



Derwent, R. G., Parrish, D. D., Simmonds, P. G., O'Doherty, S. J., & Spain, T. G. (2020). Seasonal cycles in baseline mixing ratios of a large number of trace gases at the Mace Head, Ireland atmospheric research station. *Atmospheric Environment*, 233, [117531].
<https://doi.org/10.1016/j.atmosenv.2020.117531>

Peer reviewed version

License (if available):
CC BY-NC-ND

Link to published version (if available):
[10.1016/j.atmosenv.2020.117531](https://doi.org/10.1016/j.atmosenv.2020.117531)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via [insert publisher name] at [insert hyperlink] . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

SEASONAL CYCLES IN BASELINE MIXING RATIOS OF A LARGE NUMBER OF TRACE GASES AT THE MACE HEAD, IRELAND ATMOSPHERIC RESEARCH STATION

Richard G. Derwent^{a,*}, David D. Parrish^b, Peter G. Simmonds^c, Simon J. O'Doherty^c, T. Gerard Spain^d

^a*rdscientific, Newbury, Berkshire, RG14 6LH, United Kingdom*

^b*David D. Parrish, LLC, Boulder, Colorado, USA*

^c*School of Chemistry, University of Bristol, Bristol, United Kingdom*

^d*School of Physics, National University of Ireland Galway, Galway, Ireland*

* Corresponding author.

E-mail address: r.derwent@btopenworld.com (R.G.Derwent)

Highlights

- All trace gases studied exhibited summer minima and winter-spring maxima
- Seasonal cycle minima move later in the year with increasing atmospheric lifetime
- Relative amplitudes are largest for trace gases with shortest atmospheric lifetimes

Keywords

Baseline mixing ratios, trace gases, seasonal cycle amplitudes, seasonal cycle phases

Abstract

A flexible approach for quantifying average long-term changes and seasonal cycles has been applied to the baseline mixing ratios of thirty-two trace gases monitored at the Atmospheric Research Station located at Mace Head, Ireland on the Atlantic Ocean coastline of Europe. Almost all these trace gases exhibit minima in their baseline seasonal cycles during a two-month period from mid-July to the end of September and maxima during a six-month period between November and May. Relative seasonal cycle amplitudes are largest for those trace gases with the shortest atmospheric lifetimes and smallest for the longest. Robust

relationships were found between the timings of the seasonal maxima and minima and their relative amplitudes with the atmospheric lifetimes of the trace gases. These relationships provide a basis for understanding the reasons that the seasonal cycles of a few species (that is, H₂, CCl₄ and the longest-lived gases) deviate significantly; they also have excellent potential as tools to assess global chemistry-transport model performance.

1. Introduction

Each atmospheric trace gas has its own individual spatial and temporal patterns of sources and sinks which acting together define its atmospheric life cycle. Trace gas sources and sinks are generally not constant in space and time, excepting for radioactive decay, so that it is inevitable that trace gas mixing ratios vary on all temporal scales at a monitoring location in the turbulent atmospheric boundary layer. In this study, the seasonal variations in a wide range of trace gases at a single atmospheric baseline station, Mace Head, located on the Atlantic Ocean coastline of Ireland are examined in some detail. We distinguish baseline levels from background levels. The term baseline levels here implies that the observed levels are free from any recent continental influence from man-made sources. Natural background levels are those found in the complete absence of any man-made sources; and hence cannot be directly measured; they can only be estimated from model simulations. These definitions of baseline and natural background are discussed more fully by the Task Force on the Hemispheric Transport of Air Pollution (HTAP, 2010).

At present, a comprehensive understanding of seasonal cycles of atmospheric trace species is lacking. Seasonal cycles have been discussed for certain trace gases but by no means for all. Junge (1963), for example, attributed the observed spring-time maximum in surface ozone by stratosphere-troposphere exchange through association with the spring-time peak in radioactive debris. Explanation of the origins of the seasonal cycle in tropospheric ozone are apparently not considered settled to this day and the recent evidence has been reviewed by Monks (2000). Prather et al., (1987) attributed seasonal cycles in trace gas mixing ratios to the seasonality in tropospheric transport processes such as interhemispheric exchange between the northern and southern hemispheres and between the surface and the free troposphere. For example, the seasonal cycle in convection with maximum activity over continental areas is thought to lead to an annual cycle in the surface concentrations of chlorofluorocarbons (CFCs). Emissions are held in shallow boundary layers

during winter and surface concentrations peak near sources. During summer, boundary layers are deeper, vertical exchange is more efficient and the CFCs are transported more rapidly into the free troposphere (Prather et al., 1987). Derwent et al. (1998) found that six markedly different trace gases - ozone, methyl chloroform, carbon monoxide, carbon dioxide, methane and nitrous oxide, six markedly different trace gases, all exhibited summer minima and winter-spring maxima at Mace Head. Nevison et al., (2004) reported seasonal cycles for nitrous oxide, CFC-11, CFC-113 and CFC-12 at three AGAGE stations including Mace Head. They also found well-defined summer-time minima which they attributed to down-flow of stratospheric air masses depleted in N₂O and CFCs through stratospheric photolysis, followed by a four-month time-lag in mixing to the surface. It is evident that spring-time maxima and summer-time minima are not phenomena unique to ozone; they are observed for many trace gases whether or not they have stratospheric sources.

In this study, we aim to derive a comprehensive view of the seasonality of trace gas mixing ratios at a northern mid-latitude baseline surface site by examining the observed baseline seasonal cycles for thirty-two trace gases at the Mace Head. The trace gases are grouped together into different classes to look for similarities and differences in the shapes and patterns in the seasonal cycles. In addition to tropospheric transport processes following Prather et al., (1987) and stratospheric sources and sinks following Nevison et al., (2004), we can see additionally the impact of other processes such as tropospheric destruction by hydroxyl (OH) radical reactions and natural sources in summer on these seasonal. We also show that the amplitude and phase of the seasonal cycle systematically depends on the trace gas lifetime which ranges from about two weeks to more than a thousand years in these thirty-two trace gases. Given the wide range of lifetimes, this suite of observed seasonal cycles reflects sources, sinks and transport occurring throughout the global atmosphere and thereby provides useful metrics for gauging global chemistry-transport model performance, potentially leading to improvements in the model description of emissions, tropospheric transport and loss processes.

2. Quantifying trace gas seasonal cycles at Mace Head, Ireland

2.1 Methodology

Continuous high-frequency in-situ atmospheric monitoring of a large number of trace gases has been carried out at the Mace Head Atmospheric Research Station over the last thirty years or so. The Mace Head station is located at 53°20'N, 9°54'W and 90m inland from the Atlantic Ocean coastline and has a clean air sector receiving northern hemisphere background air from 180° to 300°. Meteorological records show that on average over 60% of air masses arrive at the station in the clean air sector (www.macehead.org). Details of the site and a map showing its location is available at www.macehead.org. The Mace Head station is one of the few western European stations that has monitored high frequency mid-latitude northern hemispheric baseline concentrations over decadal time scales. Initially, the range of trace gases studied focussed on the halocarbons responsible for stratospheric ozone depletion. Monitoring methods were generally based on gas chromatography and air samples were analysed with 40-minute time resolution. More recently, the focus has extended to include those trace gases responsible for global climate change by employing gas chromatography with mass spectrometry with two-hourly time resolution. Details of the station and its instrumentation are given elsewhere (Stanley et al., 2018).

In this study, we define baseline as those conditions in which the air masses arriving at Mace Head, Ireland have not traversed land areas to the east of Mace Head and so have not been recently influenced by local sources in the vicinity of the station nor by European regional pollution sources on the European continent (HTAP, 2010). It is expected that this definition of baseline will necessarily include conditions when long-range transport brings trace gases emitted in North America and Asia and also from Europe, having travelled completely around the globe, particularly for the long-lived trace gases. Baseline monthly means for each trace gas were taken from the Carbon Dioxide Information and Analysis Center (CDIAC) archive: <http://cdiac.esd.ornl/ndps/alegage.html>, covering the period from March 1994 – December 2018. All Mace Head trace gas observations are available from the public AGAGE website (<http://agage.mit.edu/data>) and the World Data Center for Greenhouse Gases (WDCGG) (<http://gaw.kishou.go.jp/wdcgg>) as well as from CDIAC, with the exception of those for ozone which are available from: <http://ebas.nilu.no/>. These monthly mean baseline mixing ratios provide a time series for each trace gas, covering periods of length between 15 and 35 years, each terminating in 2018. Baseline allocations were made using a statistical methodology which separates polluted from baseline data (Cunnold et al., 2002).

For most of the long-lived trace gases studied here, the monthly baseline mixing ratios show trends with time and simple procedures for defining seasonal cycles do not work well for those trace gases with relatively shallow seasonal cycles. This is because the upwards or downwards trends with time during each year due to the overall trend may be as large or sometimes larger than the apparent seasonal variations within that year. It is important therefore to analyse for overall trends and seasonal cycles at the same time and employ a consistent approach. Parrish et al., (2019) have put forward such a flexible approach to the simultaneous estimation of long-term trends and seasonal cycles using tropospheric ozone and nitrous oxide as examples. This approach has been adopted in this study without modification and applied to the considerably wider range of trace gases at Mace Head.

Following the work of Parrish et al., (2019) an expression involving a polynomial with up to a cubic term and two sine terms of the form (1):

$$\text{vmr} = a + b x + c x^2 + d x^3 + a_1 \sin(x+\phi_1) + a_2 \sin(2x + \phi_2) \quad (1)$$

was fitted to the monthly mean baseline mixing ratios, vmr, using non-linear regression software (NLREG, Sherrod, 1992), where x increases continuously with each year's increment equal to 2π radians and a, b, c and d define the general changes with time. Generally speaking, the fitted equation accounted for over 98% of the variance in the baseline monthly averages and the eight fitted parameters, a, b, c, d, a_1 , a_2 , ϕ_1 and ϕ_2 were generally statistically different from zero, although for many species, the d parameter was not significant and therefore was not considered further. The last two terms of Equation (1) with four fitted parameters a_1 , a_2 , ϕ_1 and ϕ_2 , together with their 2 – σ confidence limits and expression (2),

$$\text{seasonal cycle} = a_1 \sin(x+\phi_1) + a_2 \sin(2x + \phi_2) \quad (2),$$

represents a concise and accurate means of defining the seasonal cycle in the average monthly means for each of the trace gases.

The time variable x was set to zero for some point in the middle of each time series of observations so that it would be negative for early points in the time series and positive thereafter. For the long-lived trace gases whose observations started earliest, the time origin was usefully set to the year 2000. For the more recently established observations, a

time origin of 2010 was found to be suitable. Whilst the choice of time origin made no difference to the derived description of the general changes with time, it exerted a significant influence on the $2 - \sigma$ confidence limits of the fitted parameters a , b , c and d , but made no difference to the values and confidence limits of a_1 , a_2 , ϕ_1 and ϕ_2 . The eight fitted parameters for each trace gas are provided in a Supplementary Information file.

Equation (2) with the derived parameter values and confidence limits for a_1 , a_2 , ϕ_1 and ϕ_2 provides a quantitative description of the seasonal cycle. However, we found that mathematical manipulation of that equation to determine the seasonal maxima and minima (with their $2 - \sigma$ confidence intervals) to be too complex. Instead, we chose to employ Monte Carlo sampling to derive these parameters. In this way, the timings, x_{\max} , and the magnitudes of the primary maxima, vmr_{\max} were defined for each trace gas and their corresponding timings, x_{\min} , and magnitudes, vmr_{\min} , of the primary minima in the fitted seasonal cycles. The difference in magnitudes between the fitted primary maxima and minima, $\text{vmr}_{\max} - \text{vmr}_{\min}$, defined the absolute amplitude of the baseline seasonal cycle and this was converted onto a relative or normalised basis by dividing by the fitted mixing ratio near the centre point of each dataset, a . The relative amplitude was thus $(\text{vmr}_{\max} - \text{vmr}_{\min})/a$ and hence was unit-less.

Equations (1) and (2) are the specific application of the general approach in which a power series expansion of the long-term change and a Fourier series expansion of the seasonal cycle are simultaneously fitted (Parrish et al., 2019). The power series expansion provides a method to quantify a continuous, time varying function without a priori knowledge of the underlying mathematical form, while the Fourier series provides an elegant method for the quantification of any temporally-repeating function, such as a seasonal cycle. Our method, described in some detail in Parrish et al., (2019), aims at providing a robust set of parameters that capture the statistically significant information in each observational dataset with regard to the long-term trend and seasonal cycle that can be compared quantitatively across a suite of trace gases. It is important that no physical model underpins our approach and that it is flexible enough to be appropriate to a wide range of trace gases. Each trace gas dataset defines its own most appropriate functional form of the power series and Fourier series expansions.

To illustrate our approach, we describe in some detail its application to the trace gas methane, a trace gas which shows both large long-term trends and a marked seasonal cycle. We then go on to apply this method to a wide range of trace gases which span atmospheric lifetimes from the order of a few days to tens of thousands of years.

2.2 Methane as an example

To illustrate the methodology, the analysis began with the trace gas methane (CH_4). The dataset of monthly baseline methane mixing ratios spanned the period from March 1994 to March 2018, inclusive. This dataset comprised 23 complete calendar years covering 1995 to 2017. To gain a qualitative picture of the seasonal cycle, the monthly deviations in each year from the respective annual calendar mean were calculated, together with the standard deviations of the hourly averages that made up the monthly means, and plotted in Figure 1. This figure illustrates a number of features which are common to many of the other trace gases studied.

The first main feature identified in Figure 1 was the presence of a deep summer minimum. This turned out to be a remarkably robust feature of the baseline seasonal cycle of methane as it occurred during July in seventeen out of the twenty-three years and during August during the remaining six years (2002, 2003, 2006, 2007, 2009, 2013). The second main feature identified in Figure 1 was the presence of a complex and variable, shallow maximum during the winter half of the year. In some years there were secondary maxima and minima within this period also. Overall, the picture was one of large variability in behaviour, shape and timing in terms of primary maxima versus primary and secondary maxima and secondary minima. This large variability, however, was not shown in the magnitudes of the monthly means since their $2 - \sigma$ confidence limits tended to be relatively constant throughout the year at about 10 ppb. So, the large variability seen in Figure 1 was not considered to be statistically significant.

Also shown in Figure 1, is the average seasonal cycle estimated using the fitting procedure outlined in section 2.1 above. This methodology deals accurately with the growth in baseline methane levels and returned the four fitted terms a , b , c and d , the first three of which which were highly statistically significantly different from zero (Supplementary Information). Figure 1 shows that the fitted seasonal cycle defined by the two sine terms, provided an

excellent description of the observations with a primary minimum during July and a primary maximum during March.

To quantify the primary maxima and minima in the fitted baseline seasonal cycle, Monte Carlo sampling was used to randomly sample the a_1 , a_2 , ϕ_1 and ϕ_2 terms within their confidence limits and 10,000 seasonal cycles were calculated and their primary maxima and minima were determined in terms of timing and magnitude. The primary maximum in the fitted methane seasonal cycle was found on Julian day 83 ± 4 (24 March) and the primary minimum on Julian day 207 ± 2 (26 July) (where the confidence limits here and hereafter are $2 - \sigma$ or 95% confidence limits). The absolute amplitude ($\text{vmr}_{\text{max}} - \text{vmr}_{\text{min}}$) was found to be 28.4 ± 1.4 ppb.

The two sine-term seasonal cycle fitting procedure, which gave four parameters defining the seasonal cycle, coupled with the Monte Carlo sampling has therefore been able to accurately quantify the main features in the observed baseline seasonal cycle of methane as shown in Figure 1, despite the manifest year-on-year variability in the observations.

2.3 Application to a wide range of trace gases at Mace Head

This flexible methodology was applied to a wide range of trace gases monitored at the Mace Head Atmospheric Research Station. The methodology worked well without modification for thirty-two trace gases and the results obtained are tabulated in Tables 1 – 4 and in a Supplementary Information file and are discussed in some detail in section 3. That is to say, the methodology returned fitted seasonal cycles defined by the two sine terms, together with seasonal maxima and minima, which were all statistically significant for all thirty-two trace gases.

In addition to the thirty-two trace gases mentioned in the previous paragraph, nine other trace gases were examined: HCFC142b, Halon2402, HFC23, HFC134a, HFC4310mee, HFC125, HFC227ea, HFC236fa and PFC218. The seasonal cycles for these species were not accurately defined and the $2 - \sigma$ confidence intervals surrounding the timings of the fitted seasonal maxima and minima were large. For these trace gases, the fitted seasonal cycles showed a significant amount of variability and, consequently, no conclusive assignments were made for seasonal maxima and minima. These species are undoubtedly man-made and there are

no reasons to believe that their source distributions are significantly different from the other thirty-two trace gases.

For some of the nine trace gases, seasonal cycles were weak relative to long-term trends. For others, average seasonal cycles were affected by measurement reproducibility and interannual variability because of the limited length of the observational records. For the HFCs, the shortness of the available records was potentially important, particularly when this was compounded by the HFC being a relatively recent and novel atmospheric trace gas. Under these circumstances, the trace gas would show strong upwards trends and the rate of annual increase would be large in comparison to a weak seasonal variation.

These issues should be resolved in the future when observational records are longer and substantial baseline mixing ratios have built up. It is recommended that attention should return to the HFCs as a category and their baseline seasonal cycles reanalysed after a further 10 years. No further analysis of the seasonal cycles of these nine trace gases was therefore made in this study.

3. Seasonal cycles of baseline mixing ratios of a large number of trace gases

3.1 Ozone-depleting substances

Table 1 presents the details of the fitted baseline seasonal cycles found for the ozone-depleting substances arranged in order of their increasing atmospheric lifetimes as taken from IPCC (2013) and WMO (2014). The fitted cycles of the twelve ozone-depleting substances exhibited well-defined primary minima during the late summer on Julian days between 205 and 260 (24 July to 17 September). Seven of the ozone depleting substances (CFC113, CFC114, CFC115, CFC13, Halon 12b1, Halon13b1 and N₂O) exhibited late winter to spring maxima between Julian days 40 and 130. The remaining five of this group (CFC11, CFC12, CCl₄, HCFC141b and HCFC22) exhibited late autumn to early winter maxima between Julian days 320 and 354. The timings of the seasonal cycle minima found here during August for CFC-11, CFC-12 and N₂O agree closely with those reported by Simmonds et al. (2013) for the shorter observational period up to 2010.

The amplitudes of the baseline seasonal cycles were well-defined for this group of substances. Relative amplitudes, defined by $(\text{vmr}_{\text{max}} - \text{vmr}_{\text{min}}/a)$, declined from 0.01 – 0.03

to 0.002 – 0.004 with increasing atmospheric lifetime. Indeed, visual inspection of a scatter plot of relative amplitude vs atmospheric lifetime showed a general decline over the twelve trace gases.

3.2 Trace gases with tropospheric sinks

Table 2 presents the details of the fitted baseline seasonal cycles for twelve trace gases with largely man-made sources and efficient tropospheric OH-radical sinks. This group of trace gases exhibited strong summertime primary minima between Julian days 193 – 253 (12 July to 10 September). Four trace gases exhibited primary maxima during the late autumn to early winter (CHCl₃, HFC245fa, HFC365mfc and HFC143a: Julian days 316 – 350). Eight trace gases exhibited late winter to early spring maxima (C₃H₈, C₂H₆, C₂Cl₄, CH₂Cl₂, CH₃Br, CH₃Cl, HFC152a and CH₃CCl₃: Julian days 33 – 128). Relative amplitudes decreased by two orders of magnitude from 2 to 0.02 with increasing atmospheric lifetime from C₃H₈ to HFC143a. A scatter plot of relative amplitude versus atmospheric lifetime for the twelve trace gases showed how relative amplitudes declined with increasing atmospheric lifetimes.

3.3 Trace gases with complex tropospheric source and sinks

In this section, the fitted baseline seasonal cycles are compared for five trace gases with complex tropospheric sources and sinks: tropospheric ozone (O₃), carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂) and methane (CH₄). Table 3 contains the details of the fitted parameters for these trace gases, together with the atmospheric lifetimes taken from WMO (2014). The atmospheric lifetime for carbon dioxide is not a well-defined parameter as discussed in IPCC (1990). For this trace gas, we have taken the atmospheric lifetime as 7 years based on the first exponential term in the impulse response function (IPCC, 1994; Joos et al., 2013).

All the members of this group showed strong primary minima. Four members (O₃, CO, CO₂ and CH₄) showed summer minima between Julian days 207 and 241. The fifth, H₂, showed an autumn minimum on Julian day 293 which was significantly later in the year compared with other members of this group and all other trace gases monitored at Mace Head.

Seasonal maxima were found between Julian days 79 and 111, except for H₂ which was found to be significantly later in the spring on Julian day 129. Relative amplitudes generally declined with increasing atmospheric lifetimes from ~0.4 to 0.015 for these species.

3.4 Trace gases with long atmospheric lifetimes

There are three trace gases (see Table 4) in this miscellaneous class having long atmospheric lifetimes, that is to say, at least 1000 years: sulphur hexafluoride (SF_6), perfluoroethane (PFC116) and carbon tetrafluoride (CF_4). The maxima and minima in the baseline seasonal cycles are well-defined for all three. Minima were found during the autumn in the range from Julian day 251 to 269 (7 to 25 September). Maxima were found during the spring between Julian day 118 to 150 (27 April to 29 May). Relative amplitudes declined with increasing atmospheric lifetime for all three trace gases from ~ 0.007 to 0.002 for these species.

4. Discussion and conclusions

A flexible approach (Parrish et al., 2019) to the simultaneous estimation of long-term changes and seasonal cycles has been applied to the baseline observations of thirty-two trace gases monitored at Mace Head. This approach accounted for any upwards or downwards trends in annual mean baseline mixing ratios and left the average baseline seasonal cycle to be characterised by two sine terms with four fitted parameters, together with their confidence limits. Monte Carlo sampling of these fitted parameters and their confidence limits was then used to quantify the timings and magnitudes of the primary maxima and minima and the relative amplitudes in each fitted baseline seasonal cycle.

Figure 2 summarises the timings of the seasonal cycle maxima and minima and Figure 3, the normalised amplitudes. Figure 2 is a semi-log scatter plot, where the timings are plotted against \log_{10} (atmospheric lifetime in years), with the atmospheric lifetimes taken from IPCC (2013) and WMO (2014). Figure 3 is a log – log scatter plot where \log_{10} (relative amplitudes) are plotted against the same abscissa. Despite all the variability in the atmosphere and despite the large variations in sources and sinks for all thirty-two trace gases, the timings of the maxima and minima and the relative amplitudes exhibit a simple relationship with atmospheric lifetime over the range of $\sim \frac{1}{2}$ month to 50,000 years.

Attention is first directed to the timings of the minima in Figure 2 (triangle points). The primary minima lay in a range from Julian day 200 to 269, (with the exception of H_2) and systematically advanced from mid-July (Julian day 200) to late September (Julian day 269)

with increasing atmospheric lifetime. This advance is about 11 days per 10-fold increase in atmospheric lifetime.

The square points in Figure 2 present a scatter plot of the timings of the seasonal maxima versus \log_{10} (atmospheric lifetime in years). Generally speaking, the timings of the maxima exhibit a considerable amount of variability compared to the corresponding plot of the minima. This is due to two groups of trace gases. One set spanned the range from Julian day 316 to 354 (mid-November to mid-December) and a larger set from Julian day 39 to 150 (early-February to end-May). Within both sets of trace gases, there was a marked tendency for the maxima to advance through the year with increasing atmospheric lifetime. For example, the maximum for CO, with an atmospheric lifetime of about 50 days, was found on Julian day 79 (mid-March) and that for SF₆, with an atmospheric lifetime of 3,200 years, was found on Julian day 150 (end-May). This advance amounted to about 16 days per factor of 10 increase in atmospheric lifetime.

Figure 3 presents a log – log scatter plot of \log_{10} (relative amplitude) plotted versus \log_{10} (atmospheric lifetime in years) for the thirty-two trace gases. Relative amplitudes defined by $(\text{vmr}_{\text{max}} - \text{vmr}_{\text{min}})/a$, declined steadily from 2.0 for propane with a lifetime of about ½ month to 0.0015 for CF₄ with a lifetime of 50,000 years. This implies a factor of about 10 decline in relative amplitude for every factor of 100 increase in atmospheric lifetime. The points were distributed about a log – log regression line which indicated a highly statistically significant inverse correlation with $R^2 = 0.75$ and a slope of -0.5 ± 0.12 (95% confidence intervals).

Intuitively, the more reactive trace gases are expected to be more variable in space and time (Jobson et al., 1999). In this study, this implies that seasonal cycle amplitudes should increase with decreasing atmospheric lifetime and this is clearly seen in our analysis. However, it is surprising is that a robust log – log relationship has been found between seasonal amplitude and atmospheric lifetime over all the thirty-two trace gases, despite their great diversity in sources, (that is to say, man-made versus natural) and sinks.

Many studies have related atmospheric variability in space and time to atmospheric lifetime (Junge 1974; Hamrud 1983; Ehhalt et al., 1998; Jobson et al., 1999), though, to our knowledge, this study is unique in addressing seasonal cycles for a wide range of trace gases at a single location in the atmospheric boundary layer. Jobson et al. (1999) examined the

normalised amplitude of variability of species in the remote troposphere during short period NASA field campaigns and they define a variability versus atmospheric lifetime (τ) relationship of the form: $A \tau^{-b}$, which is directly comparable to the log – log regression relationship in our Figure 3, where the slope b (which is equivalent to the exponent of Jobson et al., 1999) was found to be -0.53. Jobson et al. (1999) derived similar values, -0.46 to -0.53 for relatively remote tropospheric data from NASA field campaigns. Even the intercepts at atmospheric lifetime of 1 year are similar, $S(\ln x)$ at 1 year in Jobson et al., (1999) is about 0.11 in their Figure 5a, corresponding to a normalised variability of $\sim 11\%$, while this study gives a relative seasonal cycle amplitude of 9.8% for that same atmospheric lifetime as shown by the intercept in Figure 3. This similarity may simply reflect that the baseline filtering applied to the Mace Head data has been successful in removing any influence of recent European source contributions. However, this agreement between our Figure 3 and the variability versus atmospheric lifetime relationship of Jobson et al., (1999) is striking.

The relationships in Figure 2 and the -0.53 log – log regression slope in Figure 3 reflects a general pattern that develops from the dispersion and removal of trace gases emitted by continental sources (Jobson et al., 1999), the build-up of boundary layer concentrations in winter and continental convection venting of summer boundary layers (Prather et al., 1987). These mechanisms are of general application to all thirty-two trace gases studied here. Elucidating exactly how these mechanisms quantitatively interact must await results of detailed global chemistry-transport modelling studies that can reproduce the observed relationships. However, some deviations from the general relationships are informative. As mentioned above, the seasonal minimum of hydrogen deviated from the general relationship. This autumn minimum has been discussed previously by Derwent et al., (2019) and is thought to be caused by the observed inverted distribution of H_2 with southern hemisphere mixing ratios higher than northern hemisphere values (Simmonds et al., 2000).

The three trace gases with long atmospheric lifetimes all lie above the regression fit in Figure 3. The average mixing ratios of these trace gases (which is the denominator in the relative amplitude calculation) have not approached atmospheric steady-state since their sources are predominantly man-made and have been active for only the last few decades. As the atmospheric mixing ratios of these species rise in the future, their relative amplitudes

will decrease, bringing those points closer to the regression line. Similarly, the point furthest below the regression line is CCl_4 , a trace gas that once had large man-made emissions that have been greatly reduced. Consequently, the residual CCl_4 mixing ratio remaining in the atmosphere is now continuously decreasing and the relative seasonal amplitude will increase as the denominator decreases. One utility of the regression fits in Figure 2 and 3 is to identify outliers, such as these examples, and enhance our understanding of their seasonal cycles.

The thirty-two trace gases studied provide evidence that the maxima and minima in the baseline seasonal cycles advance steadily and robustly through the year with increasing atmospheric lifetime. Those trace gases with atmospheric lifetimes shorter than one year exhibited seasonal cycle maxima during spring and minima during summer. There was a tendency for the more longer-lived trace gases to exhibit maxima and minima considerably later in the year. The mixing ratio of a trace gas at a particular location represents the integrated temporal history of sources, sinks and transport of that species throughout the global atmosphere, with the time period of that integration determined by the species lifetime. Thus, even though the underlying observations were collected at a single northern mid-latitude surface site, these shifts in seasonal extrema and declines in relative amplitudes with increasing species lifetime constitute metrics that provide stringent tests of global chemistry-transport model performance and we provide three examples as illustrations. Firstly, Orbe et al. (2017) describe how two idealised synthetic tropospheric tracers with lifetimes of 5 days and 50 days can be used to diagnose convective parameterisations in global chemistry-transport models. This study could be straightforwardly extended using real trace gases such as propane and ethane, respectively, adding much improved realism to the model versus observation comparisons. Secondly, in a recent series of single trace gas studies, for example, of HFC152a (Simmonds et al. 2016), CFC13 and CFC114 (Vollmer et al., 2018), HFC23 (Simmonds et al., 2018) and PFC318 (Muhle et al., 2019), the Advanced Global Atmospheric Gases Experiment (AGAGE) program has applied a twelve box model (Rigby et al., 2013) to fit observed trace gas levels at Mace Head and other observation stations. To our knowledge, the AGAGE model has not been applied to multiple trace gases or a suite of them as described in this study but is generally applied on a single trace gas basis. Thirdly, our final illustrative example addresses the Atmospheric

Chemistry and Climate Model Intercomparison Project (ACCMIP) models which have been used to describe the tropospheric behaviour of ozone carbon monoxide and methane in terms of their burdens, turnover times and atmospheric lifetimes (Stevenson et al., 2013, Young et al., 2013). A study of the ACCMIP model predicted seasonal cycles for ozone pointed up significant mismatches with observations (Derwent et al., 2018), an issue taken up by the Tropospheric Ozone Assessment Report (TOAR) in TOAR-Model Performance (Young et al., 2018). Similar problems have been reported with the ozone seasonal cycles reported in three chemistry-climate models (Parrish et al., 2016). Simulating the observed seasonal cycles in a suite of trace gases, even from a single site, will provide an illuminating challenge for the chemistry-transport modelling community.

Acknowledgements

We specifically acknowledge the cooperation and efforts of the operators of the Mace Head Atmospheric Research Station and their support staff. We also thank the School of Physics, National University of Ireland, Galway, for making the research facilities at Mace Head, Ireland available. The operation of the Mace Head station was supported by the Climate and Energy: Science and Analysis Division of the Department for Energy and Climate Change (now Department for Business, Energy and Industrial Strategy) UK, under contracts EPG 1/1/130 and 142, CPEG 11, 24 and 27, GA 01081, GA 0201 and CESA 002 and also by the National Aeronautics and Space Administration (NASA grants NAGW-732, NAG1-1805, NAG5-3974 and NAG-12099).

References

Cunnold, D.M., Steele, L.P., Fraser, P.J., Simmonds, P.G., Prinn, R.G., Weiss, R.F., Porter, L.W., Langenfelds, R.L., Krummel, P.B., Wang, H.J., Emmons, L., Tie, X.X., Dlugokencky, E.J., 2002. In-situ measurements of atmospheric methane at GAGE/AGAGE sites during 1985-1999 and resulting source inferences. *Journal of Geophysical Research* 107, ACH 20-1 – ACH-20-18.

Derwent, R.G., Simmonds, P.G., Seuring, S., Dimmer, C., 1998. Observation and interpretation of the seasonal cycles in the surface concentrations of ozone and carbon monoxide at Mace Head, Ireland from 1990 to 1994. *Atmospheric Environment* 32, 145-157.

Derwent, R.G., Parrish, D.D., Galbally, I.E., Stevenson, D.S., Doherty, R.M., Naik, V., Young, P.J., 2018. Uncertainties in models of tropospheric ozone based on Monte Carlo analysis: Tropospheric ozone burdens, atmospheric lifetimes and surface distributions. *Atmospheric Environment* 180, 93-102.

Derwent, R.G., Simmonds, P.G., O'Doherty, S.J., Manning, A.J., Spain, T.G., 2019. A 24-year record of high-frequency, in situ, observations of hydrogen at the Atmospheric Research Station at Mace Head, Ireland. *Atmospheric Environment* 203, 28-34.

Ehhalt, D.H., Rohrer, F., Wahner, A., Prather, M.J., Blake, D.R., 1998. On the use of hydrocarbons for the determination of tropospheric OH concentrations. *Journal of Geophysical Research* 103, 18,981-18,997.

Hamrud, M., 1983. Residence time and spatial variability for gases in the atmosphere. *Tellus* 35B, 295-303.

HTAP 2010. Hemispheric transport of air pollution 2010. Part A.: ozone and particulate matter. *Air Pollution Studies No. 17*. United Nations, Geneva, Switzerland.

IPCC 1990. *Climate change: The IPCC scientific assessment*. Cambridge University Press, Cambridge.

IPCC 1994. *Climate change 1994. Radiative forcing of climate change and an evaluation of the IS92 emission scenarios*. Cambridge University Press, Cambridge.

IPCC, 2013. *Intergovernmental Panel on Climate Change. Working Group I. Fifth Assessment Report, Chapter 8*, Geneva, Switzerland.

Jobson, B.T., McKeen, S.A., Parrish, D.D., Fehsenfeld, F.C., Blake, D.R., Goldstein, A.H., Schauffler, S.M., Elkins, J.W., 1999. Trace gas mixing ratio variability versus lifetime in the troposphere and stratosphere: Observations. *Journal of Geophysical Research* 104, 16,091-16,113.

Joos, F., Roth, R., Fuglestad, J.S., Peters, G.P., Enting, I.G., von Bloh, W., Brovkin, V., Burke, E.J., Eby, M., Edwards, N.R., Friedrich, T., Frohlicher, T.L., Halloran, P.R., Holden, P.B., Jones, C., Kleinen, T., Mackenzie, F.T., Matsumoto, K., Meinshausen, M., Plattner, G.-K., Reisinger, A., Segschneider, J., Shaffer, G., Steinacher, M., Strassmann, K., Tanaka, K., Timmermann, A.,

Weaver, A.J., 2013. Carbon dioxide and climate impulse response functions for the computation of greenhouse gas metrics: a multi-model analysis. *Atmospheric Chemistry and Physics* 13, 2793-2825.

Junge, C.E., 1963. *Air chemistry and radioactivity*. Academic Press, New York.

Junge, C.E., 1974. Residence time and variability of tropospheric trace gases. *Tellus* 26, 477-488.

Monks, P.S., 2000. A review of the observations and origins of the spring ozone maximum. *Atmospheric Environment* 34, 3545-3561.

Mühle, J., Trudinger, C.M., Western, L.M., Rigby, M., Vollmer, M.K., Park, S., Manning, A.J., Say, D., Ganesan, A., Steele, L.P., Ivy, D.J., Arnold, T., Li, S., Stohl, A., Harth, C.M., Salameh, P.K., McCulloch, A.M., O'Doherty, S., Park, M.-K., Jo, C.O., Young, D., Stanley, K.M., Krummel, P.B., Mitrevski, B., Hermansen, O., Lunder, C., Evangeliou, N., Yao, B., Kim, J., Hmiel, B., Buizert, C., Petrenko, V.V., Arduini, J., Maione, M., Etheridge, D.M., Michalopoulou, E., Czerniak, M., Severinghaus, J.P., Reimann, S., Simmonds, P.G., Fraser, P.J., Prinn, R.G., Weiss, R.F., 2019. Perfluorocyclobutane (PFC-318, $c\text{-C}_4\text{F}_8$) in the global atmosphere. *Atmospheric Chemistry and Physics* 19, 10335–10359.

Nevison, C.D., Kinnison, D.E., Weiss, R.F., 2004. Stratospheric influences on the tropospheric seasonal cycles of nitrous oxide and chlorofluorocarbons. *Geophysical Research Letters* 31, L20103, doi:10.1029/2004GL020398.

Orbe, C., Waugh, D.W., Yang, H., Lamarque, J.-F., Times, S., Kinnison, D.E., 2017. Tropospheric transport differences between models using the same large-scale meteorological fields. *Geophysical Research Letters* 44, 1068-1078, doi:10.1002/2016GL071339.

Parrish, D.D., Galbally, I.E., Lamarque, J.-F., Naik, V., Horowitz, L., Shindell, D.T., Oltmans, S.J., Derwent, R.G., Tanimoto, H., Labuschagne, C., Cupeiro, M., 2016. Seasonal cycles of O_3 in the marine boundary layer: Observation and model simulation comparisons. *Journal of Geophysical Research: Atmospheres* 121, 538-557, doi:10.1002/2015JD024101.

Parrish, D.D., Derwent, R.G., O'Doherty, S., Simmonds, P.G., 2019. Flexible approach for quantifying average long-term changes and seasonal cycles of tropospheric trace gases. *Atmospheric Measurement Techniques Discussions* <https://doi.org/10.5194/amt-2019-38>.

Prather, M., McElroy, M., Wofsy, S., Russell, G., Rind, D., 1987. Chemistry of the global troposphere: Fluorocarbons as tracers of air motion. *Journal of Geophysical Research* 92, 6579-6613.

Rigby, M., Prinn, R. G., O'Doherty, S., Montzka, S. A., McCulloch, A., Harth, C. M., Mühle, J., Salameh, P. K., Weiss, R. F., Young, D., Simmonds, P. G., Hall, B. D., Dutton, G. S., Nance, D., Mondeel, D. J., Elkins, J. W., Krummel, P. B., Steele, L. P., Fraser, P. J., 2013. Re-evaluation of the lifetimes of the major CFCs and CH₃CCl₃ using atmospheric trends, *Atmospheric Chemistry and Physics* 13, 2691–2702.

Simmonds, P.G., Derwent, R.G., O'Doherty, S., Ryall, D.B., Steele, L.P., Langenfelds, R.L., Salameh, P. Wang, H.J., Dimmer, C.H., Hudson, L.E., 2000. Continuous high-frequency observations of hydrogen at the Mace Head baseline atmospheric monitoring station over the 1994-1998 period. *Journal of Geophysical Research* 105, 12,105-12,121.

Simmonds, P.G., Manning, A.J., Athanassiadou, M., Scaife, A.A., Derwent, R.G., O'Doherty, S., Harth, C.M., Weiss, R.F., Dutton, G.S., Hall, B.D., Sweeney, C., Elkins, J.W., 2013. Interannual fluctuations in the seasonal cycle of nitrous oxide and chlorofluorocarbons due to the Brewer-Dobson circulation. *Journal of Geophysical Research* 118, 10,694-10,706.

Simmonds, P.G., Rigby, M., Manning, A.J., Lunt, M.F., O'Doherty, S., McCulloch, A., Fraser, P.J., Henne, S., Vollmer, M.K., Mühle, J., Weiss, R.F., Salameh, P.K., Young, D., Reimann, S., Wenger, A., Arnold, T., Harth, C.M., Krummel, P.B., Steele, L.P., Dunse, B.L., Miller, B.R., Lunder, C.R., Hermansen, O., Schmidbauer, N., Saito, T., Yokouchi, Y., Park, S., Li, S., Yao, B., Zhou, L.X., Arduini, J., Maione, M., Wang, R.H.J., Ivy, D., Prinn, R.G., 2016. Global and regional emissions estimates of 1,1-difluoroethane (HFC-152a, CH₃CHF₂) from in situ and air archive observations. *Atmospheric Chemistry and Physics* 16, 365–382.

Simmonds, P. G., Rigby, M., McCulloch, A., Vollmer, M. K., Henne, S., Mühle, J., O'Doherty, S., Manning, A. J., Krummel, P. B., Fraser, P. J., Young, D., Weiss, R. F., Salameh, P.K., Harth, C. M., Reimann, S., Trudinger, C. M., Steele, L.P., Wang, R. H. J., Ivy, D. J., Prinn, R. G.,

Mitrevski, B., Etheridge, D. M., 2018. Recent increases in the atmospheric growth rate and emissions of HFC-23 (CHF₃) and the link to HCFC-22 (CHClF₂) production, *Atmospheric Chemistry and Physics* 18, 4153–4169.

Sherrod, P.H. (1992). NLREG: Non-linear regression software. <http://www.nlreg.com>.

Stanley, K.M., Grant, A., O'Doherty, S., Young, D., Manning, A.J., Stavert, A.R., Spain, T.G., Salameh, P.K., Harth, C.M., Simmonds, P.G., Sturges, W.T., Oram, D.E., Derwent, R.G., 2018. Greenhouse gas measurements from a UK network of tall towers: technical description and first results. *Atmospheric Measurement Techniques* 11, 1437-1458.

Stevenson, D.S., Young, P. J., Naik, V., Lamarque, J.-F., Shindell, D.T., Voulgarakis, A., Skeie, R. B., Dalsoren, S. B., Myhre, G., Berntsen, T. K., Folberth, G. A., Rumbold, S. T., Collins, W. J., MacKenzie, I. A., Doherty, R. M., Zeng, G., van Noije, T. P. C., Strunk, A., Bergmann, D., Cameron-Smith, D., Plummer, D.A., Strode, S. A., Horowitz, L., Lee, Y. H., S., Sudo, K., Nagashima, T., Josse, B., Cionni, I., Righi, M., Eyring, V., Conley, A., Bowman, K. W., Wild, O., Archibald, A., 2013. Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). *Atmospheric Chemistry and Physics* 13, 3063-3085.

Vollmer, M.K., Young, D., Trudinger, C.M., Mühle, J., Henne, S., Rigby, M., Park, S., Li, S., Guillevic, M., Mitrevski, B., Harth, C.M., Miller, B.R., Reimann, S., B., Steele, L.P., Wyss, S.A., Lunder, C.R., Arduini, J., McCulloch, A., Wu, S., Rhee, T.S., Wang, R.H.J., Salameh, P.K., Hermansen, O., Hill, M., Langenfelds, R.L., Ivy, D., O'Doherty, S., Krummel, P.B., Maione, M., Etheridge, D.M., Zhou, L., Fraser, P.J., Prinn, R.G., Weiss, R.F., Simmonds, P.G., 2018. Atmospheric histories and emissions of chlorofluorocarbons CFC-13 (CClF₃), ΣCFC-114 (C₂Cl₂F₄), and CFC-115 (C₂ClF₅). *Atmospheric Chemistry and Physics* 18, 979–1002.

WMO UNEP, 2014. Scientific assessment of ozone depletion: 2014. World Meteorological Organization. Global Ozone Research and Monitoring Project – Report No. 55, WMO, Geneva, Switzerland.

Young, P.J., Archibald, A.T., Bowman, K.W., Lamarque, J.-F., Naik, V., Stevenson, D.S., Tilmes, S., Voulgarakis, A., Wild, O., Bergmann, D., Cameron-Smith, P., Cionni, I., Collins, W.J., Dalsoren, S.B., Doherty, R.M., Eyring, V., Faluvegi, G., Horowitz, L.W., Josse, B., Lee, Y.H., MacKenzie, I.A., Nagashima, T., Plummer, D.A., Righi, M., Rumbold, S.T., Skeie, R.B., Shindell,

D.T., Strode, S.A., Sudo, K., Szopa, S., Zeng, G., 2013. Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP). *Atmospheric Chemistry and Physics* 13, 2063-2090.

Young, P.J., Naik, V., Fiore, A.M., Gaudel, A., Guo, J., Lin, M.Y., Neu, J.L., Parrish, D.D., Rieder, H.E., Schnell, J.L., Tilmes, S., Wild, O., Zhang, L., Ziemke, J., Brandt, J., Delcoo, A., Doherty, R.M., Geels, C., Hegglin, M.I., Hu, L., Im, U., Kumar, R., Luhar, A., Murray, L., Plummer, D., Rodriguez, J., Saiz-Lopez, A., Schultz, M.G., Woodhouse, M.T., Zeng, G., 2018. Tropospheric Ozone Assessment Report: Assessment of global-scale model performance for global and regional ozone distributions, variability and trends. *Elementa Science of the Anthropocene* 6: 10, doi:<https://doi.org/10.1525/elementa.265>.

Table 1. Details of the fitted baseline seasonal cycles found for twelve ozone-depleting substances arranged in order of increasing atmospheric lifetime.

Substance	Lifetime, years	x_{\min} , Julian day	x_{\max} , Julian day	Amplitude, vmr	Relative amplitude
HCFC141b	9	230±7	337±7	0.31±0.06	0.013
HCFC22	12	205±74	333±7	2.04±0.3	0.014
Halon12b1	16	253±10	110±16	0.038±0.006	0.0086
CCl ₄	26	209±115	332±7	0.26±0.06	0.0026
CFC11	52	229±3	352±5	1.12±0.08	0.0043
Halon13b1	72	235±13	122±13	0.023±0.006	0.0079
CFC113	93	228±11	68±33	0.42±0.07	0.0051
CFC12	102	224±4	354±7	1.41±0.1	0.0026
N ₂ O	123	240±3	104±8	0.66±0.04	0.0021
CFC114	189	247±19	39±22	0.033±0.006	0.0020
CFC115	540	260±30	41±54	0.027±0.01	0.0032
CFC13	640	254±112	130±18	0.013±0.004	0.0043

Notes:

vmr: units in ppt (1 ppt = 1 part in 10¹² parts), except for N₂O which is in ppb (1 ppb = 10⁹ parts).

2 – σ confidence limits shown.

Relative amplitude is given by $(\text{vmr}_{\max} - \text{vmr}_{\min})/a$.

Table 2. Details of the fitted baseline seasonal cycles found for twelve trace gases with efficient tropospheric OH oxidation sinks arranged in order of increasing atmospheric lifetime.

Trace gas	Lifetime, years	x_{\min} , Julian day	x_{\max} , Julian day	Amplitude, vmr	Relative amplitude
C ₃ H ₈	0.036	193±8	33±2	645±16	2.02
C ₂ H ₆	0.14	220±2	60±2	1419±24	1.09
C ₂ Cl ₄	0.28	228±2	64±6	2.41±0.07	0.42
CH ₂ Cl ₂	0.39	244±2	106±3	13.3±0.4	0.35
CHCl ₃	0.41	199±5	327±5	1.53±0.12	0.13
CH ₃ Br	0.8	240±9	128±7	0.60±0.1	0.055
CH ₃ Cl	0.9	249±2	103±3	85.4±2	0.16
HFC152a	1.6	245±3	110±7	1.45±0.08	0.16
CH ₃ CCl ₃	5.0	253±10	120±12	1.42±0.2	0.028
HFC245fa	7.9	227±8	342±8	0.070±0.01	0.046
HFC365mfc	8.7	219±60	316±60	0.027±0.008	0.039
HFC143a	51	229±7	350±9	0.21±0.03	0.018

Notes:

vmr: units in ppt (1 ppt = 1 part in 10¹² parts).

2 – σ confidence limits shown.

Relative amplitude is given by $(\text{vmr}_{\max} - \text{vmr}_{\min})/a$.

Table 3. Details of the fitted baseline seasonal cycles found for five trace gases with complex tropospheric sources and sinks arranged in order of increasing atmospheric lifetime.

Trace gas	Lifetime, years	x_{\min} , Julian day	x_{\max} , Julian day	Amplitude, vmr	Relative amplitude
O ₃	0.06	218±2	97±2	15.2±0.6	0.38
CO	0.15	214±3	79±3	58.8±2	0.47
H ₂	2.1	293±3	129±6	33.8±1	0.066
CO ₂	7*	241±0.9	111±2	13.7±0.3	0.037
CH ₄	9.1	207±2	83±4	28.4±1	0.015

Notes

*: the atmospheric lifetime of carbon dioxide is not a well-defined quantity, see text. This figure refers to the first exponential term in the multi-exponential decay of a pulse of carbon dioxide (IPCC, 1994).

vmr: units in ppb (1 ppt = 1 part in 10⁹ parts), except for CO₂ which is in ppm (1 ppb = 10⁶ parts).

2 – σ confidence limits shown.

Relative amplitude is given by $(\text{vmr}_{\max} - \text{vmr}_{\min})/a$.

Table 4. Details of the fitted baseline seasonal cycles found for three trace gases with long atmospheric lifetimes arranged in order of increasing atmospheric lifetime.

Trace gas	Lifetime, years	x_{\min} , Julian day	x_{\max} , Julian day	Amplitude, vmr	Relative amplitude
SF ₆	3,200	251±6	150±16	0.034±0.006	0.0074
PFC116	10,000	269±68	118±18	0.014±0.004	0.0041
CF ₄	50,000	252±11	127±82	0.11±0.03	0.0015

Notes:

vmr: units in ppt (1 ppt = 1 part in 10¹² parts).

2 – σ confidence limits shown.

Relative amplitude is given by $(\text{vmr}_{\max} - \text{vmr}_{\min})/a$.