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# Long-term trends in ozone in baseline and European regionally-polluted air at Mace Head, Ireland over a 30-year period.

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HIGHLIGHTS

- 30 years of ozone observations for Mace Head, Ireland are presented
- The importance of sorting the observations by air mass is stressed
- Northern hemisphere baseline ozone levels have increased, levelled off and begun to decline

ABSTRACT

Observations of surface ozone, $O_3$, have been made at the Mace Head Atmospheric Research Station on the North Atlantic Ocean coastline of Ireland over a 30-year period from April 1987 through to April 2017. Using meteorological analyses and a sophisticated Lagrangian dispersion model, the hourly observations have been sorted by air mass histories to separate out the observations for northern hemisphere mid-latitude baseline air masses. Monthly average baseline levels showed a pronounced seasonal cycle with spring maxima and summer minima. Baseline levels have shown an increase during the 1980s and 1990s which has been stronger in the winter and spring and weaker in the summer. The rate of this increase has slowed to the extent that baseline levels have been relatively constant through the 2000s and started to decline in 2010s. The unsorted $O_3$ data has shown different long-term trends from the baseline data because of the influence of European regional $NO_x$ and VOC emissions which have reduced wintertime $O_3$ levels below the baseline levels and enhanced summertime $O_3$ levels above them. Episodic peak $O_3$ levels have

declined steadily during the study period but 50 ppb 1-hour exceedances are likely to continue for the foreseeable future.

## 1. Introduction

Tropospheric ozone ($O_3$) is important both as an oxidant and as a source of hydroxyl (OH) and hydroperoxyl ($HO_2$) radicals (Levy, 1971). It is widely recognised as an important air pollutant with widespread impacts on human health, crops and vegetation (Monks et al., 2015). $O_3$ is also a tropospheric greenhouse gas (IPCC, 2007: Stevenson et al., 2013). Because of these impacts, it is the focus of much policy-making activity, the aim of which is to reduce $O_3$ levels to meet air quality standards and guidelines (WHO, 2006).

Much of the understanding that is the bedrock of policy-making has come from $O_3$ observations and a number of authoritative reviews are available (Vingarazan, 2004; Oltmans et al., 2006; Cooper et al., 2014). Surface $O_3$ levels over Europe have doubled from the 1950s to around 1990 (Feister and Warmbt, 1987) and in the Swiss Alps the records demonstrate much the same (Staehelin et al., 1994). Ozonesonde data over Europe have shown an increase during the 1980s and 1990s but a decrease in the 2000s (Logan et al., 2012). Studies by Parrish et al., (2012) and Cooper et al., (2010) have demonstrated increases in surface $O_3$ in spring on the Pacific Ocean coast of the USA. There are preliminary indications of a slowing of this increase and perhaps a reversal of the trend (Parrish et al., 2012; 2014; 2017). Strong increases have been reported for Mount Happo, Japan also during spring (Tanimoto, 2009).

An important issue for policy-makers has been the role played by intercontinental $O_3$ transport and the growth in the hemispheric $O_3$ background. Regional-scale $O_3$ episodes are superimposed upon this hemispheric $O_3$ background and so any rising ozone background may erode the benefits of regional-scale $O_3$ precursor emission reductions (Jacob, 1999). Decreases in the baseline $O_3$ entering the USA from across the North Pacific Ocean as monitored at Trinidad Head and Lassen National

Park may ease the difficulties faced by policy-makers in achieving air quality standards (Parrish et al., 2017). However, ozone levels monitored at the Mount Bachelor Observatory in Central Oregon appear to be increasing due to global sources and regional wildfire events (Zhang and Jaffe, 2017).

Baseline $O_3$ can be readily monitored in maritime air masses at Mace Head, Ireland, located on the western fringe of Europe, having recently travelled across the North Atlantic Ocean without local influence. Previously, increasing $O_3$ mixing ratios in baseline air masses have been reported over the period from 1987 to 2003 (Simmonds et al., 2004). This increasing baseline may have partially offset the improvement in European air quality due to $O_3$ precursor emission reductions (Derwent et al., 2003). More recently, baseline levels have remained roughly constant during the 2000s (Derwent et al., 2013) and have now begun to decline during the 2010s. Here we present a further analysis of the Mace Head $O_3$ record which has been extended to include 30 years of data from April 1987 onwards.

## 2. Experimental Methods

Ozone ($O_3$) measurements were acquired using commercial UV spectrometers and three separate analysers were used over the period of this study. The periods of use were from April 1987 to March 2003 (model ML8810, Monitor Labs, San Diego CA), from March 2003 to April 2016 (model 49C, Thermo Electron Inc, Franklin, MA) and from April 2016 to April 2017 (model 49i, Thermo Electron Inc. Franklin, MA). The instruments were operated within the UK Rural Ozone Network, latterly the Automatic Urban/Rural Network (AURN). As part of that network, their calibration was audited 2-4 times per year against a National Physical Laboratory-traceable UV photometer transfer standard (Sweeney and Stacey, 1992). The raw voltage output of the Monitor Labs ML8810 was converted to concentration values based on these audits. The Thermo Electron instruments output mixing ratio values directly and have required no adjustments to response factors. Since 1995, the measurements are shared with the national pollution network operated by the Irish Environmental Protection Agency (EPA) who audit the instrument annually against their own NPL-traceable transfer standard. In all cases, the results were found to be within 5% of nominal values. In addition, the

instruments (other than the current instrument) have been regularly validated by a system and performance audit (https://www.empa.ch/web/s503/wcc-empa) conducted by the World Calibration Centre for surface ozone, (Zellweger et al., 2013) and the performance criteria have consistently been passed as good. These audits are necessarily more rigorous than the more frequent network audits and give a high degree of confidence in the measurements.

All analysers operate on a 10 second measurement cycle and data are reported as hourly averages. Prior to 1996, data were recorded as hourly averages. From 1996 onward, data were recorded as one minute averages and, after filtering, averaged to one hour. This permitted a better assessment of instrumental performance and reduced data loss due to short duration events such as filter changes etc. The sampling inlet comprised an inverted PTFE cup to prevent rain ingress, 1/4" PTFE sample tubing and a PTFE filter, 5-um pore size, changed monthly to exclude particulate contamination. The sample inlet was mounted initially at 3m and in March 2005 it was moved to 7m using the same tubing and in December 2014 it was installed at 10m using new tubing. The new tubing had previously been tested and $O_3$ loss was found to be less than 1ppb. In January 2015, the tubing was sheathed in 1/2" Synflex to exclude light and to ease removal and replacement. At this time, a second, sheathed line was installed at the same height to facilitate instrument inter-comparisons. The filters used were either Pall Zylon P4PH047 (Pall Life Sciences, Ann Arbor, MI) or Millipore Mitex LSWP04700 (Merck Millipore, Carrigtoohil, Co. Cork, Ireland)) both of which were found to produce minimal ozone loss.

Central to the analysis and interpretation of the $O_3$ record at Mace Head, Ireland is the selection of the $O_3$ measurements in air masses that are representative of the unpolluted Northern Hemispheric marine boundary layer. The $O_3$ levels in these unpolluted air masses are referred to as baseline levels and, by definition, they should be uninfluenced by local effects or recent regional $NO_x$ emissions from Ireland or Continental Europe. Baseline levels are to be distinguished from background levels which are model constructs describing levels due to natural sources (HTAP, 2010). Over the 30 years

of continuous $O_3$ observations at Mace Head, a number of methods have been developed to assign $O_3$ mixing ratios to specific air masses (Simmonds et al., 1997), of which two methods have been used here as described previously by Derwent et al., (2013).

(1). Pollution filtering. Co-incident measurements of anthropogenic traces such as halocarbons and carbon monoxide are simple but effective indicators of 'polluted' air masses (Cunnold et al., 1986; Simmonds et al., 1993). Halocarbons or carbon monoxide were first flagged as 'polluted' if their values exceeded baselines by 3 standard deviations. To define a pollution event the mixing ratios of at least two other species must show concurrent increases of at least 2 standard deviations, over several consecutive measurement periods. If and only if these two independent species showed simultaneously elevated levels, the values were reported as 'polluted', otherwise the data were reported as 'unpolluted' or baseline, (Cunnold et al., 1986; Simmonds et al., 1993).

(2). Lagrangian dispersion modelling. A sophisticated numerical atmospheric dispersion model has been used to indicate air mass histories in terms of 'baseline', 'European', 'southerly', or 'local', as described by Manning et al., (2011). Baseline observations exclude times when the air was modelled to have come significantly from populated regions east of Mace Head (i.e. Ireland, UK and the rest of Europe) or southern latitudes (latitudes less than 35$^{o}$N), or when the air was not well mixed (i.e. in stable atmospheric conditions). This is our preferred method for sorting air masses but unfortunately it is limited to the period after 1$^{st}$ February 1989 and up to the present date.

Because of the presence of the significant levels of $O_3$ in unpolluted maritime air masses, care had to be taken separating 'polluted' and 'unpolluted' air masses for those months before February 1989 when the dispersion model method was not available. With the phase-out of European production and usage of halocarbons and the implementation of vehicle exhaust gas catalysts, the magnitudes of the halocarbon and carbon monoxide peaks from Europe have become smaller with time. As a result, the pollution filtering method has become more inaccurate particularly for ozone and the dispersion model method has become the preferred method for sorting air masses. The 1987 – 2017

period has therefore been split into three sections. The section from April 1987 to January 1989, inclusive, utilised the pollution filtering method to sort the ozone data according to whether the air masses were 'polluted' or 'unpolluted'. The section from February 1989 to December 1994 provided a six year overlap period when both methods were operated side-by-side. The section from January 1995 to April 2017 utilised the dispersion model method. As detailed in Derwent et al., (2013), a careful analysis of the overlap period indicated that the pollution filtering method gave somewhat lower monthly mean baseline mixing ratios by 1.6 ± 1.9 (1 standard deviation sd) ppb compared with the dispersion model method. This correction was added to the pollution filtering results for the period from 1st April 1987 to 31st January 1989.

Over the intervening period since the Lagrangian dispersion modelling sorting method (Manning et al., 2011) has been applied to the Mace Head data, improvements have been made to the sorting algorithm. A population map is now combined with the air history map to infer the total influence of populated regions, including Africa, USA and Eastern Europe on any measurement during each 2-hour period. Additionally, for each 2-hour period, the percentage of model particles leaving the air history domain from the north west (NW) sector (northern Canada and the Arctic regions), southern and upper troposphere edges is estimated. 2-hour periods are defined as being representative of the well-mixed Northern Hemisphere baseline when the overall and land local influences are low (no significant influence from any local emissions), when the influence of European populated regions, Africa, USA and Eastern Europe are all low, and the vast majority of the model particles have left the model domain through the NW sector. With this improved baseline allocation, two or more hours were assigned to the baseline in 317 out of the 339 months between February 1989 and April 2017, leaving 22 months for which the less restricted baseline allocation method of Manning et al., (2011) was employed.

A merged baseline dataset was then constructed from the 22 monthly records from the pollution filtering method, 317 monthly records from the improved baseline allocation method employing the

Lagrangian dispersion model, back-filled with 22 records from the Manning et al., (2011) method. This merged dataset has been used in the subsequent analyses below and is presented in Figure 1 and in electronic form in the Supplementary Information.

## 3. Ozone levels in Northern Hemisphere baseline air masses

### 3.1 Baseline trends

Using the pollution sorting and dispersion model methods, the $O_3$ observations have been sorted by air mass origins into distinct and robust categories. We begin with an analysis of the $O_3$ levels that have been assigned to the baseline category. This category largely excludes air masses that may have been influenced by the highly populated and industrialised regions of Europe, with the majority of the baseline air masses arising from the most northerly regions of North America. With the more restricted allocation methodology employed here within the Lagrangian dispersion model, 11.7% of the available hourly $O_3$ observations were assigned to the baseline category compared with 36.2% previously with the less restricted allocation methodology (Derwent et al., 2013). The hourly baseline sorted $O_3$ observations were accumulated up to a monthly basis and the monthly average baseline levels were estimated from whatever baseline allocations were available during that month. Figure 1 presents the complete time series of baseline monthly average $O_3$ mixing ratios obtained by combining the pollution filtering baseline levels with those from the dispersion model. Visual inspection of the complete time series shows the presence of a well-developed seasonal cycle during each year with a springtime maximum and a summertime minimum, an early period of increasing mixing ratios, a later period of relatively constant mixing ratios and significant year-on-year variability as indicated by the high year in 1999 and the low year in 1987.

In most studies of $O_3$ trends, linear regression is used to fit a straight line through the data to determine the slope of the fit in units of ppb $yr^{-1}$ (for example: Collette et al., 2016; Cooper et al., 2014; Oltmans et al., 2013). Trends in the annual average baseline $O_3$ mixing ratios in Figure 1 were analysed and assessed using the Mann-Kendall test (Salmi et al., 2002). The annual averages showed

a highly statistically significant (at the 0.01 or 99% level of significance) upwards trend over the 1987 – 2017 period. The non-parametric Sen's method (Salmi et al., 2002) indicated an upwards trend of $+0.22\ ^{+0.10}_{-0.08}$ ppb $yr^{-1}$ (where the quoted confidence limits here and throughout the study are 95% or 2 – σ confidence limits). In previous studies, we have reported +0.31 ± 0.12 ppb $yr^{-1}$ (Derwent et al., 2007) and +0.25 ± 0.09 ppb $yr^{-1}$ (Derwent et al., 2013) for shorter periods, 1987 – 2007 and 1987 – 2012, respectively. However, all three linear fits only poorly represented the observations as indicated by the residuals which were negative up to 1995 and after 2010 and were positive between 1998 and 2010. The behaviour of the residuals could be explained if the increase in the baseline had slowed, levelled out and perhaps declined in the later part of the record.

To test for any levelling off in the observed trend, a quadratic function of the form:

$$Y = a + bt^2 + ct \qquad (1).$$

was fit through the baseline data where t is the time through the record relative to t = 0 in the year 2000. Non-linear regression analysis, (NLREG, Sherrod, 1992), returned a slope (c) of 0.34 ± 0.07 ppb $year^{-1}$ and an acceleration (or deceleration) term (b) of -0.0225 ± 0.008 ppb $year^{-2}$, both of which terms were highly statistically significant at the 95% level of significance. This points to constantly decreasing annual growth rates over the 1987 – 2017 period. The slowing in the annual rate of increase has advanced to the point that annual baseline ozone levels have begun to level off and decrease. The apparent time of maximum, $t_{max}$, could be quantified using:

$$t_{max} = -c/(2*b) + 2000 \qquad (2).$$

Combining the slope and deceleration terms together points to the fitted quadratic function levelling out in 2007 or thereabouts, with a 2 – σ confidence range of ± 6 years. The quadratic fit explained about 80% of the variance in the data whereas the simple linear fit without the acceleration term accounted for about 56%. It is concluded therefore that the baseline Mace Head observations are best explained by the quadratic function, that is to say, by an initially steep rising trend that declines,

203 levels out and ultimately declines during the later years of the record, rather than a simple steady
204 linear trend.

205 The linear fit, (Y = a + ct), provides an estimate of the average annual increase in $O_3$ over the 1989 –
206 2017 data record of + 0.27 ± 0.09 ppb $year^{-1}$. The quadratic fit, ($Y = a + bt^2 + ct$), provides an estimate
207 for the average annual rate of change of the $O_3$ growth rate, indicating a constantly decreasing rate
208 of growth over the 1989 – 2017 data record. It must be noted that neither analysis implies that $O_3$
209 necessarily varied in a linear or quadratic manner and they do not imply how annual mean $O_3$ levels
210 will change in the future. They merely provide a convenient way of summarising the observed long-
211 term $O_3$ changes. Figure 2 presents the annual average baseline $O_3$ data for 1987 – 2016, together
212 with linear and quadratic fits and their residuals. The superior quality of the quadratic fit is evident,
213 as is the recent decline in ozone levels from 2009 onwards. Inspection of the residuals in Figure 2 for
214 the linear fit showed that the linear fit overestimated the observations at the start and end of the
215 record and underestimated them in the middle. In contrast, the residuals from the quadratic fit were
216 scattered above and below the observations evenly throughout the record.

217 The trend in annual baseline $O_3$ has not been realised evenly through the months of the year. The
218 trend in the month of January has been different to that in the month of February and so on, as is
219 shown in Table 1, where the quadratic fits have been applied to the Januarys, Februarys and so on.
220 The quadratic fits are highly statistically significant in all months, except for August and October.
221 Also shown in Table 1 are the quadratic fits to the 3-month seasonal averages because the seasonal
222 averaging decreases the confidence limits and thus eases the discussion of statistical significance.
223 Monthly baseline levels showed an initial phase of high growth during the period from 1987 to 1997
224 which was particularly marked during winter and spring months and weaker during the summer
225 months. This initial growth rate has slowed from 1998 onwards. The slowing down of the rate of
226 increase has been most marked during spring and has been least marked in autumn. As a result, the
227 interpolated times of the maxima in the monthly time series using equation (2) have varied from

2004 during May and June through to 2017 in August. Spring levels peaked earliest in 2005 whereas autumn levels peaked some six years later in 2011.

### 3.2 Seasonal variations

Visual inspection of the time series of monthly baseline average $O_3$ levels in Figure 1 shows clear evidence of a seasonal cycle with maxima in the months from March through to May and minima in July through to August. Seasonal cycles with springtime maxima are a clear feature of the ozone records at most marine boundary layer stations though the reasons underpinning these maxima have yet to be unambiguously explained (see Monks 2000 and the references therein). Inevitably, different trends in different months of the year may lead to changing seasonal cycles. This has been investigated by Parrish et al., (2013) using eleven mid-latitude data sets including the baseline Mace Head record up to 2012. The conclusion was that there had been an apparent shift in the seasonal cycle at Mace Head but that it was not statistically significant. With the longer baseline record available in this study, we return to the issue of changing seasonal cycles at Mace Head.

To accurately characterise the seasonal cycles in the baseline observations, sine curves were fitted through the monthly mean ozone mixing ratios ($O_3$) using non-linear regression software (NLREG, Sherrod, 1992) which returned five fitted parameters: $Y_0$, $A_1$, $A_2$, $\phi_1$ and $\phi_2$, representing:

$$O_3 = Y_0 + A_1 \sin(\chi + \phi_1) + A_2 \sin(2\chi + \phi_2) \quad (1)$$

where $\chi$ takes the values from 0 to $2\pi$ radians in covering one complete year from 1st January to 31st December, $Y_0$ is the long-term average ozone mixing ratio, $A_1$ and $A_2$ are the amplitudes of the fundamental and second harmonics and $\phi_1$ and $\phi_2$ are their phase angles. The 1987 – 2017 baseline record was split into six five-year periods and the average seasonal cycles were calculated for each five-year period and sine curves were fitted through them. The fitted parameters for each five-year period are presented in Table 2.

The long-term average value terms ($Y_0$) clearly show evidence of an increase between 1988 – 1992 and 2012 – 2016 which is statistically significant, as would be expected based on section 3.1 above. The amplitudes of the fundamental ($A_1$) also appear to increase between 1988 – 1992 and 2012 – 2016 but by no more than would be expected based on the increase in the $Y_0$ values. In contrast, the phase angles of the fundamentals ($\phi_1$) increased steadily from 1988 – 1992 to 2012 – 2016 by 0.015 ± 0.005 radians per year (0.85 ± 0.3 day per year), an increase which was statistically significant. The amplitudes of the second harmonics ($A_2$) showed a slight downwards trend which was not statistically significant. The phase angles of the second harmonics ($\phi_2$) showed no evidence of any significant change throughout the study period.

In summary then, it is likely that the differential trends between the different months over the 1987 – 2017 period have led to a statistically significant increasing trend of 0.85 ± 0.3 day per year in the phase angle of the fundamental term, $A_1 \sin(\chi + \phi_1)$, of the baseline seasonal cycle, see Table 2. This is equivalent to the maximum in the baseline $O_3$ seasonal cycle shifting by 0.85 ± 0.3 day per year, or about 8.5 days per decade, earlier in the year as illustrated in Figure 6. This is somewhat larger than the 3.0 ± 3.7 days per decade shift reported by Parrish et al., (2013) which was not statistically significant. The increasing confidence in the shift of the ozone maximum earlier in the year reported here is presumably due to the longer baseline record now available.

## 4. Analysis of the unsorted Mace Head data

Data repositories (for example: Schultz et al., 2017) and literature reviews (Collette et al., 2016; Cooper et al., 2014; Oltmans et al., 2006) focus on the unsorted Mace Head ozone data because of its widespread availability and ease of access. The unsorted data differs from the baseline data analyses in section 3 above because it includes data for air masses arriving from the continent of Europe, southerly latitudes and those air masses which have been influenced by local ozone sinks. In Figure 3, the monthly average unsorted ozone data are presented, together with the difference between the monthly averages of the baseline data and the unsorted data. Visual inspection of the

276 unsorted data in Figure 2 and the baseline data in Figure 1 reveals many similar features, namely,
277 increasing trends and marked seasonal cycles. The difference plot shows that the unsorted monthly
278 averages are generally lower than the baseline averages and that this difference also shows the
279 presence of trends and marked seasonal cycles.

280 The annual averages of the unsorted $O_3$ data exhibited similar behaviour over the 1987 – 2017
281 period compared with the baseline data. A linear fit to the unsorted data returned a year 2000 value
282 of 35.6 ± 0.55 ppb and a slope of +0.17 ± 0.06 ppb $yr^{-1}$ which is significantly smaller than the linear
283 slope found for the baseline data of +0.27 ± 0.09 ppb $yr^{-1}$. A quadratic fit to the unsorted data
284 returned a year 2000 value of 36.4 ± 0.67 ppb, a linear term of +0.22 ± 0.06 ppb $yr^{-1}$ and a
285 deceleration term of -0.0123 ± 0.007 ppb $yr^{-2}$, implying a turnover during 2008 ± 6. These fitted
286 parameters are different from the fitted annual baseline parameters reported in Table 1. The
287 differences in the year 2000 values and the deceleration terms were statistically significant at the 2 –
288 σ confidence level but those in the linear terms were only significant at the 1 – σ level. The two sets
289 of annual averages and their quadratic fits are illustrated in Figure 4, showing how different their
290 time series behaviours are on visual inspection. Baseline levels have risen faster than unsorted
291 levels, leading to an increasing divergence between the two datasets with time. There is also a
292 difference in the turn-over behaviour, with a delay in the turnover of the unsorted data which has
293 led to decreasing divergence with time.

294 Visual inspection of the difference plot in Figure 3 shows that the monthly averages of the unsorted
295 mixing ratios were less than the baseline mixing ratios, generating a positive difference (monthly
296 average baseline > unsorted). The differences were largest during the winter months and these
297 wintertime differences appear to have declined during the study period. The differences were most
298 negative (unsorted > baseline) during the summer months and these negative differences also
299 appear to have declined during the study period.

Quadratic functions were fitted through the monthly average differences, revealing that the annual average difference increased steadily, then reached a maximum in 2007, before starting to decline, see Table 3. Fitted differences in 2000 were largest in December and least in July. November differences declined steadily, reached a minimum in 2004, before increasing again. In contrast, July differences increased steadily throughout the study period, showing the steepest annual gradient, without any statistically significant evidence of levelling off. Springtime differences rose initially, then levelled off in the early 2000s, before starting to decline towards the end of the record, following the behaviour of the baseline data.

Baseline and unsorted $O_3$ mixing ratios would be closely similar and the (baseline – unsorted) differences would be small, were it not for the $O_3$ levels found in European regionally polluted air masses arriving at Mace Head and for local influences from the immediate vicinity of the Mace Head Atmospheric Research Station. During winter, European regional $NO_x$ emissions cause depletion of $O_3$ and so $O_3$ mixing ratios in the unsorted data drop markedly below baseline levels (Derwent et al., 1998), producing the positive differences evident in Figure 3. During summer, European photochemical $O_3$ formation from European regional $NO_x$ and VOC emissions drives up $O_3$ mixing ratios above baseline levels producing the negative differences evident in Figure 3.

European $NO_x$ emissions have declined to 48% of their 1990 values by 2015 (European Environment Agency, 2017) and this has reduced the scavenging of $O_3$ by $NO_x$, particularly in the winter and in urban areas. Consequently, this has reduced the intensity of $NO_x$-depletion in the air masses arriving at Mace Head and so decreased the size of the positive differences in Figure 3 with time. Not only have European regional $NO_x$ emissions declined with time but those of VOC emissions have also declined to 51% of their 1990 values by 2015 (European Environment Agency, 2017). This has reduced the intensity of photochemical $O_3$ formation in polluted air masses arriving at Mace Head (Collette et al., 2016: 2017; Derwent et al., 2013) and so decreased the magnitude of the negative summertime differences in Figure 3 with time.

By way of confirmation of the impact that the reductions in European regional $NO_x$ and VOC emissions have had on European regional photochemical $O_3$ formation, we examine the time series of the number of 50 ppb 1-hour ozone exceedances and the maximum 1-hourly mean $O_3$ level in each year in Figure 5. The number of 50 ppb exceedances starts at a relatively low level in the 1980s, rises to a maximum in the 2000s and then declines towards the end of the study period. A quadratic fit returned a linear term of +9.8 ± 10.2 $yr^{-1}$ and a deceleration term of -1.6 ± 1.0 $yr^{-2}$, both of which were highly statistically significant, implying a turnover during 2003. This behaviour follows from the increasing spring-time baseline ozone early in the study period and from the decreasing regional scale photochemical ozone formation later in the study period, following on from Figures 3 and 4.

In contrast, the maximum 1-hour ozone levels declined steadily throughout the study period, see Figure 5, under the influence of the regional scale ozone precursor emission controls. In this case, a quadratic fit returned a highly statistically significant linear term of -0.84 ± 0.48 ppb $yr^{-1}$ and a deceleration term which was not statistically significant. The fit also returned a year 2000 maximum 1-hour mean ozone level of 71 ± 4 ppb, implying that it will not be until 2025 before maximum 1-hour ozone levels declined to the 50 ppb level, if present trends continue. This 50 ppb metric was selected based on the World Health Organisation air quality guideline of 50 ppb maximum 8-hour $O_3$ concentration (WHO, 2006). However, this analysis is merely illustrative and is intended to illustrate the influence of the European regional $NO_x$ and VOC emission reductions on photochemical $O_3$ formation. It is not an attempt to infer or quantify human health effects. Indeed, the remote nature of the location of the Mace Head Atmospheric Research Station precludes such human health considerations. No policy significance is implied by our selection of the 1-hour averaging time period.

## 5. Discussion and Conclusions

We have analysed the Mace Head $O_3$ measurement record with a view to quantifying the changes that have occurred at northern mid-latitudes over the past 30 years. An important aspect of our analysis of the Mace Head $O_3$ record has been our use of meteorological analyses and a

sophisticated Lagrangian dispersion model to sort the hourly observations by air mass histories. In this way, we have assembled a time series of $O_3$ levels in baseline northern hemisphere mid-latitude air masses which have had minimal influence from continental Europe. The 1987 – 1992 baseline observations revealed a seasonal cycle with a spring maximum and a summer minimum and evidence of an annual trend of +0.37 ppb $year^{-1}$, (Derwent et al., 1994). The 1987 – 1995 baseline observations exhibited a small increasing trend of +0.19 ppb $year^{-1}$ (Simmonds et al., 1997). The 1987 – 2003 baseline observations showed a trend of +0.49 ppb $year^{-1}$, with largest trends in the winter and weakest trends in the summer (Simmonds et al., 2004). During the 2000s, baseline $O_3$ levels exhibited evidence of decline and stabilisation, with an average trend of +0.31 ppb $year^{-1}$ over the 20-year 1987 – 2007 period (Derwent et al., 2007) and +0.25 ppb $year^{-1}$ over the 25-year period (Derwent et al., 2013). Logan et al., (2012) set the Mace Head baseline observations in the context of European ozone-sondes, measurements on board regular aircraft and alpine mountain-top sites and pointed to $O_3$ increases from 1987 to 1997, with relatively constant levels since 1999. Parrish et al., (2012) examined the Mace Head baseline levels together with ten other global $O_3$ datasets of which five were European in origin, with a view to characterising $O_3$ changes over several decades. Here, the above assessments of changes in tropospheric $O_3$ at Mace Head have been extended through to April 2017, thus producing a high quality, 30-year monitoring record.

We have been able to demonstrate that the long-term $O_3$ trends and behaviour are markedly different for the complete unsorted $O_3$ dataset and that of the baseline $O_3$ dataset. The differences in the apparent trends between the baseline and unsorted data may seem of academic interest but they do have important policy implications. The linear trend in the unsorted data is about 60% of that found in the baseline data. This becomes an issue when it comes to the evaluation of the performance of the global models in describing the growth in tropospheric $O_3$ levels since pre-industrial times. Parrish et al., (2014) describe how global models underestimate the growth in tropospheric $O_3$ since the 1950s and how this is particularly the case for the 1987 – 2012 baseline $O_3$ record at Mace Head. If the unsorted $O_3$ record had been employed for the Parrish et al., (2014)

376 comparison then the situation would have been viewed much more advantageously for the global
377 models and their inadequacies would have been hidden. However, there is no evidence that the
378 coarse spatial scale global models are able to describe accurately the impact of European regionally-
379 polluted air masses on baseline $O_3$ levels as revealed in section 4 above and so any apparent
380 agreement between the global models and the unsorted $O_3$ trends at Mace Head must be
381 coincidental.

382 By way of example, we examine the global model study of Lamarque et al., (2010) which compared
383 the global model trends of +0.17 ppb $yr^{-1}$ from CAM-Chem and G-PUCCINI with the unsorted Mace
384 Head trend of +0.18 ppb $yr^{-1}$ because they felt that the unsorted observations were more
385 representative of the global model $O_3$ fields. However, the global models employed by Lamarque et
386 al., (2010) were too coarse in their spatial resolution (1.9° x 2.5°) and could not accurately represent
387 the regional $NO_x$-driven ozone sink processes that accounted for the reduction in the trends
388 between the baseline and unsorted datasets. A more rigorous comparison should have been made
389 with the baseline data trend of +0.27 ppb $yr^{-1}$ and then a large global model underestimation would
390 have been apparent. In a further example, we take the GISS-E2 study of Shindell et al., (2013) in
391 which a comparison was made between their global model trend of +0.04 to +0.17 ppb $yr^{-1}$ at Mace
392 Head between November 1987 and September 2006 and the observed unsorted trend of +0.18 ppb
393 $yr^{-1}$, concluding that their model performance was satisfactory. However, a more rigorous
394 comparison should have been made with the much higher baseline trend of +0.27 ppb $yr^{-1}$ and then
395 the global model would appear to underestimate the observed trend as it has since the 1950s
396 (Parrish et al., 2014).

397 A more straightforward and direct comparison between the Mace Head baseline ozone and global
398 model predictions could be achieved if high time resolution (hourly, say) output were to be made
399 available. The comparison with baseline observations could then be restricted to the conditions
400 when the models themselves predict baseline transport.

In previous studies, we have shown how rising baseline $O_3$ levels may have offset the benefits of European regional $O_3$ precursor emission controls, particularly in the western fringes of Europe (Derwent et al., 2003). $O_3$ levels in central Europe may well remain roughly level because the increasing influence of North American and Asian emissions on North Atlantic inflow is counterbalanced by decreasing $O_3$ production from European regional $NO_x$ and VOC emissions from central Europe itself. It is now clear that the rise in baseline $O_3$ in air masses entering Europe from across the North Atlantic Ocean has finished and that baseline $O_3$ levels have now levelled off and begun to decline. As a result, the offsetting and counterbalancing effects should begin to diminish and Europe should begin to see more strongly the benefits of European regional emission reductions on European $O_3$ air quality. Episodic peak $O_3$ levels have declined steadily during the study period at Mace Head but 50 ppb 1-hour exceedances are likely to continue for the foreseeable future as the decline in baseline $O_3$ takes time to work through.

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Table 1. Linear, c, and deceleration coefficients, b, obtained by fitting quadratic functions of the form: $Y = a + bt^2 + ct$, through the monthly baseline average ozone levels at Mace Head, Ireland over the period from April 1987 to April 2017.

| Month | Linear coefficient, ppb $year^{-1}$ | Deceleration coefficient, ppb $year^{-2}$ | Year 2000 value, ppb | Interpolated year of maximum[b] |
|---|---|---|---|---|
| January | +0.40 ± 0.09 | -0.0215 ± 0.010 | 41.65 ± 1.0 | 2009 ± 5 |
| February | +0.46 ± 0.15 | -0.0234 ± 0.016 | 42.91 ± 1.6 | 2009 ± 7 |
| March | +0.33 ± 0.11 | -0.0227 ± 0.012 | 45.84 ± 1.2 | 2007 ± 7 |
| April | +0.42 ± 0.13 | -0.0311 ± 0.015 | 47.53 ± 1.6 | 2006 ± 4 |
| May | +0.28 ± 0.16 | -0.0342 ± 0.020 | 45.96 ± 1.9 | 2004 ± 1 |
| June | +0.29 ± 0.12 | -0.0302 ± 0.015 | 38.31 ± 1.5 | 2004 ± 3 |
| July | +0.32 ± 0.11 | -0.0167 ± 0.014 | 31.80 ± 1.4 | 2009 ± 8 |
| August | +0.29 ± 0.14 | -0.0083 ± 0.017[a] | 31.97 ± 1.7 | 2017 ± 19 |
| September | +0.22 ± 0.14 | -0.0127 ± 0.017 | 35.82 ± 1.7 | 2008 ± 6 |
| October | +0.26 ± 0.14 | -0.0087 ± 0.017[a] | 37.62 ± 1.7 | 2015 ± 16 |
| November | +0.34 ± 0.15 | -0.0152 ± 0.018 | 40.06 ± 1.8 | 2011 ± 14 |
| December | +0.32 ± 0.09 | -0.0114 ± 0.010 | 40.34 ± 1.0 | 2014 ± 7 |
| | | | | |
| Winter (DJF) | +0.39 ± 0.08 | -0.0218 ± 0.010 | 41.78 ± 0.9 | 2009 ± 4 |
| Spring (MAM) | +0.30 ± 0.10 | -0.0272 ± 0.012 | 46.44 ± 1.1 | 2005 ± 2 |
| Summer (JJA) | +0.30 ± 0.10 | -0.0184 ± 0.012 | 34.03 ± 1.2 | 2008 ± 6 |
| Autumn (SON) | +0.28 ± 0.09 | -0.0124 ± 0.011 | 37.83 ± 1.1 | 2011 ± 11 |
| | | | | |
| Annual | +0.34 ± 0.07 | -0.0225 ± 0.008 | 40.10 ± 0.8 | 2007 ± 6 |

[a] Not considered significantly different from zero.

[b] For an explanation of the interpolated year of maximum, see text

Table 2. Fitted parameters ($Y_0$, $A_1$, $A_2$, $\phi_1$, $\phi_2$) quantifying the seasonal cycles in baseline ozone over five-year periods at Mace Head, Ireland.

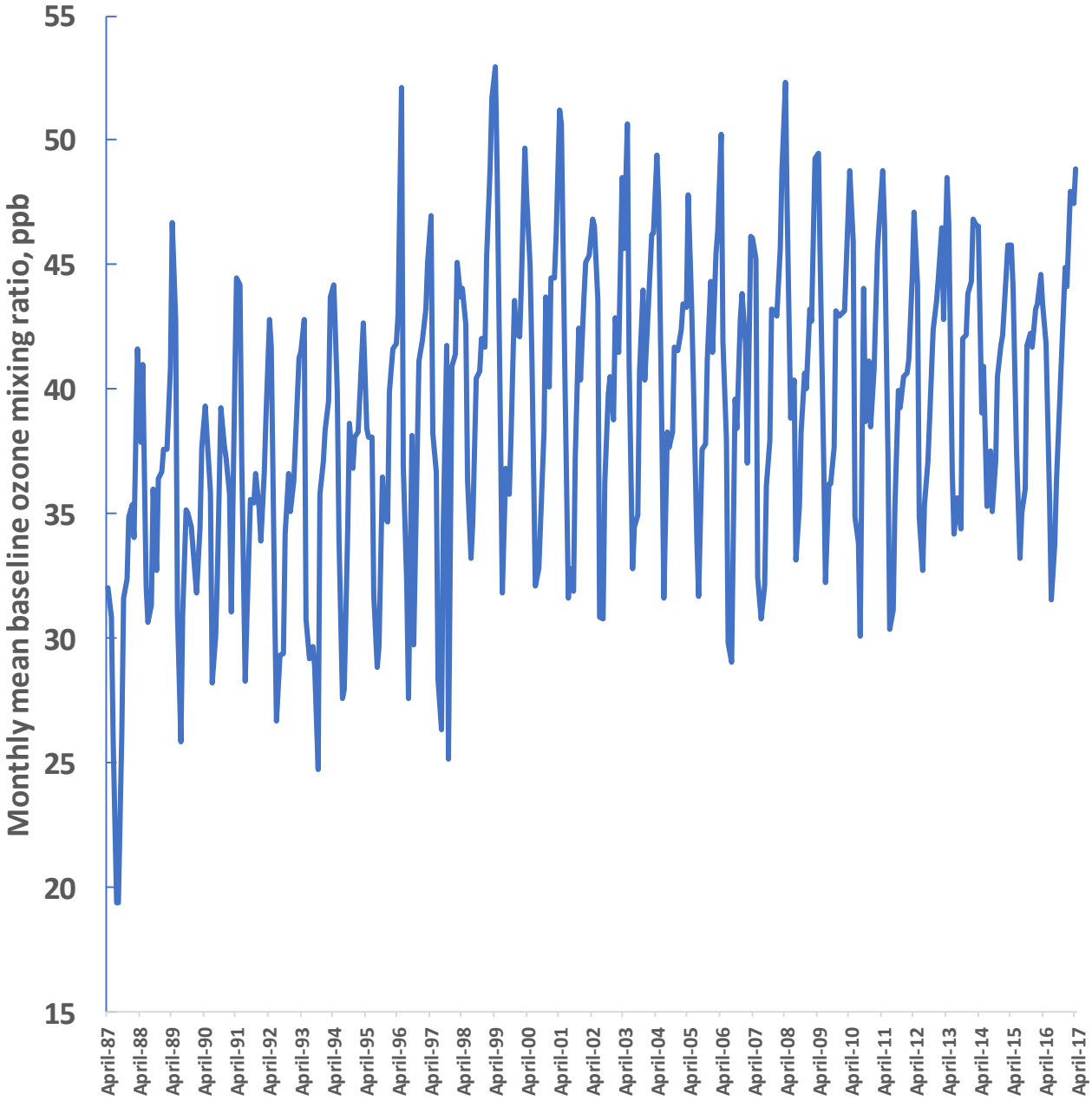
| Period | $Y_0$, ppb | $A_1$, ppb | $A_2$, ppb | $\phi_1$, radians | $\phi_2$, radians |
|---|---|---|---|---|---|
| 1988 - 1992 | 35.5 ± 0.8 | 3.7 ± 1.1 | 4.0 ± 1.1 | 0.37 ± 0.30 | -2.38 ± 0.27 |
| 1993 – 1997 | 36.7 ± 0.9 | 6.2 ± 1.2 | 2.3 ± 1.2 | 0.41 ± 0.20 | -2.43 ± 0.52 |
| 1998 – 2002 | 41.2 ± 0.7 | 6.5 ± 1.0 | 3.2 ± 1.0 | 0.47 ± 0.16 | -2.44 ± 0.32 |
| 2003 – 2007 | 40.7 ± 0.7 | 5.7 ± 1.0 | 3.6 ± 1.0 | 0.61 ± 0.17 | -2.49 ± 0.27 |
| 2008 – 2012 | 40.9 ± 0.6 | 6.1 ± 0.9 | 3.8 ± 0.9 | 0.57 ± 0.15 | -2.40 ± 0.23 |
| 2012 – 2016 | 40.7 ± 0.5 | 5.2 ± 0.8 | 2.2 ± 0.8 | 0.74 ± 0.15 | -2.41 ± 0.35 |
| | | | | | |
| 1988 – 2016 | 39.2 ± 0.5 | 5.5 ± 0.7 | 3.1 ± 0.7 | 0.51 ± 0.13 | -2.40 ± 0.23 |
| Trend @ 2000 | 40.0 ± 0.6 | 6.1 ± 0.8 | 3.3 ± 0.8 | 0.43 ± 0.13 | -2.45 ± 0.24 |

562 Table 3. Linear, c, and deceleration coefficients, b, obtained by fitting quadratic functions of the
563 form: $Y = a + bt^2 + ct$, through the monthly excess baseline mixing ratios over unsorted mixing ratios
564 at Mace Head, Ireland over the period from April 1987 to April 2017.

| Month | Linear coefficient, ppb $year^{-1}$ | Deceleration coefficient, ppb $year^{-2}$ | Year 2000 value, ppb | Interpolated year of maximum |
|---|---|---|---|---|
| January | +0.063 ± 0.18[a] | -0.018 ± 0.020 | 6.5 ± 1.9 | 2002 ± 5 |
| February | +0.160 ± 0.14 | -0.011 ± 0.016 | 4.6 ± 1.6 | 2007 ± 12 |
| March | +0.079 ± 0.11 | -0.004 ± 0.012[a] | 4.1 ± 1.2 | b |
| April | +0.073 ± 0.08 | -0.008 ± 0.010 | 3.4 ± 1.0 | 2005 ± 8 |
| May | +0.096 ± 0.15 | -0.015 ± 0.018 | 3.3 ± 1.8 | 2003 ± 6 |
| June | +0.107 ± 0.14 | -0.002 ± 0.016[a] | 1.5 ± 1.6 | b |
| July | +0.182 ± 0.12 | -0.002 ± 0.014[a] | 0.6 ± 1.4[a] | b |
| August | +0.125 ± 0.12 | -0.000 ± 0.014[a] | 0.9 ± 1.4 | b |
| September | +0.101 ± 0.09 | -0.004 ± 0.012[a] | 2.3 ± 1.2 | b |
| October | +0.004 ± 0.13[a] | -0.006 ± 0.016[a] | 3.6 ± 1.6 | b |
| November | -0.090 ± 0.10 | 0.010 ± 0.012 | 4.1 ± 1.2 | 2004 ± 7 |
| December | -0.103 ± 0.15 | -0.009 ± 0.018 | 7.1 ± 1.8 | b |
| | | | | |
| Annual | +0.069 ± 0.07 | -0.005 ± 0.038 | 3.5 ± 0.4 | 2007 ± 7 |

567 [a] Not considered significantly different from zero at the 1 – σ level of confidence.

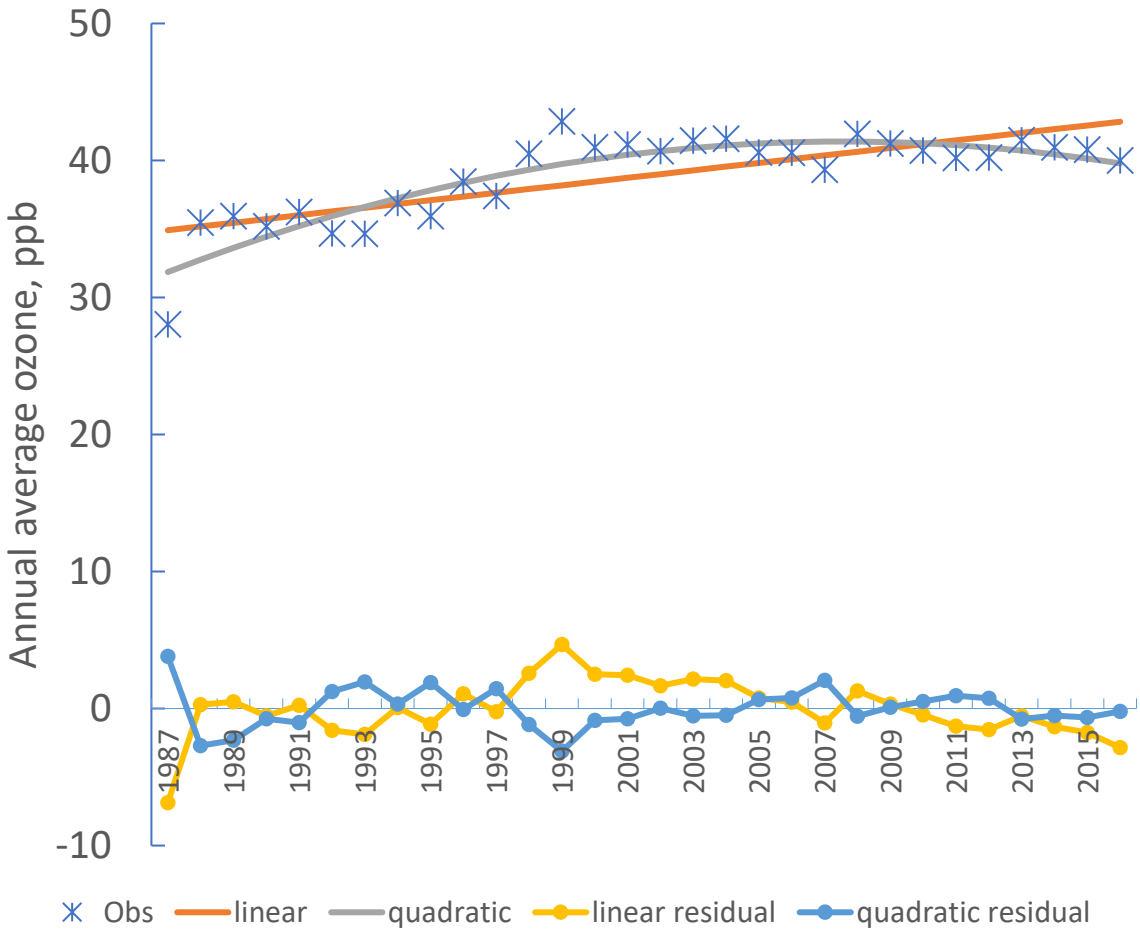
568 b: no statistically significant levelling off.




574

575 Figure 1. Baseline monthly average $O_3$ mixing ratios at the Mace Head Atmospheric Research Station
576 over the period from April 1987 to April 2017.

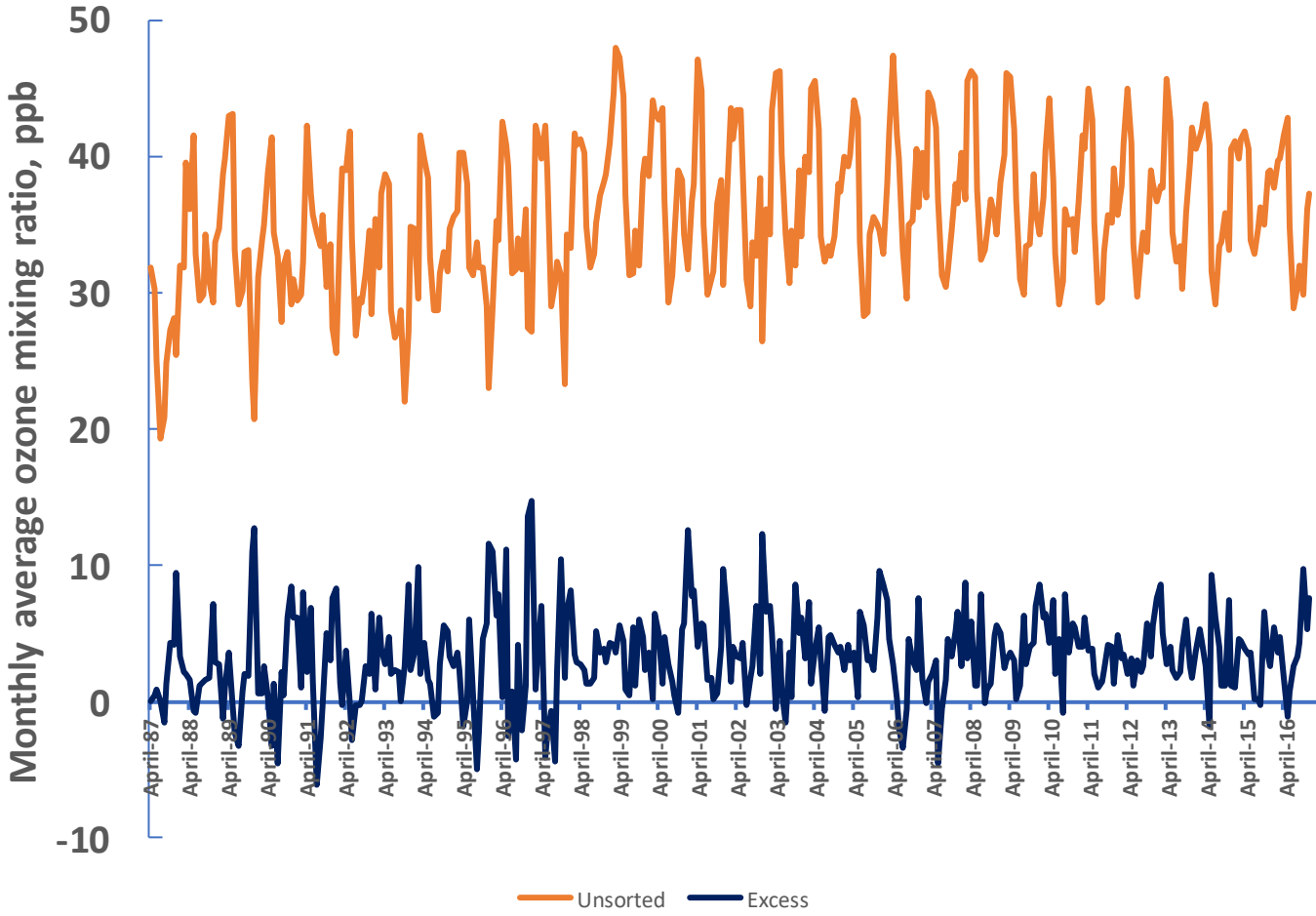
577




578

579 Figure 2. Annual average baseline $O_3$ data for 1987 – 2016, together with linear and quadratic fits
580 and their residuals.

581

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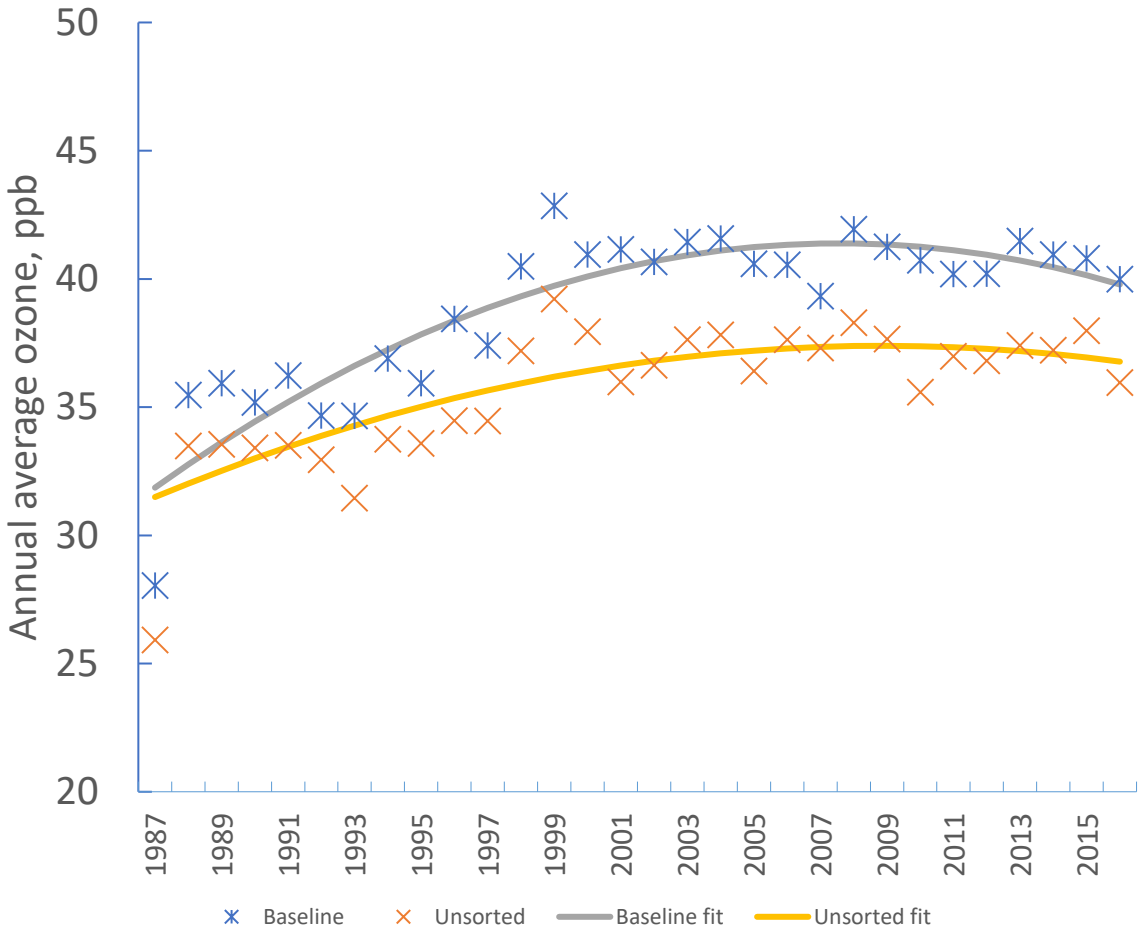
583

584 Figure 3. Monthly average unsorted ozone mixing ratios and their differences from the baseline
585 monthly average $O_3$ mixing ratios at the Mace Head Atmospheric Research Station over the period
586 from April 1987 to April 2017.

587

588




589

590 Figure 4. Annual average baseline and unsorted $O_3$ data for 1987 – 2016, together with quadratic
591 fits.

592

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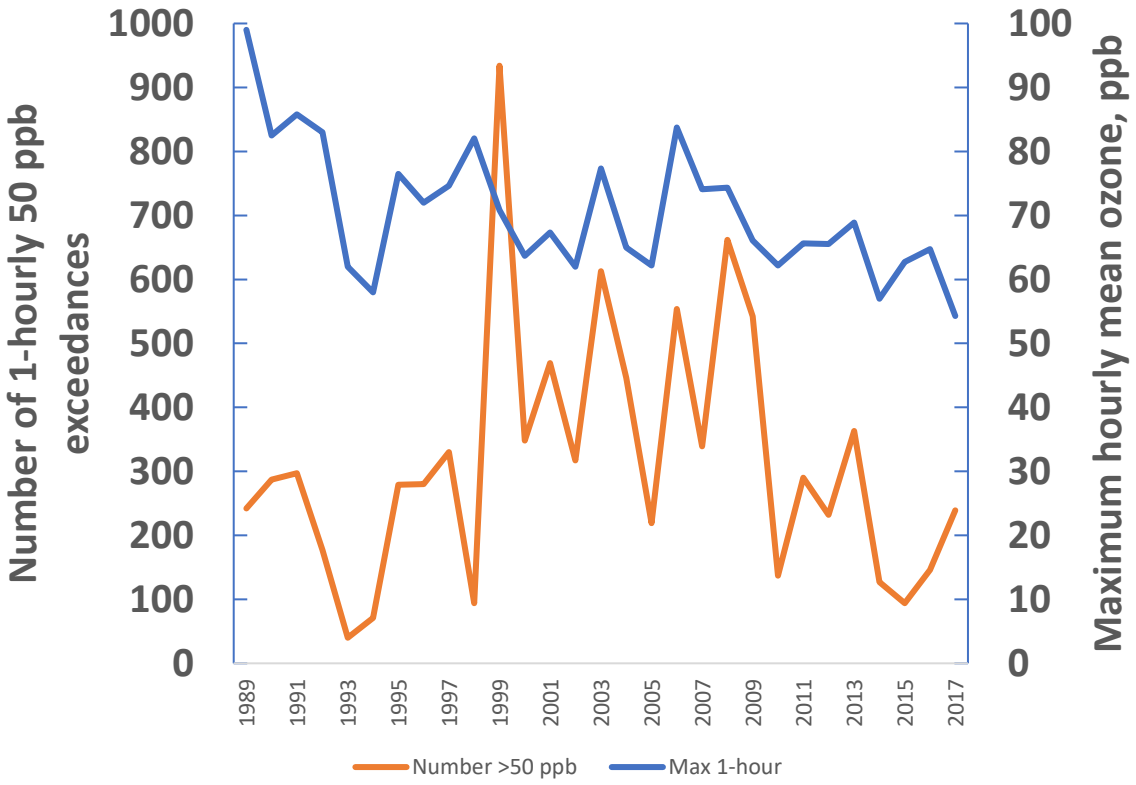
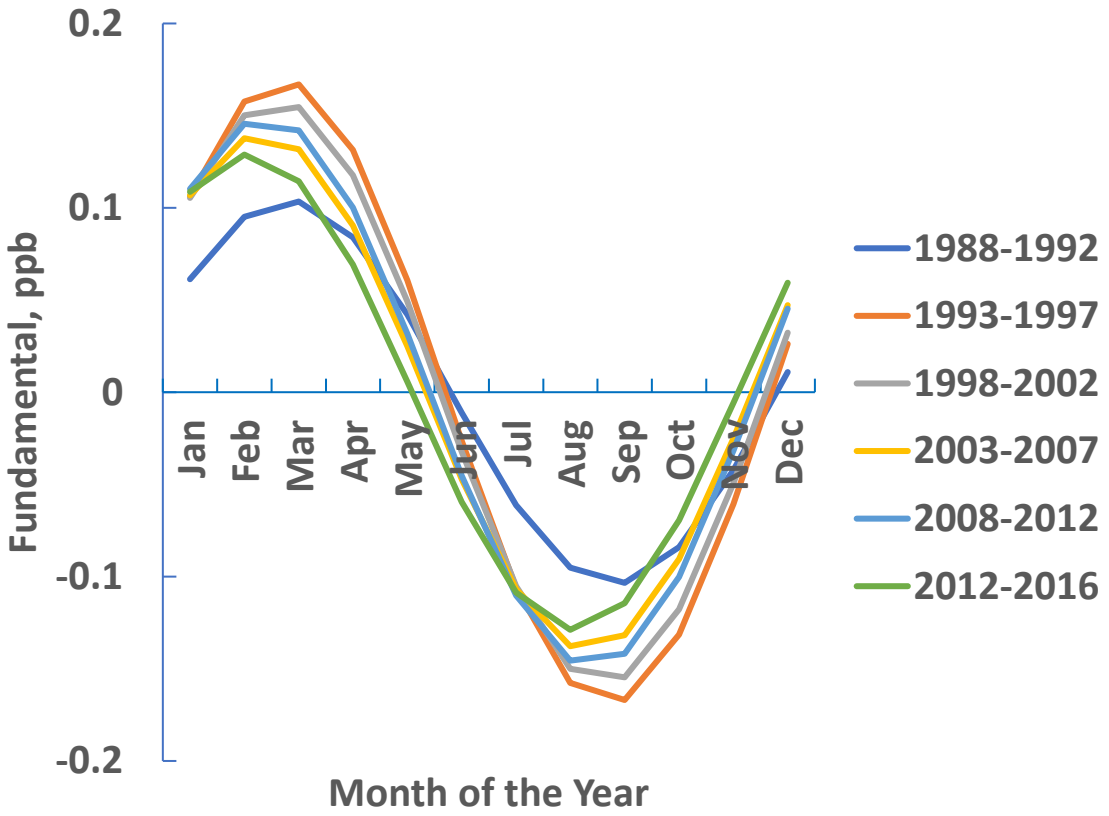



Figure 5. Number of 1-hourly ozone levels above 50 ppb and the maximum 1-hourly mean ozone level in each year between 1987 and 2017 at Mace Head, Ireland.




599

600 Figure 6. Fundamental terms of the seasonal cycles in baseline ozone for the five-year periods 1988-
601 1992, 1993-1997, 1998-2002, 2003-2007, 2008-2012, 2012-2016.