

## Lower tropospheric ozone at northern midlatitudes: Changing seasonal cycle

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[1] At northern midlatitudes the abundance of tropospheric O<sub>3</sub> has increased by a factor of approximately 2 since the 1950s. The cause of this increase is generally attributed to increasing anthropogenic precursor emissions, but present chemical and transport models cannot quantitatively reproduce its magnitude. Here we show another manifestation of changes in O<sub>3</sub> abundance—a shift of the seasonal cycle at northern midlatitudes so that the observed peak concentrations now appear earlier in the year than in previous decades. The rate of this shift has been 3 to 6 days per decade since the 1970s. We examine possible reasons to explain this shift and suggest it is due to changes in atmospheric transport patterns combined with spatial and temporal changes in emissions. Detailed modeling is necessary to test these hypotheses; this investigation will provide useful guidance for improving global chemistry-climate models and stringent tests of the model results. **Citation:** Parrish, D. D., K. S. Law, J. Staehelin, R. Derwent, O. R. Cooper, H. Tanimoto, A. Volz-Thomas, S. Gilge, H.-E. Scheel, M. Steinbacher, and E. Chan (2013), Lower tropospheric ozone at northern midlatitudes: Changing seasonal cycle, *Geophys. Res. Lett.*, 40, 1631–1636, doi: 10.1002/grl.50303.

### 1. Introduction

[2] Ozone (O<sub>3</sub>) is one of the most important trace constituents of the troposphere, where it acts as a pollutant in rural and urban areas [Royal Society, 2008], as a greenhouse gas, thereby contributing to global climate change [Gauss *et al.*, 2006], and as the precursor of the hydroxyl radical, which is responsible for oxidation and removal of many atmospheric

pollutants [Levy, 1971]. In the troposphere, O<sub>3</sub> originates from downward transport from the stratosphere and from photochemical production from precursors emitted by natural and anthropogenic sources. It is destroyed photochemically and by dry deposition at the surface [Crutzen, 1973]. Ozone and its precursors are also transported between continents. It can also be formed over downwind regions from decomposition of nitrogen oxide (NO<sub>x</sub>) reservoirs, in particular peroxyacetyl nitrate. Thus, O<sub>3</sub> concentrations over a particular region depend not only on local and regional emissions, but also on import from upwind emission regions [HTAP, 2010].

[3] Analysis of surface data from northern midlatitudes shows that the abundance of tropospheric O<sub>3</sub> has changed, increasing by about a factor of 2 since the 1950s, with generally increasing surface O<sub>3</sub> in all seasons at relatively remote sites at northern midlatitudes [e.g., Staehelin *et al.*, 1994; Parrish *et al.*, 2012, and references therein]. This increase slowed, at least over Europe, by the late 1990s, and at some European sites O<sub>3</sub> has begun to decrease, particularly in summer [e.g., Logan *et al.*, 2012]. Chemical transport models generally attribute this general O<sub>3</sub> increase to increasing anthropogenic precursor emissions and changes in meteorology or natural emissions [e.g., Stevenson *et al.*, 2012]. However, attribution varies significantly between studies and models have difficulties quantitatively reproducing the magnitude of observed trends [e.g., Pozzoli *et al.*, 2011]. Here we show another manifestation of changes in O<sub>3</sub> abundance, a shift of the seasonal cycle at northern midlatitudes so that observed seasonal maxima now appear earlier in the year than they did 20 years ago.

[4] Over populated continental areas at northern midlatitudes, surface O<sub>3</sub> exhibits a well-known summertime maximum that is generally attributed to the peak in local and regional photochemical production at this time of year. Over more remote continental areas surface O<sub>3</sub> generally has a late spring maximum attributed to both enhanced stratospheric input and hemisphere-wide photochemical production during that season [Holton *et al.*, 1995; Monks, 2000]. Sites within the marine boundary layer exhibit a spring maximum with a summer minimum due to enhanced photochemical destruction in that season. The general long-term O<sub>3</sub> increase has important seasonal differences that necessarily imply a concurrent change in the seasonal cycle of O<sub>3</sub>. For example, at Hohenpeissenberg in Germany, where O<sub>3</sub> has been continuously measured since 1971, summer was the season of maximum O<sub>3</sub> throughout at least the first three decades of the data record. However, in recent years O<sub>3</sub> concentrations in spring have been comparable to those in summer [see Parrish *et al.*, 2012, Figure 2]. Here we quantitatively examine how the seasonal cycle in tropospheric O<sub>3</sub> at northern midlatitudes has evolved over the past four decades, possibly

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in response to changing anthropogenic emissions, natural variability, and changing global climate.

## 2. Data Sets and Analysis

[5] To quantify long-term changes in lower tropospheric O<sub>3</sub> concentrations at northern midlatitudes, Parrish *et al.* [2012] examined 11 data sets that included measurements in Europe, North America, and Asia. Here we examine five of those data sets that are most appropriate (those with longest continuous data records from single sites with year-round coverage) for quantifying the evolution of the O<sub>3</sub> seasonal cycle over decadal time scales. These data sets include four European records: two from alpine sites (Zugspitze, Germany and Jungfrauoch, Switzerland), a lower elevation, midcontinental site (Hohenpeissenberg, Germany) and a marine boundary layer site (Mace Head, Ireland). The European data were provided by coauthors of this paper; the German and Swiss data are as described by Gilge *et al.* [2010]. The Jungfrauoch and Hohenpeissenberg data are also available from the World Data Centre for Greenhouse Gases at <http://ds.data.jma.go.jp/gmd/wdcgg/>. The Mace Head data are filtered for baseline conditions based on the NAME Lagrangian dispersion model as described by Derwent *et al.* [2007]. A single North American site is also examined. Monthly averages at Lassen NP were calculated from hourly average data provided by the U.S. National Park Service, Air Resources Division (available at <http://www.nature.nps.gov/air/monitoring/network.cfm>). Parrish *et al.* [2012] give more details of these data sets and sites, including a map of site locations. For all sites, the full data records are included in the analyses.

[6] We use two approaches to quantify the O<sub>3</sub> seasonal cycle change and its uncertainty at a particular site. First is to fit a sine function to monthly average data from 5 year time periods at the beginning and at the end of the data record, and then to determine if the parameters of the functional fits are statistically significantly different between the two time periods. These fits are to a three-parameter equation

$$y = y_o + A^* \sin(x + \phi), \quad (1)$$

where  $y_o$  is the annual average O<sub>3</sub>,  $A$  is the magnitude of the seasonal cycle,  $\chi$  the month (where 12 months corresponds to  $2\pi$  radians), and  $\phi$  is the phase shift of the seasonal cycle. The derived value of  $\phi$  allows calculation of the date of the year of the annual O<sub>3</sub> maximum:  $(\pi/2 - \phi) * 365/2\pi$ . Equation (1) also can be fit to sequential, overlapping 5 year periods over the entire data record at each site, which then provides a determination of the continuous evolution of the parameters in equation (1). In this latter application, the  $y_o$  parameter in equation (1) is obtained from the average of the seasonal averages over the 5 year period. The seasonal O<sub>3</sub> averages for each year are directly available from the quadratic fits to the seasonal O<sub>3</sub> trends presented by Parrish *et al.* [2012]. This reduces the least-squares regression fit from three to two parameters. Three-parameter regressions to equation (1) give results in close (statistically not significantly different) agreement with the two-parameter fits, but the two-parameter fits give somewhat more precise determinations of the  $A$  and  $\phi$  parameters. Confidence limits for all derived parameters are calculated from standard propagation of error techniques, properly accounting for the number of independent data points included in the regressions.

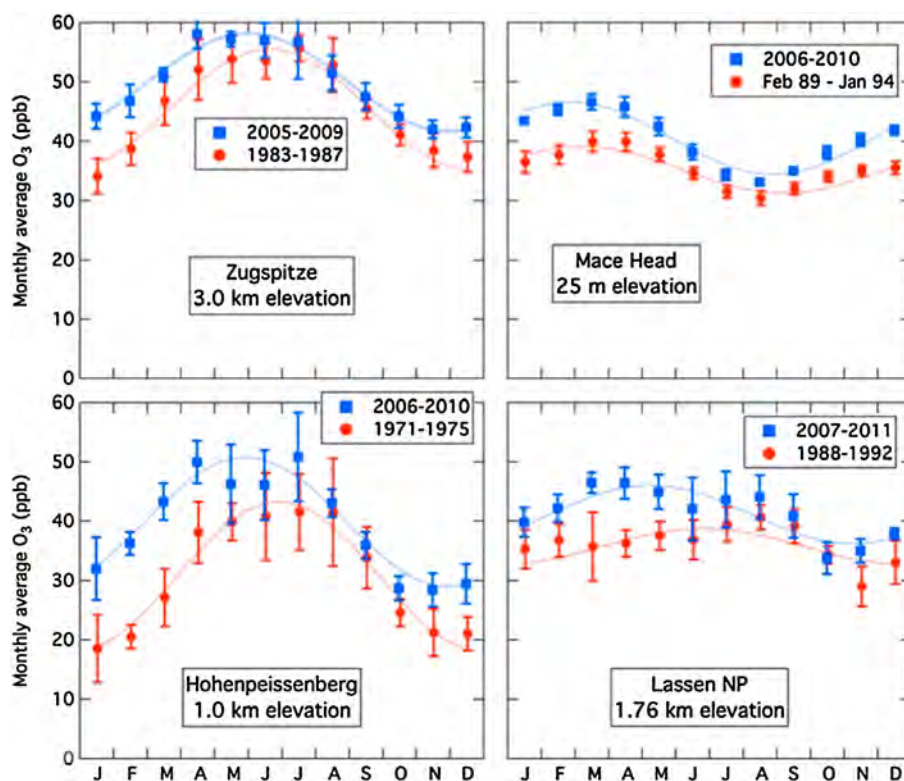
[7] The second approach is to calculate the date of the year when the cumulative ozone concentration reaches 50% of the year's total. This date is determined through three steps designed to be least affected by any gaps of missing data. First, the cumulative hourly O<sub>3</sub> concentration for the entire year is calculated by summing the accumulated hourly average O<sub>3</sub> concentrations in each of the 12 months. The accumulated hourly average O<sub>3</sub> concentration for each month is calculated as the product of the monthly average O<sub>3</sub> concentration multiplied by the hours in the month. Second, the monthly accumulated hourly averages are examined to determine the month during which the cumulative ozone concentration reaches 50% of the year's total. In all cases to be considered that month is either June or July. Third, sequential hourly O<sub>3</sub> averages before or after July 1 are summed to find the date and time corresponding to 50% of the year's total; periods of a few hours or less of missing data are linearly interpolated. This process allows for the unbiased treatment of data sets with some missing data, as long as the data are complete enough to (1) allow calculation of accurate monthly average O<sub>3</sub> concentrations for all months of the years considered, and (2) provide nearly continuous records during the June–July period that includes the 50% cumulative O<sub>3</sub> date. The one data set treated in this manner (Lassen NP) meets these criteria for all years considered.

[8] In the final section, we will discuss column NO<sub>2</sub> maps. They are derived from monthly gridded data from the polar-orbiting GOME and SCIAMACHY sensors, produced and made freely available by the Tropospheric Emission Monitoring Internet Service in The Netherlands ([www.temis.nl](http://www.temis.nl)). These products are based on the methodology of Boersma *et al.* [2004]. Data are available for 1996–2011 at  $0.25^\circ \times 0.25^\circ$  horizontal resolution.

## 3. Results

[9] There is substantial evidence that the seasonal cycle has shifted to earlier in the year at all five of the sites investigated here. For the four sites included in Figure 1, the seasonal maximum occurred 10 to 48 days earlier during the later 5 year period compared to the earlier period; however, only at the two sites with the longest data records, Zugspitze and Hohenpeissenberg, are the differences significant at the 95% confidence level. As expected, significant increases in annual average O<sub>3</sub> are also evident at all sites, reflecting the general O<sub>3</sub> increase that has occurred at northern midlatitudes [e.g., Parrish *et al.*, 2012].

[10] The temporal evolution of the date of the seasonal maximum obtained from fitting a sine function to running 5 year periods (Figure 2) indicates a shift of the seasonal cycle to earlier in the year for all five stations. Table 1 gives the parameters for the linear, least-squares fits to these seasonal maxima as a function of the centers of the 5 year periods. The three European continental sites all have late spring to early summer maxima (dates interpolated to the year 2000 are given in Table 1) that move to earlier in the year at statistically significant and similar rates of 5 to 7 days per decade. Mace Head, a European marine boundary layer site, has a late winter to early spring maximum that also moves to earlier in the year, although the rate of evolution ( $3.0 \pm 3.7$  days/decade) is smaller than found at the continental sites, and is not statistically significant at the 95% confidence limit. Oltmans *et al.* [2013] also noted an indication of a shift



**Figure 1.** Comparison of  $\text{O}_3$  seasonal cycles at three European and one North American site for two periods separated by 17 to 35 years. The data points and error bars indicate 5 year averages and standard deviations of monthly averaged data for the indicated time periods. The curves of the respective colors are sine function fits to the data.

(from April–May to April) of monthly average maximum  $\text{O}_3$  concentrations at Mace Head. These months are later than the March seasonal maxima shown in Figure 2. However, *Oltmans et al.* [2013] considered the full data set rather than the baseline-selected data considered here. Their results are likely affected by episodes of  $\text{NO}_x$ -driven depletion and/or photochemical production of  $\text{O}_3$  in polluted European air masses transported to Mace Head. Nevertheless, the seasonal shift they note parallels that in Figure 2. Lassen NP (the one North American site) has a seasonal cycle that is only poorly represented by a sine function, but also shows indications of a seasonal cycle similar to the European sites together with a similar shift although the shift is not statistically significant. A statistically significant shift in the date of the year when the cumulative ozone concentration reaches 50% of the year's total at Lassen NP ( $3.6 \pm 3.0$  days/decade) is apparent (Figure 2). The magnitude of this shift cannot be directly compared to the shift in the seasonal cycle maxima given in Table 1, because these are different measures of the phase of the seasonal cycle.

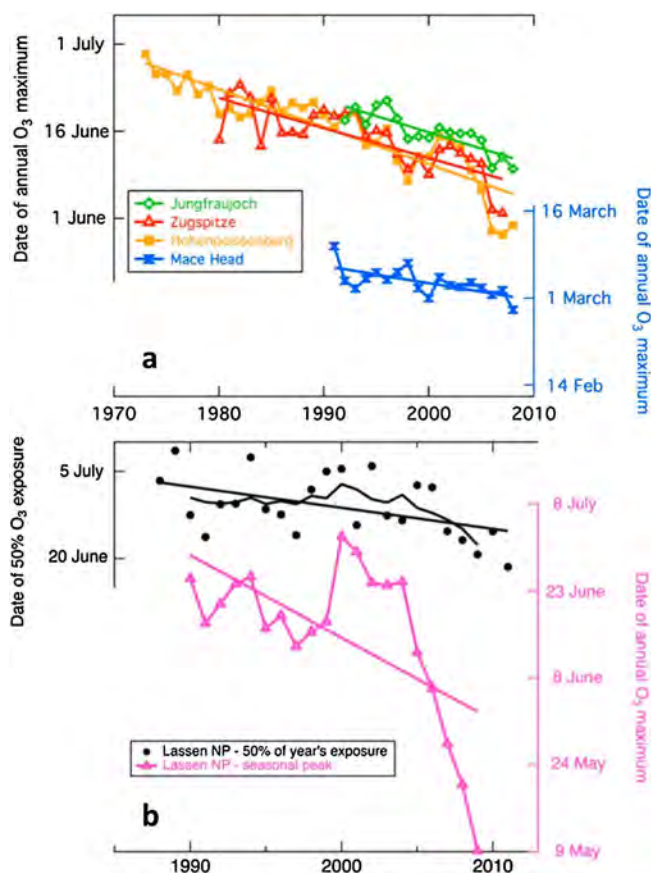
[11] In summary, these five sites, which provide the longest continuous records of surface  $\text{O}_3$  concentrations at relatively remote sites in the northern midlatitudes, all show substantial evidence for the seasonal cycle shifting so that the yearly maximum  $\text{O}_3$  appears earlier in the year. Long-term increases in northern midlatitude, lower troposphere  $\text{O}_3$  have occurred from the 1950s to the present [e.g., *Staehelin et al.*, 1994; *Parrish et al.*, 2012]. The  $\text{O}_3$  seasonal cycle has changed concurrently with this increase in concentrations (Figures 1 and 2). Importantly, this seasonal cycle shift is not due simply to local or regional influences. The Mace Head data analyzed here have been filtered to remove recent European influence [see *Parrish et al.*, 2012]. A separate analysis of

a Jungfraujoch data set that was similarly filtered [*Cui et al.*, 2011] yields a seasonal shift statistically consistent with those shown in Figure 2a. Although these sites provide only sparse coverage of the northern midlatitudes, the sites do represent baseline (here understood as representative of continental to hemispheric scales)  $\text{O}_3$  [*Parrish et al.*, 2012], so we hypothesize it is a hemisphere-wide phenomenon. To support this hypothesis, it would be useful to extend this analysis to other  $\text{O}_3$  data sets (e.g., those described in *Logan et al.* [2012]), although we note that few existing long-term records are appropriate for this type of analysis. We now discuss possible causes for this seasonal cycle shift.

#### 4. Discussion

[12] The seasonal cycle in tropospheric  $\text{O}_3$  at northern midlatitudes has evolved over the past four decades in response to changing anthropogenic emissions, natural variability on annual or decadal time scales, and changing global climate. Climate change may have caused changes in stratosphere to troposphere transport, tropospheric transport patterns, and increased temperatures, water vapor, and changes in natural emissions (e.g., lightning, forest fires, and vegetation). Here we suggest possible hypotheses to explain the observed changes in the  $\text{O}_3$  seasonal cycle. The following discussion considers several possibilities related to (1) changes in transport and pollution transport pathways, (2) changes in emissions and ozone photochemistry, and (3) factors related to climate change.

[13] First, changes in atmospheric transport may have influenced pollution transport pathways or transport of  $\text{O}_3$  from the stratosphere, possibly in response to changing climate. Transport of stratospheric  $\text{O}_3$  to the troposphere is at



**Figure 2.** Temporal evolution of O<sub>3</sub> seasonal cycle at a) four European sites and b) one North American site. Three of the ordinates indicate the date of the maximum of a sine function fit to a 5 year period of monthly average data. The left ordinate in b) gives the date when each year's cumulative integrated O<sub>3</sub> concentration reached 50%. The lines indicate linear, least-squares fits to the points, and the solid black curved line in Figure 2b indicates 5 year smoothed results.

a maximum in spring [Tang *et al.*, 2011], while photochemical O<sub>3</sub> production maximizes in summer. Hence, the observed shift of the O<sub>3</sub> maximum concentration to earlier in the year may imply that the relative contribution from the stratosphere is increasing. Strong correlations between observed O<sub>3</sub> anomalies in the lower stratosphere and, for example, European mountain sites, support this hypothesis, although no trend in air mass fluxes across the tropopause was found [Ordóñez *et al.*, 2007]. Changes in the large-scale circulation in the troposphere may have also played a role. For example, an increased prevalence of stronger westerly flow over the North Atlantic, related to changes in the North Atlantic Oscillation, from the late 1980s up to the late 1990s may have led to increased O<sub>3</sub> in northwestern Europe in the winter and spring [Pausata *et al.*, 2012]. These changes may result in enhanced transport of pollution from North America to Europe at this time of year [Creilson *et al.*, 2003] due to more active frontal transport [Eckhardt *et al.*, 2003]. They may also be related to increased downward transport of stratospheric O<sub>3</sub> [Sprenger and Wernli, 2003]. However, although certain studies suggest significant stratospheric influence, even at surface sites [e.g., Hess and Zbinden, 2013], other analyses show larger contributions from upwind regions compared to the stratosphere (e.g., Cui *et al.* [2011] find that only 4–8% of air masses at Jungfraujoch have strong stratospheric influence). This suggests that enhanced, more efficient intercontinental transport of O<sub>3</sub> and its precursors in winter and spring may have contributed to changing seasonality.

[14] Second, changing emissions and subsequent photochemical production within the troposphere may also have played a role in the shift of the O<sub>3</sub> seasonal cycle. Over the past two decades, global anthropogenic emissions of O<sub>3</sub> precursors have remained approximately constant in magnitude [Granier *et al.*, 2011], but their spatial distribution has changed significantly. North American and European emissions have generally decreased, while eastern Asian emissions have increased. The satellite data presented in Figure 3 demonstrate that this effective shift of emissions is not only between continents, but also from more northerly to more southerly latitudes. This may have led to an earlier onset of significant photochemical production, supported by observations of earlier O<sub>3</sub> maxima at southerly Japanese sites [Tanimoto *et al.*, 2005]. Earlier spring-time photochemical O<sub>3</sub> production over Asia may also be leading to increased peroxyacetyl nitrate production that could lead to increased ozone production during transport and/or over downwind continents. These factors coupled with more efficient springtime vertical and westward transport of Asian pollution and more efficient O<sub>3</sub> production in lofted air masses [Wild and Akimoto, 2001] may explain the increase in springtime O<sub>3</sub> concentrations in more recent years over North America and Europe. Significant increases in springtime free tropospheric O<sub>3</sub> over North America, particularly in air masses originating in East Asia, have been reported by Cooper *et al.* [2010, 2012]. Multimodel apportionment studies also support enhanced springtime contributions from Asian emissions to European lower

**Table 1.** Temporal extent of data records and results of linear regressions (Figure 2) to the parameters of the sine function least-squares fits (based on Eq. (1)) to five data sets. Indicated uncertainties are 95% confidence limits of the respective quantities

Site	Lat./ Long.	Elev. (km)	Data Record	Date of Seasonal Maximum in 2000	Shift in Seasonal Maximum (Days/Decade)
Jungfraujoch, Switzerland	46°33'N/7°59'E	3.6	1990–2010	14 June $\pm$ 2.0 days	5.6 $\pm$ 4.1
Zugspitze, Germany	47°25'N/10°59'E	3.0	1978–2009	10 June $\pm$ 3.6 days	5.1 $\pm$ 3.5
Hohenpeissenberg, Germany	47°48'N/11°01'E	1.0	1971–2010	9 June $\pm$ 3.3 days	6.4 $\pm$ 2.4
Mace Head, Ireland	53°10'N/9°30'W	0.02	1989–2010	2 March $\pm$ 1.9 days	3.0 $\pm$ 3.7
Lassen NP, California, USA	40°32'N/121°35'W	1.8	1988–2011	14 June $\pm$ 11 days	14 $\pm$ 19

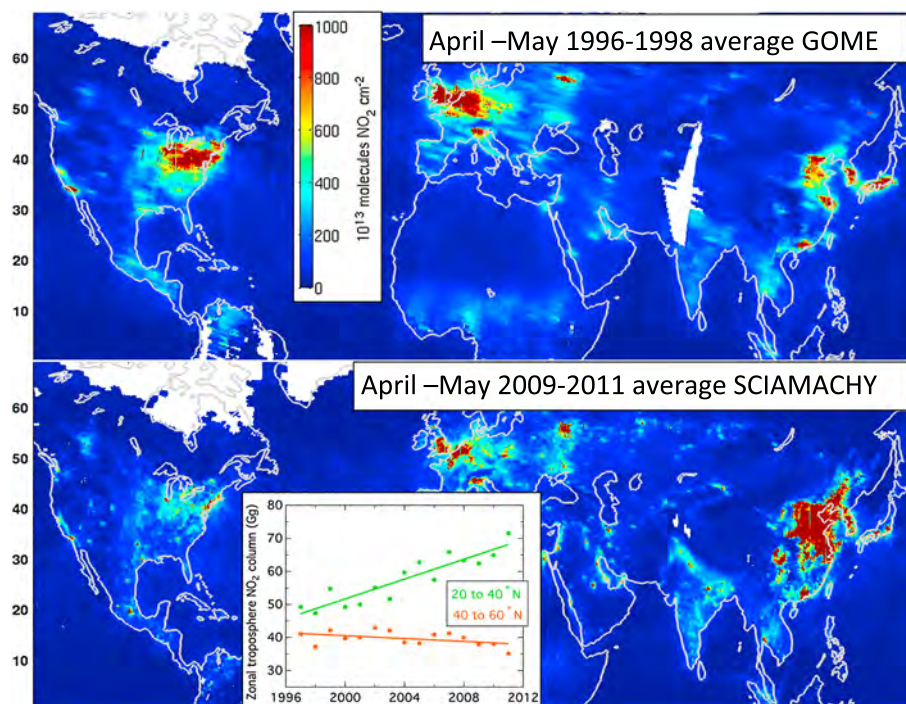
tropospheric O<sub>3</sub> over the last 2 decades (Oliver Wild et al., manuscript in preparation, 2013).

[15] In contrast, within Europe and North America, decreasing O<sub>3</sub> precursor emissions have led to reductions in peak summertime ozone concentrations at surface continental sites [Royal Society, 2008; Cooper et al., 2012]. At the same time decreasing NO<sub>x</sub> emissions have resulted in less loss of O<sub>3</sub> via NO titration in winter and early spring [e.g., Jonson et al., 2006], manifesting itself in positive wintertime O<sub>3</sub> trends at European and North American sites [e.g., Wilson et al., 2012; Parrish et al., 2012; Cooper et al., 2012]. It is worth noting that stronger seasonal cycle changes are seen in unfiltered Mace Head data (not shown) most likely driven by reductions in European NO<sub>x</sub>, especially in winter. Hence, reduced summertime photochemical production and reduced winter/early spring photochemical removal of O<sub>3</sub> at more northerly European and North American latitudes, combined with increased springtime photochemical production of O<sub>3</sub> at

more southerly Asian latitudes, may synergistically act to yield an earlier seasonal O<sub>3</sub> maximum.

[16] Third, changes in other processes linked to climate change or natural variability may have also played a role. Variations in temperature, water vapor, and natural emissions, driven by meteorological conditions, contribute to surface O<sub>3</sub> variability on interannual or multiannual time scales, although there are large differences between factors found to be important in different studies [e.g., Hess and Mahowald, 2009; Pozzoli et al., 2011]. While the impacts of climate change due to increases in anthropogenic emissions on the O<sub>3</sub> seasonal cycle are currently unknown, some studies [e.g., Stevenson et al., 2012] suggest that climate change between preindustrial times and present day has affected Northern Hemisphere lower tropospheric O<sub>3</sub> by just a few ppbv.

[17] Without detailed global chemical model simulations that can accurately reproduce the observed O<sub>3</sub> seasonal cycle, including its magnitude, changing phase, and spatial variation,

**Figure 3.** Comparison of satellite measured springtime tropospheric NO<sub>2</sub> columns during two time periods separated by 13 years. See Methods Summary for data reference. The inset shows the temporal change in the total zonal troposphere NO<sub>2</sub> column for two Northern Hemisphere Latitude bands. See Methods Summary for more details and data reference.

it is not possible to definitively test these hypotheses, determine which is dominant, or perhaps to discover more realistic ones. Reproducing the seasonal cycle of tropospheric O<sub>3</sub> at different locations, and its temporal evolution, will provide useful benchmarks of model performance leading to improved causal attribution and tropospheric O<sub>3</sub> predictions as the atmosphere is progressively more affected by climate change. The use of tracers in long multiannual simulations, representing CO emissions over different regions, or the stratospheric ozone flux into the troposphere, for example, can be used to discriminate between O<sub>3</sub> changes due to emissions or transport from the stratosphere. Runs with fixed emissions or meteorology can be used to tease out the effects of emissions versus transport pathway changes. As a first step, it is planned to examine the evolution in the seasonal cycle over the 60 years of model simulations performed as part of the Chemistry-Climate Model Initiative (see <http://www.igacproject.org/CCMI>).

[18] This observed shift in the O<sub>3</sub> seasonal cycle has implications for O<sub>3</sub> pollution control policies based on exceedances above ambient ozone concentration thresholds impacting human health and vegetation (e.g., 35 and 40 ppbv, respectively, in Europe [Royal Society, 2008]). Populations may be exposed to higher concentrations for a greater time during the year resulting in increased health effects, and crops and forests may be susceptible to damage by higher concentrations in the early part of the growing season.

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