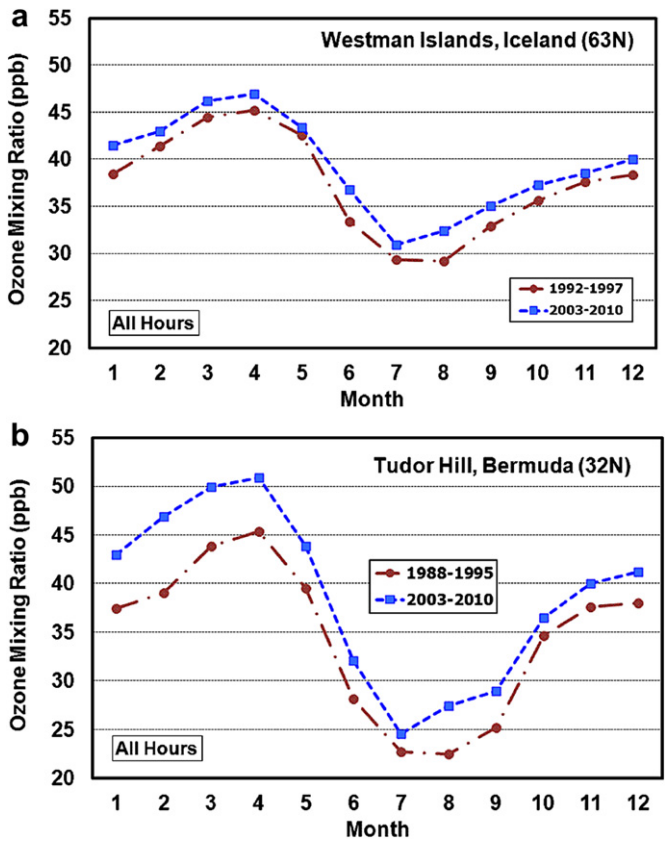

Fig. 5. The seasonal variation of O_3 for various time periods at two sites in the North Atlantic; a) Westman Islands, Iceland and b) Tudor Hill, Bermuda. The length of the time periods varies between 6 and 8 years depending on the data record and overall length of the record.

measurements beginning in 1988 that are amendable to time series analysis. The sites at Bermuda and Iceland provide snapshots for 6–8 year periods at the beginning and end of 1988–2010 (Fig. 5). These two sites exhibit increases from the earlier time period to the later period that include most months of the year. Though the differences between the earlier and later periods for individual months are not significant, the differences through the full year are significant. However, without a continuous time series it is not possible to determine the progression of these changes.

Derwent et al. (2007) indicate that Mace Head shows increasing values from its inception in 1987 until the late 1990s with a flattening observed thereafter. This is the pattern shown in Fig. 6, although it should be kept in mind that Fig. 6 analysis is based on all daytime data and has not been screened for background conditions as in the Derwent et al. (2007) analysis. Tripathi et al. (2010) also noted this pattern. Using monthly averages, Logan et al. (2012) indicate that there are two periods of relatively constant O_3 at Mace Head (1988–1995 and 1998–2009), with an increase in between. From the comparison of the average seasonal variation (Fig. 6b) during three time periods (1988–1995, 1996–2002, and 2003–2010), the changes occur in the winter and spring between the 1988–1995 period and the subsequent two periods. There is also an indication that the monthly average maximum concentrations may have shifted over the period of record from April–May to April. These seasonal shifts are significant as shown by the changes in the distribution (Fig. 6c) where the frequency of the lower hourly average concentrations (30–40 ppb) move upward to the 50–60 ppb bins. The running 15-year trends of the W126 metric at Mace Head (Fig. 6d) show only small non-significant positive changes with the largest increases occurring during 3 of the 15-year running periods (i.e., 1992–2006, 1993–2007, and 1994–2008). However, the running 15-year W_Low metric (Fig. 6e) shows that the frequency shift from the lower to the mid-level concentrations was most predominant during the earlier part of the record, while in the most recent 15-year period, the shift has changed direction. The trend in the W_Low (shift from lower to middle levels) reflects changes in the winter months (Fig. 6b and c) that contribute more prominently to the W_Low metric.

At the high-elevation site at Izaña, Canary Islands, the downslope (nighttime) measurements used in this analysis are generally representative of the lower free troposphere (Cuevas et al., 2012). The time series of the observations (Fig. 7a) shows a rapid increase to higher values in the mid to late 1990s. This change is reflected throughout the seasonal cycle (Fig. 7b). This is seen in the running 15-year trends for both the W126 and W_Low metrics (Fig. 7c and d) that indicate upward shifts in both the higher and lower portions of the distribution but a transition to non-significant changes in the later periods. The somewhat abrupt change in O_3 levels in the mid 1990s may reflect a shift in the phase of the North Atlantic Oscillation (NAO) altering the transport pattern to Izana (Cuevas et al., 2012). The influence of the change in the NAO phase on transport is worthy of investigation as a possible cause of changes to higher O_3 amounts at other North Atlantic sites in the mid and late 1990s.

3.2.3. Eastern North America

Four sites with longer-term records are identified in eastern North America. The Churchill (59N) and Goose, Canada (53N) sites have ozonesonde records that begin in 1980 (not shown). Similar to the other Canadian higher-latitude sites, a period of declining tropospheric O_3 amounts in 1980s to mid 1990s has been followed by a period of increasing values; thus, the overall 30-year trend is very small. The higher-elevation surface site at Whiteface Mountain, New York has one of the longer surface records extending back to 1973 (Fig. 8), although in the mid 2000s, there are some gaps in the measurement record. The longest ozonesonde record in the United States, going back to 1970, is Wallops Island, Virginia. The electrochemical concentration cell (ECC) technique has been used throughout the measurement program. The Whiteface record suggests a small overall increase (2.1 ± 1.7%/decade, 0.09 ± 0.07 ppb/decade) from the beginning of the record that results from an increase during the first 15 years of the record so that the most recent 20 years shows a decline (−5.3 ± 2.8%/decade, −0.22 ± 0.12 ppb/decade). At Wallops Island, there were very high O_3 amounts in the late 1980s, but no significant change over the 40-year period of record. The most recent decades show little change throughout the troposphere (see e.g. Cooper et al., in press).

3.2.4. Western North America

Several recent studies (Jaffe and Ray, 2007; Parrish et al., 2009; Cooper et al., 2010) have placed particular emphasis on possible changes in this region related to the impacts of growing Asian emissions of O_3 precursors (Jaffe et al., 2003; Jaffe and Ray, 2007). These emissions may not only impact the western coast of North America, but also be observed as far inland as the Rocky Mountain region (Oltmans et al., 2010). Two ozonesonde sites, Edmonton, Alberta and Boulder, Colorado have records longer than 25 years (Fig. 9). However, both locations are likely to be influenced in the lowest portion of the profile by regional pollution sources. Emphasis for these records is placed on the troposphere above the boundary layer. At Edmonton, Alberta (Fig. 9a and b) and Boulder, Colorado (Fig. 9c and d), the overall changes through the troposphere are small and computed trends are not significant. There

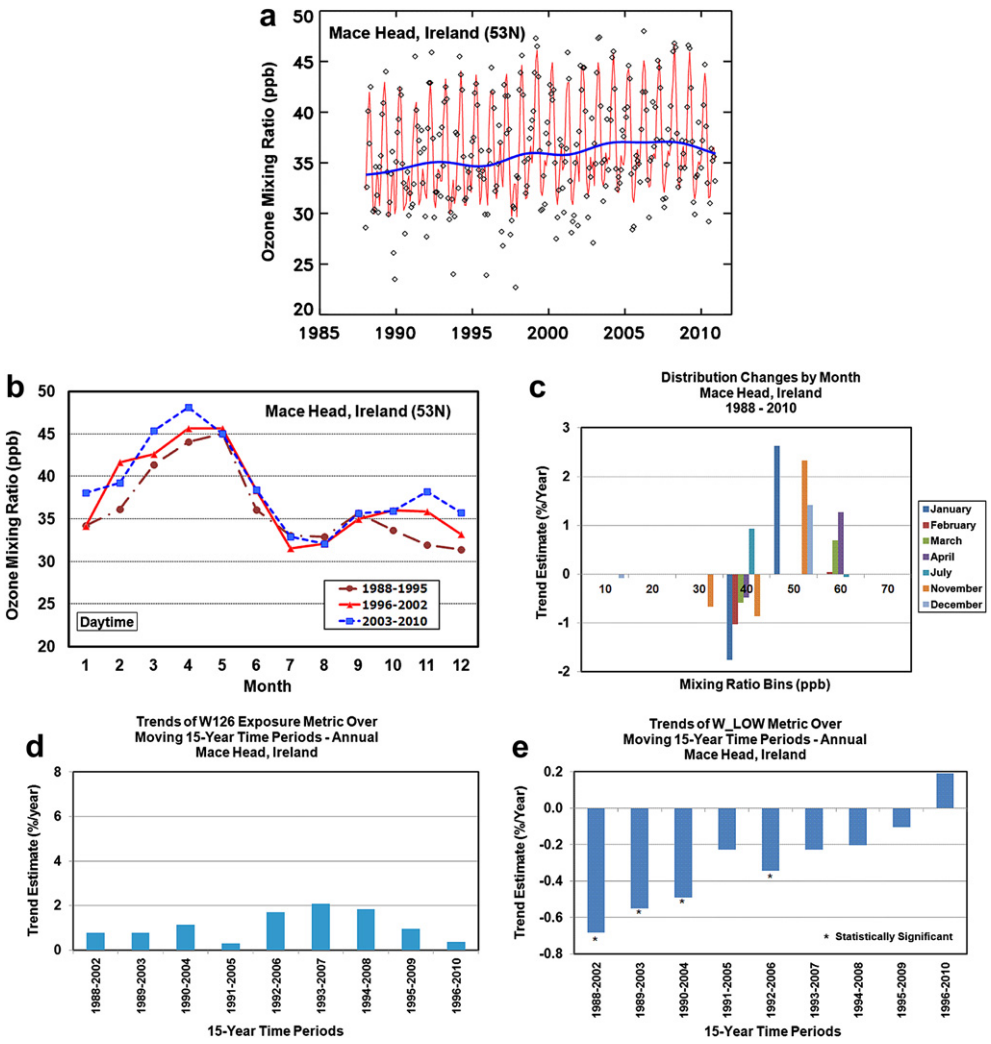

Fig. 6. a) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Mace Head, Ireland; b) The seasonal variation of daytime surface ozone at Mace Head for three periods (1988–1995, 1996–2002, and 2003–2010); c) Change in occurrence of O_3 values in 10 ppb bins for months with significant changes; d) Moving 15-year trends at Mace Head of the W126 exposure metric; e) Moving 15-year trends at Mace Head of the W_Low metric.

appears to be a similar pattern of change at these two sites during the overlapping period of record (Fig. 9a and c). Both records show higher values in the late 1980s, a dip in the mid 1990s and a slight increase thereafter. Although the annual variation in the 850–700 hPa at Boulder, which includes the near surface region, is larger, the correspondence of the longer time scale variations suggests that such changes occur over a broad enough scale that conclusions on changes can be drawn on a regional level.

Several relatively remote surface sites (Denali National Park (NP), Alaska; Lassen Volcanic NP, California; Glacier NP, Montana; Pinedale, Wyoming; and Rocky Mountain NP, Colorado) with records of more than 20 years that may be impacted at times by regional influences, but are likely to reflect broader scale patterns, have also been analyzed for this region (Fig. 10). The site at Denali NP is at relatively high latitude but can be influenced by flow from Asia (Oltmans et al., 2010) and so is considered here with the western North America locations. During the first one third of the record at Denali (Fig. 10a) the late winter and spring months were on average lower than during the latter two thirds of the record. The increase from the late 1980s (the beginning of the record) into the early 1990s seems to be reflected in the record at several of the western U.S. locations such as Lassen NP (Fig. 10b–f) and Pinedale (Fig. 10g) but not at Glacier NP (Fig. 10g). The running 15-year trends at Pinedale (Fig. 10e) indicate that early in the record surface O_3 may have increased but this has been followed by a consistent pattern with little or no change and most recently by statistically significant declining amounts. The W126 trend patterns at Rocky Mountain NP (not shown) over six running 15-year periods showed statistically significant positive trends during 1989–2003, 1990–2004, 1991–2005, and 1992–2006. This is similar to the results reported by Lefohn et al. (2010). Following the 1992–2006 period, the 15-year trend pattern showed non-significant trends with values close to zero for 1995–2009 and 1996–2010.

It has been shown recently that both stratospheric-tropospheric exchange (Langford et al., 2012; Lin et al., 2012a) and transport from Asia (Lin et al., 2012b) can have significant impacts on western North America, including the ability to attain air quality standards. Changes have also been noted over a longer-time horizon (Cooper et al., 2010) in the lower free troposphere above the boundary layer. It has been hypothesized that increases will continue with growing Asian emissions (Tanimoto et al., 2009). Using the entire record, at Lassen NP, the monthly means computed from daytime mixing ratios (Fig. 10b, Table 2) show a year-round increase of

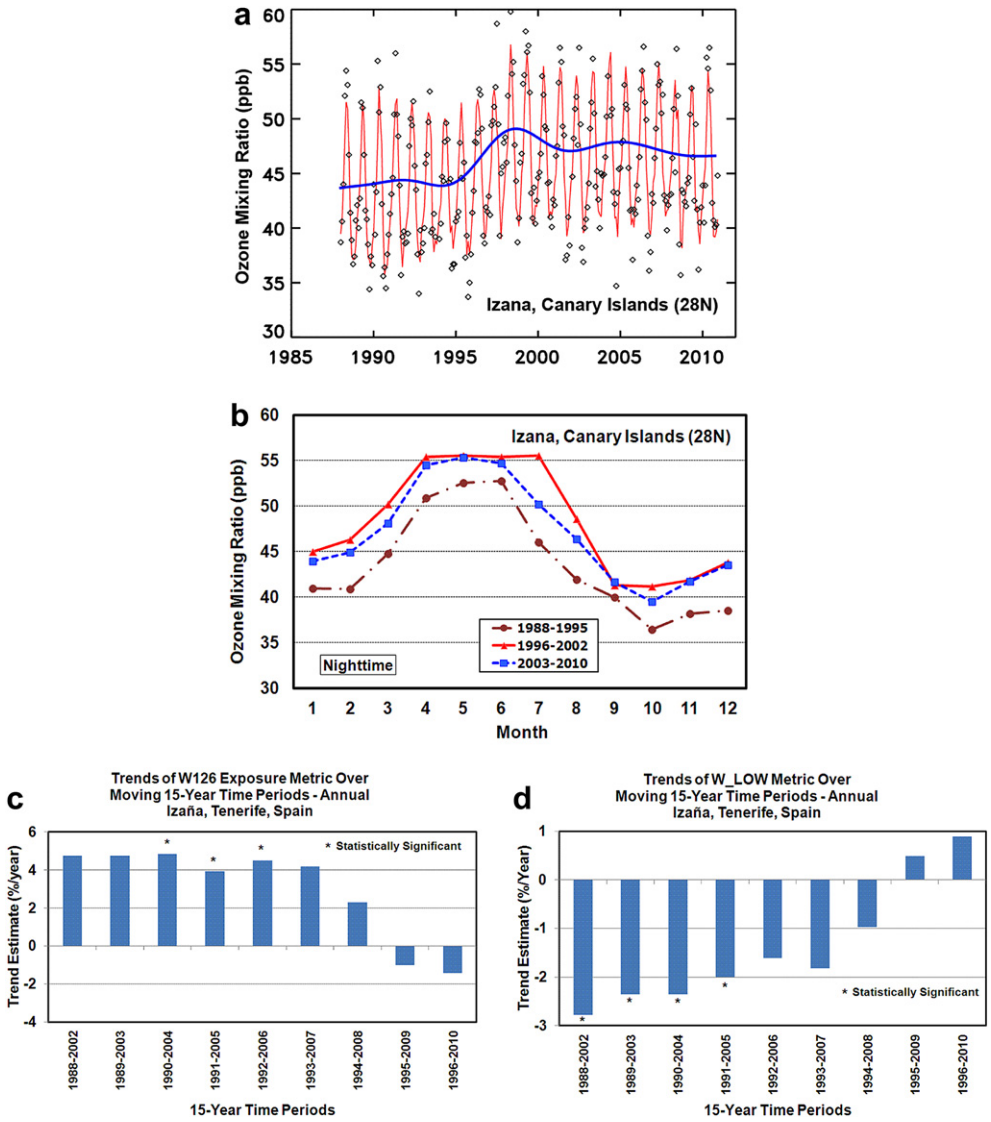

Fig. 7. a) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Izana, Canary Islands. b) The seasonal variation of nighttime surface O_3 at Izana for three periods (1988–1995, 1996–2002, and 2003–2010). c) Moving 15-year trends at Izana of the W126 exposure metric. d) Moving 15-year trends at Izana of the W_Low metric. Significant trends are marked with an asterisk.

4.4 ± 2.3%/decade (0.19 ± 0.10 ppb/decade). However, the figure also indicates that the pattern begins to flatten starting around 2000, continuing through the present. Because of the flattening of the trend at Lassen NP, the running 15-year trends of the W126 values (Fig. 10c) do not show any significant trends for individual 15-year periods. However, the overall pattern for the 15-year running trends suggests that there has been a declining tendency in the change. Over the period of record, there is an indication that the frequency of the lower hourly average mixing ratios (20–40 ppb) have shifted upward (i.e., 50–70 ppb). Although not statistically significant, the running 15-year W_Low metric illustrates that the shifting from the lower to the mid-level concentrations has lessened over the period of record suggesting that the influence of NO titration has weakened.

3.2.5. *Japan*

In Japan there are two long-term ozonsonde records at Tsukuba (36N) and Sapporo (43N) that exceed 40 years in length. In both cases there are significant periods of missing or very sparse measurements. Since 1991 soundings at these sites have been made weekly. Neither of these locations is free of local influences from precursor emissions, especially Tsukuba, which is near Tokyo. In addition, a surface site at Ryori, Japan (38N) has made measurements for 20 years. This site is located in a forested area on the eastern shore of Honshu Island. Although this location is impacted by regional O_3 sources, its relatively remote location and length of record in a region with few such records makes it worth examining. At Tsukuba and Sapporo, the 40-year time series (Fig. 11a and b) suggests increasing tropospheric amounts up to about 1990 and relatively little change thereafter. However in the late 1970s and 1980s, both these data sets have rather spotty records. Overall from the beginning of the record, tropospheric O_3 showed a modest increase (Fig. 11c). However, with only weekly profiles there is a large uncertainty in the estimates of these changes. The time series at Ryori (Fig. 11d), using the daytime averages (13–20 Local Time), shows a definite increase into the mid 1990s with a flattening in the record in the last 15 years. This is somewhat similar to the pattern observed in western North America but suggests more recent increases than the Japan ozonesonde data from Tsukuba and Sapporo (Fig. 11a and b).

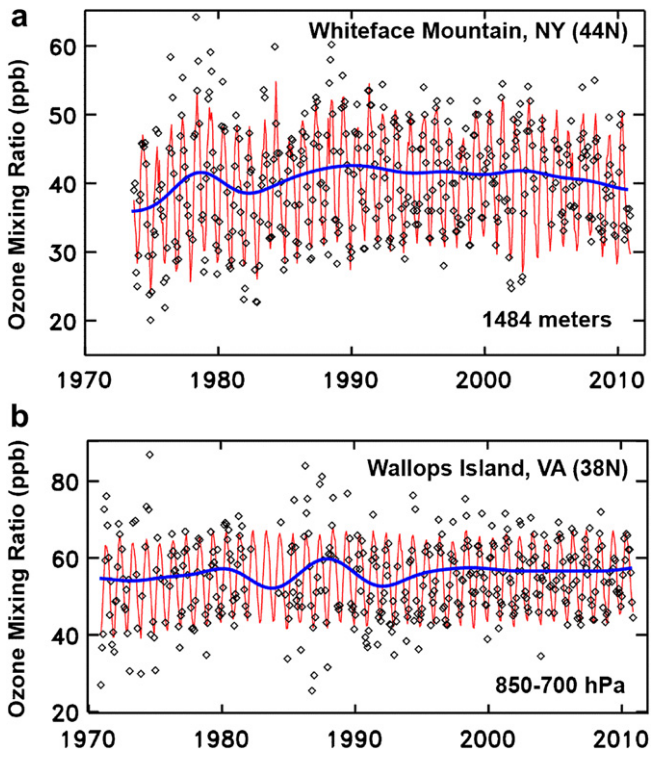

Fig. 8. a) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Whiteface Mountain, New York. b) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 850–700 hPa (~1.5–3 km) layer from ozonesondes at Wallops Island, Virginia. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Subtropical Pacific (Hawaii)

Over the vast expanse of the North Pacific, there is only a single location with a continuous long-term measurement record. The Mauna Loa, Hawaii site (19N) at 3.4 km began surface O_3 observations in 1973 (Fig. 12a). Over the entire period of record there has been a significant year-round increase of 3.8 ± 0.9%/decade (0.16 ± 0.04 ppb/decade) and there has been a seasonal dependence to this change (Fig. 12b). The 15-year running trend based on the W126 metric (Fig. 12c), that is more heavily weighted by changes in the distribution at O_3 values greater than 50 ppb (Fig. 1a), presents a picture of an increasing trend into the earlier 2000s but a decline in this increasing pattern after that. In the earliest period, there was an increase primarily in the spring that is reflected in the W126 O_3 maximum where the higher spring values receive greater weight. In the most recent decade, the increase has come exclusively during the seasonal minimum in autumn and early winter (Fig. 12b). As was noted in an earlier analysis (Oltmans et al., 2006), this change resulted from a shift in the transport pattern with more flow from higher latitudes in the most recent period. There is a significant ENSO signal in the Mauna Loa record, with generally higher O_3 amounts during the warm phase. Both the transport-related increase in the autumn and the ENSO signal have been well reproduced in a recent model simulation (M. Lin – private communication, 2012). The warm event in 2009–2010 resulted in high O_3 readings that have had some impact on the overall trend, with the change through 2009 being about 30% less than when 2010 is included. This is also observed in the 15-year running trend pattern with the last 15-year period showing an increase above the previous 15-year period (Fig. 12c). After 1980 the surface record shows a smaller increase of 3.3 ± 1.0%/decade driven by the change in the seasonal minimum. Since 1982, a near continuous record of weekly O_3 profiles has been made from the nearby sea level site in Hilo (Fig. 12e). The ozonesonde record that reflects the period after 1980 also shows increases (Fig. 12d) but the much less frequent sampling compared to the surface data resulted in these changes being non-significant.

A station with a record a bit shorter than 20 years (1994–2010), Minamitorishima, Japan, located at 24N and about 4000 km east of southern China, may reflect flow from southern China, including the Pearl River delta and Shanghai that reaches the mid-Pacific. The time series at this site (Fig. 13a) shows a decreasing trend in the overall record. Looking at the seasonal pattern for two periods (1995–2002 and 2003–2010), however, indicates that much of this change has occurred after 2005 since the earlier period has slightly less O_3 through all months than the later period. At Naha, Japan in Okinawa, which is within 800 km of the Chinese mainland, O_3 in the troposphere may have increased (Fig. 13b) although the year-round trend estimates are not significant. The extent to which O_3 resulting from emissions in China is continuing to raise O_3 levels over the subtropical Pacific is difficult to determine from the limited measurements.

3.4. Tropical South Pacific (American Samoa)

The 35-year surface O_3 record at American Samoa shows minimal change (Fig. 14) with a small decline in the earlier portion of the record, a period of no change in the middle, and a small increase over the last 5 years. None of these changes are statistically significant. The Southern Hemisphere Additional Ozonesonde (SHADOZ) network includes measurement records of ~10–15 years in length (Thompson et al., in press and references therein). The most complete ozonesonde record is also at American Samoa and is nearly 15 years in length through 2010. Although these data were not analyzed in the same manner as the longer ozonesonde records, there appears to be little change over this period. Two other SHADOZ stations in the tropical South Pacific (Suva, Fiji and San Cristobal, Galapagos) have less complete records and have not been analyzed. The minimal change in this region appears to be consistent with the lack of O_3 precursor sources as well as the strong O_3 sink in this very low NO_x regime (MacFarland et al., 1979).

3.5. Mid-latitudes of the southern hemisphere

Two sites in the mid-latitudes of the S.H. have surface O_3 records approaching 30 years in length (Cape Grim, Australia and Cape Point, South Africa) while the ozonesonde record at Lauder, New Zealand has 25 years of profile data. All three of these sites are consistent in showing significant increases (Fig. 15a–c). Using the overlapping period from 1991 to 2010 when all of the stations have data there is an increase ranging from 7.3 ± 0.7%/decade at Cape Point to 2.8 ± 0.4%/decade at Cape Grim. At Lauder there is a significant increase of ~5% per decade throughout the lower and middle troposphere. The surface site at Baring Head, New Zealand shows an increase of similar magnitude to the change at Lauder, but with a less complete data record, so that the change is not statistically significant. The lack of a trend in the upper troposphere at Lauder suggests that changes in transport from the lower stratosphere/upper troposphere are not directly responsible for the increase lower in the troposphere. Possible transport changes within the troposphere itself, including both short and long-term changes in ENSO, are currently under investigation (Galbally et al., 2011) as cause for these changes. In the N.H. it has been shown that interannual variability, such as ENSO, can have a substantial influence on tropospheric O_3 that may lead to longer-

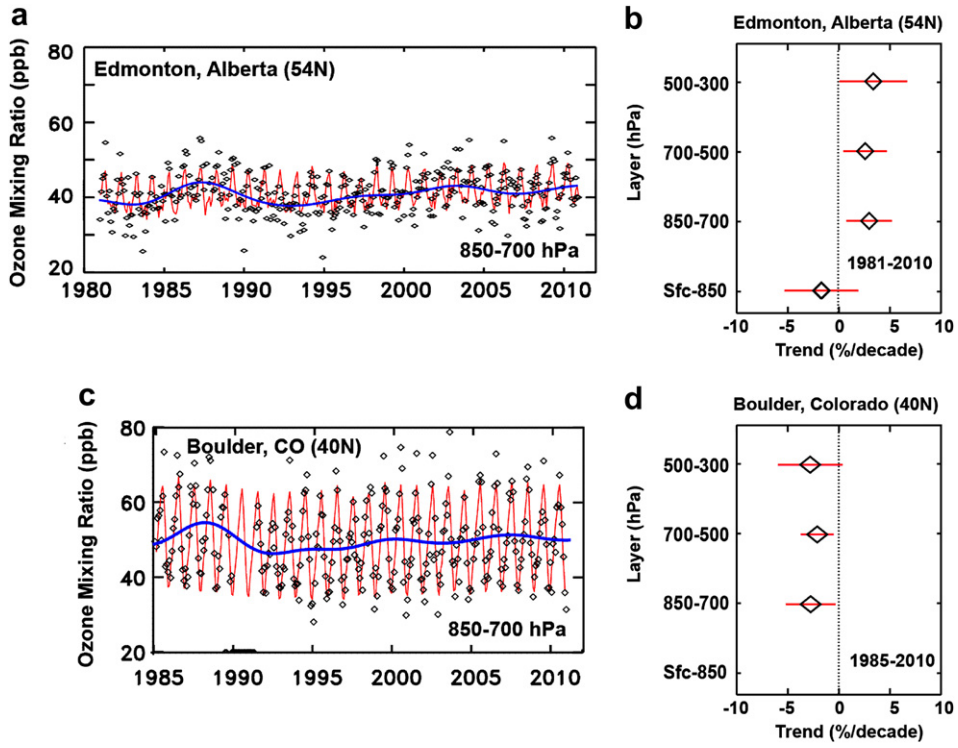

Fig. 9. a) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 850–700 hPa (~1.5–3 km) layer from ozonesondes at Edmonton, Alberta. b) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Edmonton. c) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 850–700 hPa (~1.5–3 km) layer from ozonesondes at Boulder, Colorado. d) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Boulder. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

term changes related to the frequency of the ENSO events (M. Lin – private communication, 2012; Langford et al., 1998).

3.6. South Polar (Antarctica)

Unlike the north polar region, much of the south polar region is encompassed by the Antarctic continent and surrounding permanent and seasonal ice cover. This region is also much more isolated from the influence of populated continental areas of the S.H. The continuous surface record at South Pole begins in 1975. Continuous (weekly) ozonesonde measurements at South Pole begin in 1986. At Syowa Station near the Antarctic coast ozonesonde measurements began in the mid 1960s but the record is not continuous. Continuous measurements began at Syowa in 1987. At the surface at South Pole (Fig. 16a), there is gradual decline from the beginning of the record into the mid 1990s and a slow recovery so that overall there has been no change. Ozone mixing ratios during both the seasonal maximum (winter) and minimum (late summer) follow this pattern. The overlapping continuous ozonesonde records from South Pole and Syowa beginning in 1987 show no change (Fig. 16b). From 1991 at the time of the minimum in the South Pole surface record both sonde records show a small increase at most levels that is not statistically significant. Thus the surface and sonde records are consistent in showing the gradual increase after the mid 1990s.

4. Discussion and summary

The wide spectrum of processes that influence the distribution and possible longer-term changes in tropospheric O_3 suggest that regional differences will often dominate. The approach taken in this analysis is to look at data from a variety of locations spread over a number of geographic regions. On a global basis, these rather broadly defined geographic regions each have a limited number of locations with measurement records of 20 years or longer. In the Arctic, the longest continuous records are limited to North America from Canada and Alaska. The 30-year ozonesonde record at the Canadian high Arctic site has shown a decadal decrease followed by an increase (Fig. 3a) that has been associated with changes in the stratosphere (Tarasick et al., 2005) but the overall change has been small. Kivi et al. (2007) examined several Arctic ozonesonde records, including the European Arctic, during the period 1989 to 2003 and found a significant increase during the winter and early spring months. This is consistent with the results found here and those of Tarasick et al. (2005) where O_3 increased in the 1990s and early 2000s (Table 3 and Fig. 3a). The Barrow data, during this overlapping 30-year period, generally present a similar pattern for the surface observations (Fig. 2a). Whether the significant increase at Barrow, prior to the early 1980s (Fig. 2c), is related to this decadal variability is not clear. As discussed below, several of the mid-latitude locations also showed increases in the earliest portion of the record that likely were not associated with changes in the stratosphere.

At mid-latitudes of the N.H., where the bulk of O_3 precursors are emitted, there are more numerous tropospheric O_3 measurements with extended records (Fig. 17a and b). In western Europe, the evidence appears strong that tropospheric O_3 increased substantially into the early 1990s, when restrictions on precursor emissions appear to have led to a flattening or even a decline in O_3 concentrations (Logan et al., 2012). Even over the North Atlantic, where there is evidence of earlier increases, here also a pattern is observed where increases have ceased, for example at Mace Head and Izaña. As noted in Oltmans et al. (2006), increases into the early 2000s reported by Lelieveld et al. (2004) in the 20°–40°N band over the North Atlantic are consistent with the O_3 changes seen at Izana. The lack of change seen in the 40°–60°N band over the same period reported by Lelieveld et al. (2004) is different from the increases

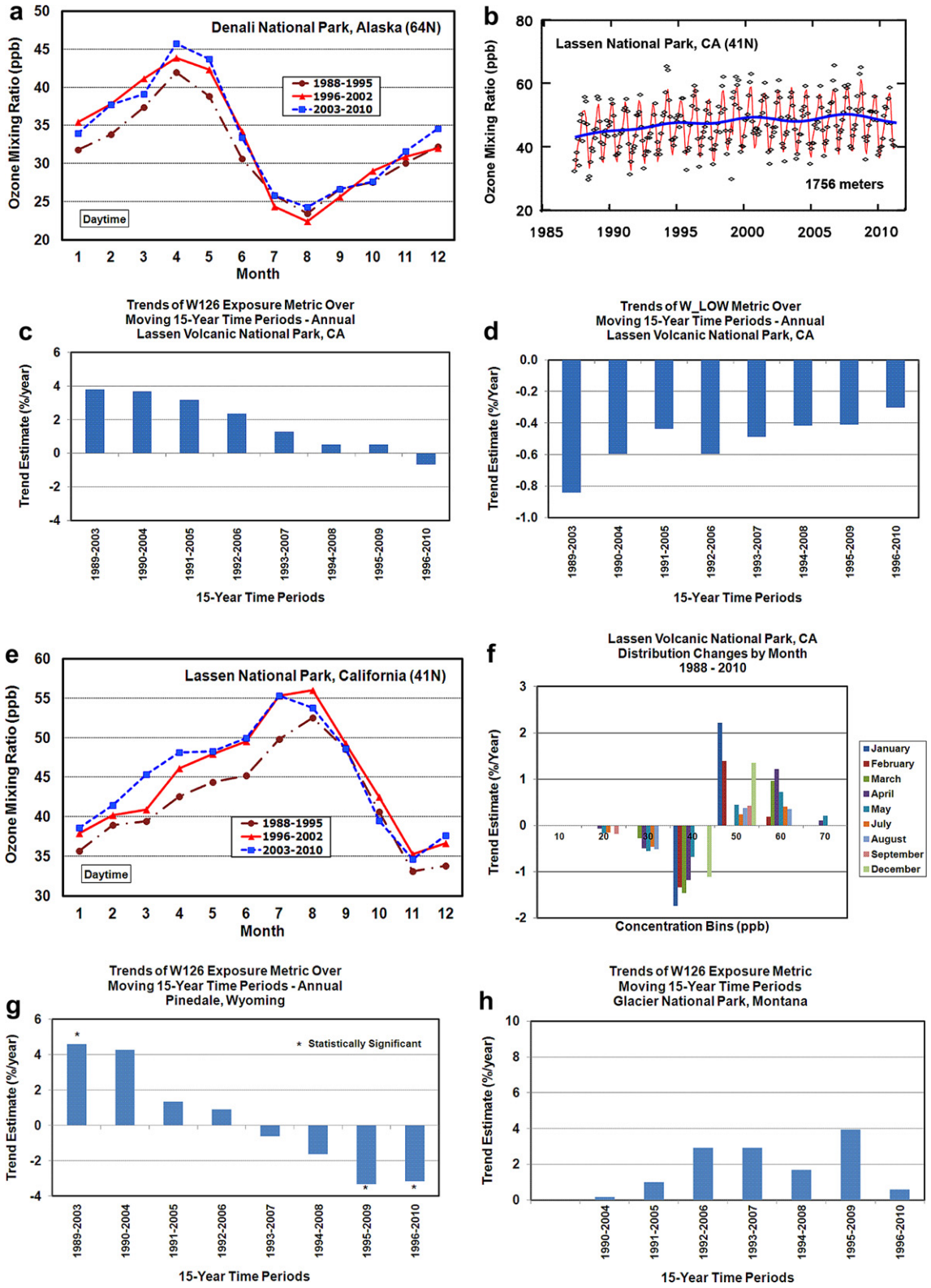

Fig. 10. a) The seasonal variation of daytime surface O_3 at Denali National Park, Alaska for three periods (1988–1995, 1996–2002, and 2003–2010); b) Monthly mean, model fit and smooth trend curve of the O_3 mixing ratio at Lassen Volcanoes NP, California; c) Moving 15-year trends at Lassen NP of the W126 exposure metric; d) Moving 15-year trends of the W_Low metric at Lassen NP. Significant trends are marked with an asterisk; e) The seasonal variation of daytime surface O_3 at Lassen NP for three periods (1988–1995, 1996–2002, and 2003–2010); f) Change in occurrence of O_3 values in 10 ppb bins at Lassen NP for months with significant changes. g) Moving 15-year trends at Pinedale, Wyoming and h) moving 15-year trends at Glacier NP, Montana of the W126 exposure metric. Significant trends are marked with an asterisk.

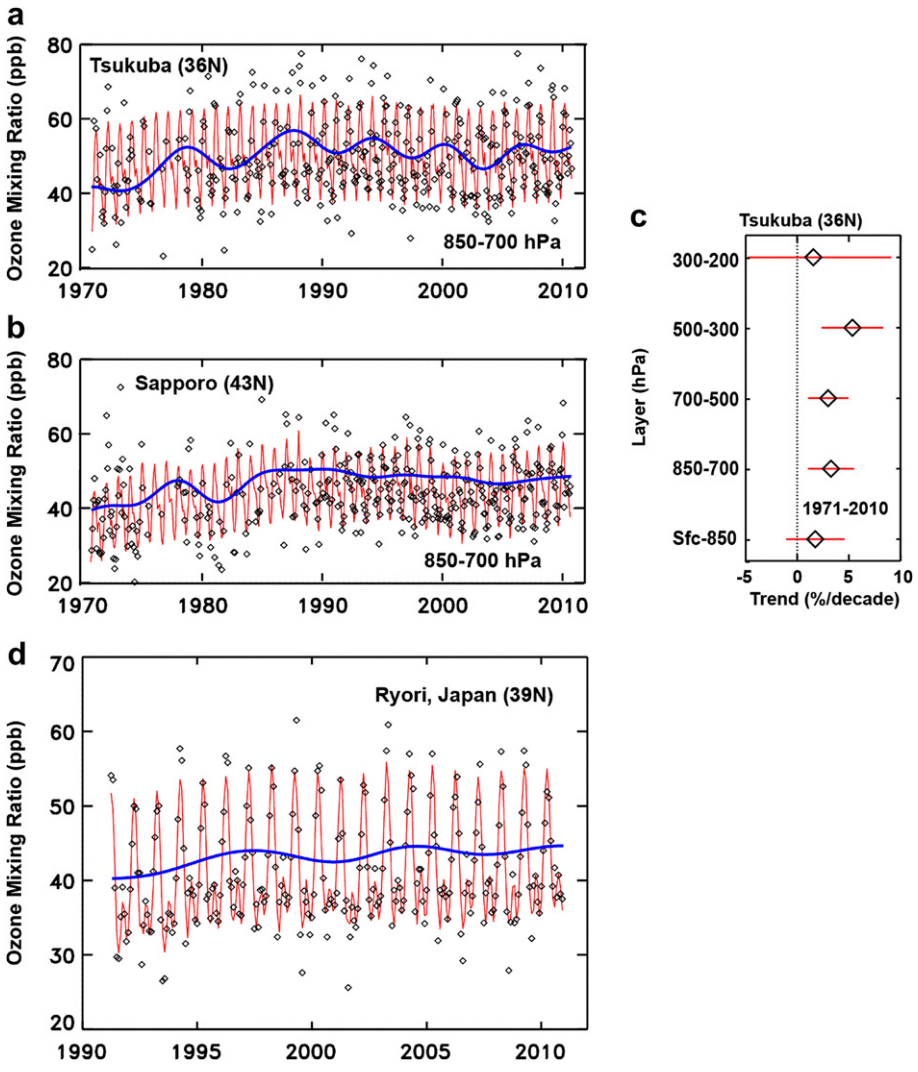

Fig. 11. Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the O_3 mixing ratio in the 850–700 hPa (~1.5–3 km) layer from ozonesondes at a) Tsukuba, Japan and b) Sapporo, Japan. c) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Tsukuba, Japan. d) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) for the surface O_3 mixing ratio at Ryori, Japan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reported here for the North Atlantic locations, where the leveling off is more recent. In eastern North America there does not appear to be as strong a pattern of earlier increases as observed in western Europe, but at Whiteface Mountain, there is a definite flattening and decline in the last couple of decades. In western North America, the time series only extend back into the mid-1980s. At several locations, there has been no substantial change, while a few sites indicate a modest initial increase that has recently flattened. Assessing changes in Asia presents the greatest uncertainty because long records are only available from Japan. The extent to which these records reflect changes primarily in Japan or are also indicative of changes over continental East Asia is not clear. The Japanese ozonesonde records depict a pattern that is not greatly different from that observed in Europe and North America, with increases in the early portion of the record but generally flat or declining trends more recently.

Although details appear to vary between regions in the N.H., it appears that for the last 10–15 years a pattern of no substantial change is predominant. This likely reflects the reduction of precursor emissions in stable developed economies. Lefohn et al. (1998) noted that the shift from the lower concentrations upward appeared to be associated with lack of NO_x scavenging as precursors were reduced. Our current results show that over some periods the frequency of the lower hourly average concentrations is decreasing with a shift from the lower concentrations upward into the mid-level concentration range and the higher concentrations downward. The frequency of lower concentrations has decreased due to NO_x titration and higher concentrations reduced from less photochemical production as precursors are reduced. This shifting of low- and mid-level values is slowing down and in some cases, changing direction. At Mace Head, the running 15-year W_Low metric indicates that hourly average O_3 was shifting from the lower to the mid-level concentrations during the earlier part of the record (Fig. 6), slowing down for the most recent 15-year periods, and changing direction (i.e., mid-level concentrations shifting to the lower levels) for the last 15-year period. Similar patterns are observed for the sites at Zugspitze (Fig. 4) and Izaña (Fig. 7). These observations are important for assessing whether changes in the lower end of the distribution may be associated with processes related to reduced regional emissions or changes in background O_3 levels. Mace Head, Izaña, and Zugspitze show recent indications that the frequency of mid-level concentrations is shifting from the

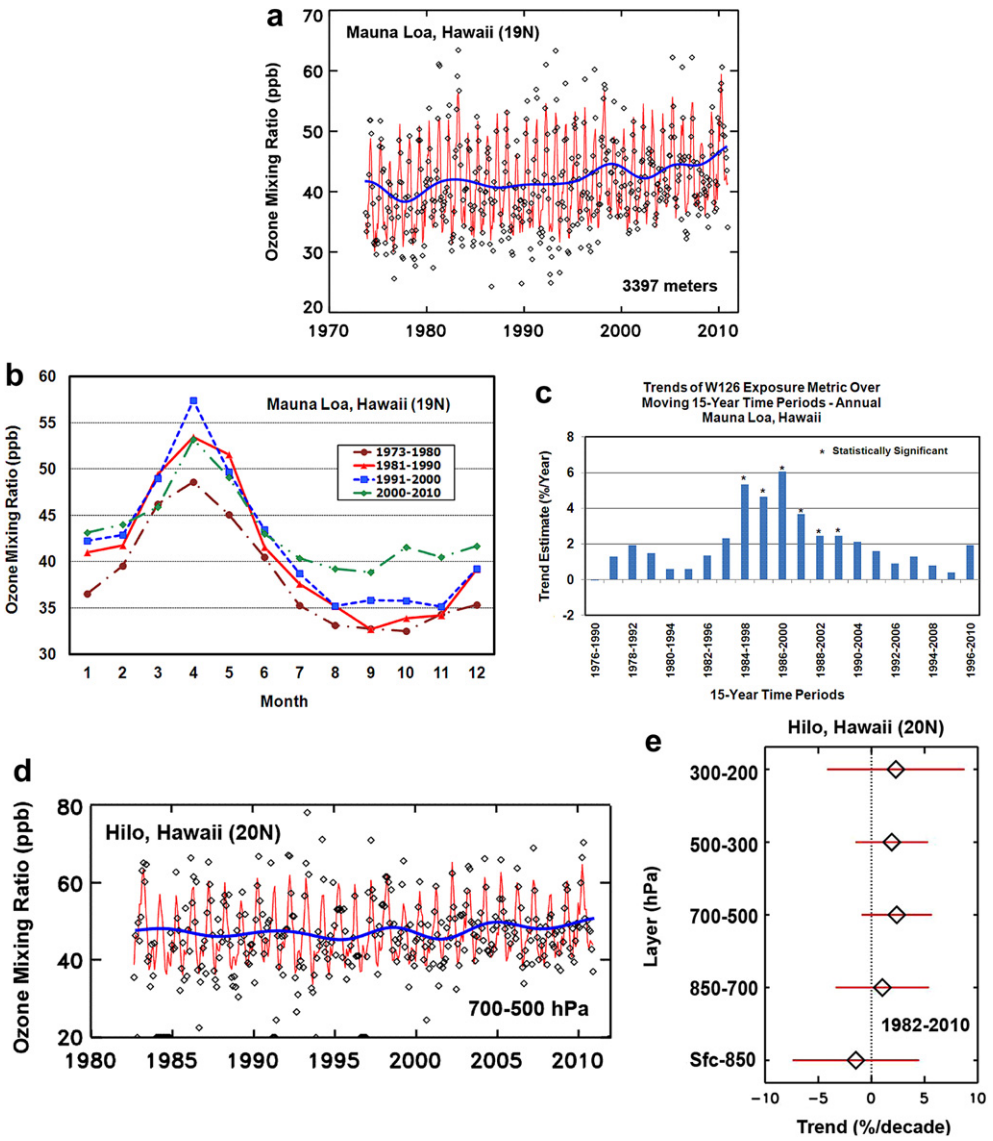

Fig. 12. a) Monthly mean (black diamonds), model fit (red line) and smooth trend curve (blue line) of the O_3 mixing ratio at Mauna Loa, Hawaii. b) The seasonal variation of surface O_3 for 10-year periods at Mauna Loa. c) Moving 15-year trends at Mauna Loa of the W126 metric. d) Monthly mean, model fit and smooth trend curve for the O_3 mixing ratio in the 700–500 hPa (~3–6 km) layer from ozonesondes at Hilo, Hawaii. e) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Hilo. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

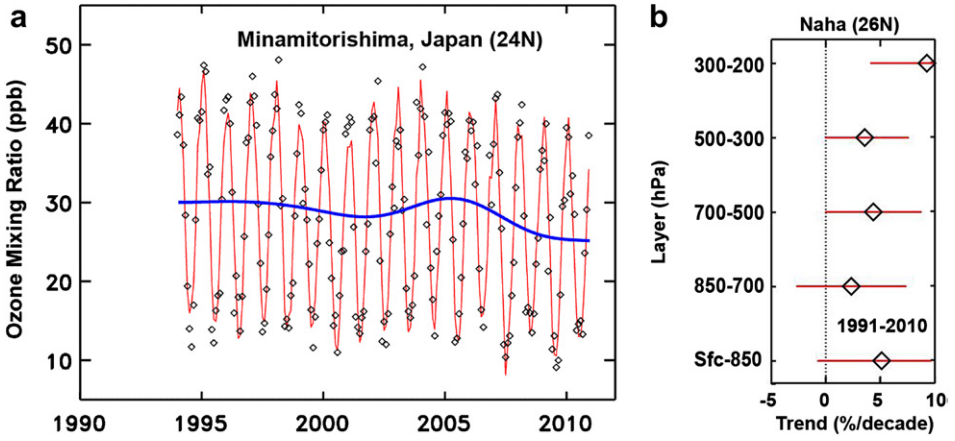

Fig. 13. a) Monthly mean, model fit, and smooth trend curve of the surface O_3 mixing ratio at Minamitorishima, Japan. b) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Naha, Japan.

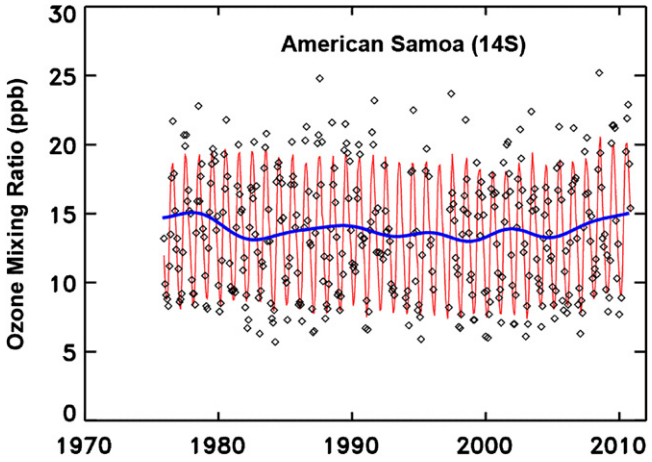

Fig. 14. Monthly mean, model fit, and smooth trend curve of the surface O_3 mixing ratio at American Samoa.

mid-level down into the lower concentrations range and may indicate a stabilizing or decline in background O_3. Were reduced NO_x scavenging or increased background O_3 responsible, one would anticipate a shift from the lower concentrations to the mid-levels.

The extent to which the stations investigated are sensitive to the impact of growing Asian emissions on the hemispheric background is unclear. Recent evidence suggests that the contributions of stratosphere-to-troposphere exchange (STE) on surface O_3 in the western US may be greater than from Asian emissions (Ambrose et al., 2011; Lin et al., 2012b). STE contributes to the variability but it is not clear to what extent it may contribute to longer-term changes. For Lassen NP, the concentration values are lower in the earlier part of the record and then begin to rise but begin to flatten by 2000. The running 15-year W126 trends at Lassen NP are not statistically significant but overall there has been a declining trend in the running 15-year periods. The lack of a statistically significant trend pattern was noted by Lefohn et al. (2010). Although not statistically significant, the running 15-year W_Low metric shows that the rate of shifting from the lower to the mid-level concentrations has lessened over the period of record. These results, coupled with those reported earlier by Oltmans et al. (1998, 2006) and recently by Logan et al. (2012) suggest that on a hemispheric scale it is currently difficult to observe the projected increases in tropospheric O_3 that models indicate may occur from growing Asian emissions. This may result from the lack of such O_3 increases or that changes resulting from precursor reductions in North America and Europe have made the influence of Asian precursor emissions more difficult to detect. Changes in hourly average O_3 distributions at the low-, mid- and high-level ranges for sites investigated in this study do not indicate that background O_3 concentrations continue to increase in the most recent decades. As indicated in our analysis and others, at many of the investigated sites earlier O_3 increases have reached a plateau and in some cases begun to decrease. Reductions in NO_x emissions of 45% in the US (http://www.epa.gov/airtrends/nitrogen.html) and ~40% in Europe (http://www.eea.europa.eu/data-and-maps/indicators/eea-

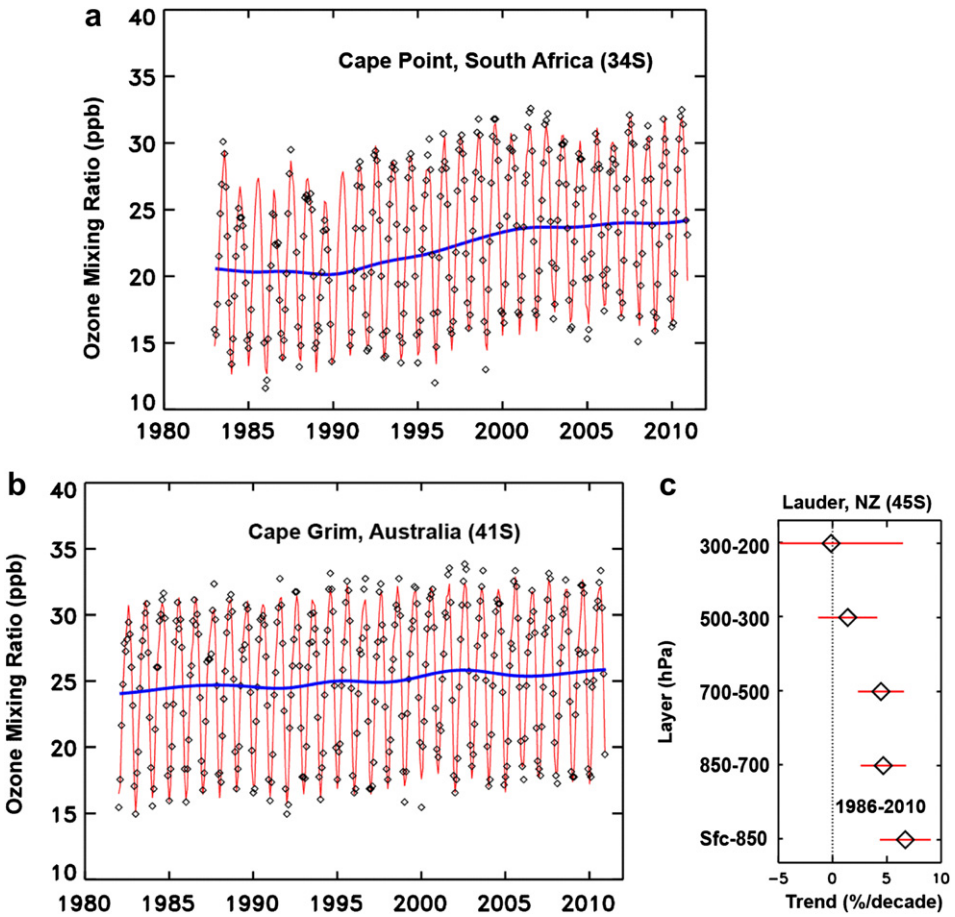

Fig. 15. Monthly mean, model fit, and smooth trend curve of the surface O_3 mixing ratio at a) Cape Point, South Africa and b) Cape Grim, Australia. c) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Lauder, New Zealand.

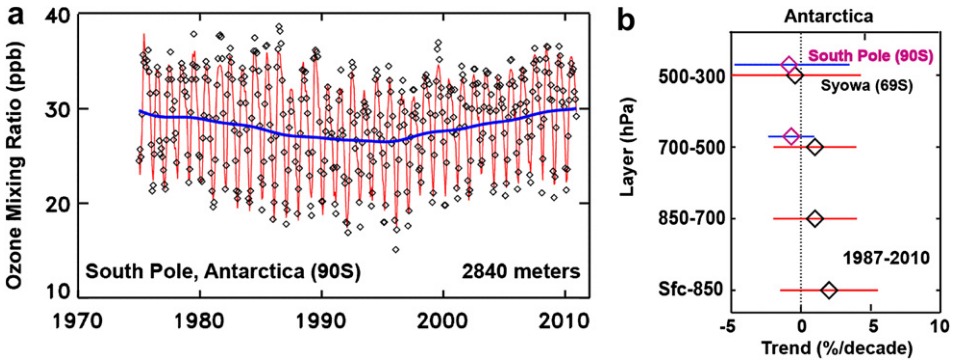

Fig. 16. a) Monthly mean, model fit, and smooth trend curve of the surface O_3 mixing ratio at South Pole, Antarctica. b) Year-round linear trend of the monthly mean O_3 in layers in the troposphere at Syowa and South Pole, Antarctica.

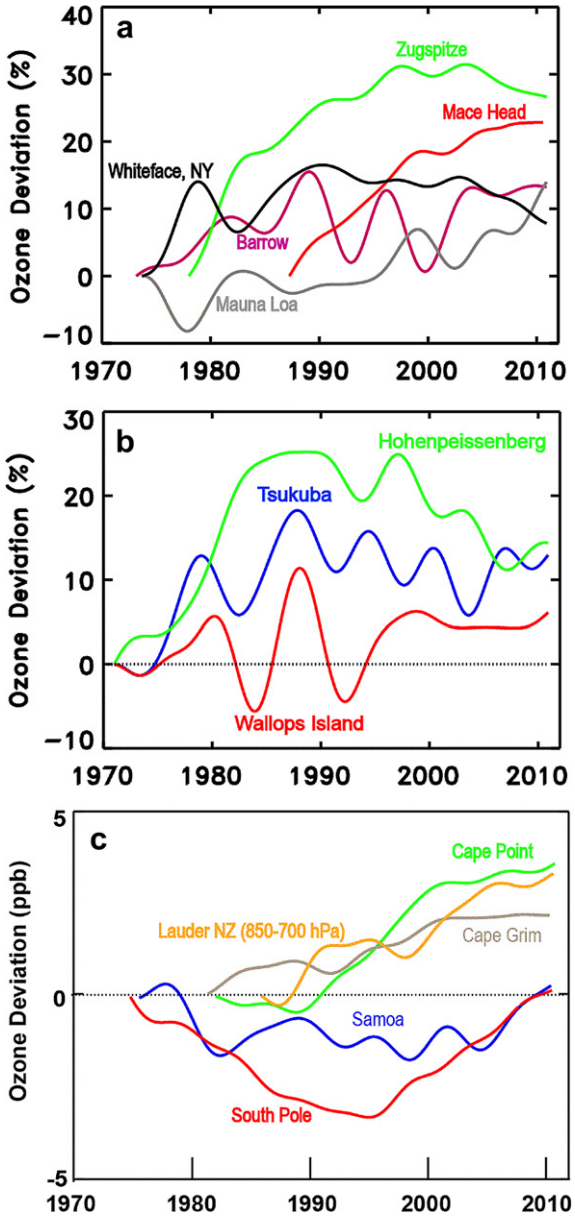

Fig. 17. a) Summary of trend of four N.H. surface O_3 locations. b) Summary of O_3 trend curves for the 850–700 hPa layer at three N.H. ozonesonde sites. c) Summary of O_3 trends for S.H. stations. The trend curves are taken from the smoothed fit to the modeled monthly residuals.

32-nitrogen-oxides-nox-emissions/eea-32-nitrogen-oxides-nox) over the past two decades suggest that background O_3 increases associated with NO_x emission increases may have peaked within the past decade. Ten to 15 year O_3 records from China (Ding et al., 2008; Wang et al., 2009, 2012) show increasing O_3 although several downwind Japanese locations do not appear to reflect these changes. With emission slowdowns in China (Lin and McElroy, 2011) and planned further reductions (www.chinadaily.com.cn/bizchina/2012-/02/01/content_14519125.htm), it will be important to monitor possible O_3 changes in China to see if what appears to be a flattening or decline of O_3 in the mid-latitudes of the N.H. is sustained.

S.H. tropical and polar locations (Fig. 17c) show decadal periods of increasing and decreasing O_3, but over the 40-year horizon there has been little overall change. In the future the SHADOZ sites in both the tropical South Pacific and South Atlantic may enable a broader perspective on changes in the tropics. At S.H. mid-latitudes there have been significant increases but over the most recent decade there is some indication that these increases have moderated (Fig. 17c). The increases reported by Lelieveld et al. (2004) in the South Atlantic into the early 2000s are consistent with the measurements at Cape Point. The inclusion of an additional decade of observations at Cape Point shows the moderation of this increase. The limited tropical data analyzed in this work does not provide additional perspective on the increases reported for the upper troposphere in the work of Bortz et al. (2006) for the nine year (1994–2003) MOZAIC record.

In order to follow future trend patterns, it will be important to use techniques that capture the time evolution of O_3 changes such as the running 15-year trend periods used here or other methods that detect these changes. In particular it will be important to determine if the widespread flattening or declining O_3 concentrations reported here reflect longer-term changes in precursor O_3 emissions.

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