Trends and drivers of ozone human health and vegetation impact metrics from UK EMEP supersite measurements (1990 - 2013)

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Abstract

Analyses have been undertaken of the spatial and temporal trends and drivers of the distributions of ground-level O_3 concentrations associated with potential impacts on human health and vegetation using measurements at the two UK EMEP supersites of Harwell and Auchencorth. These two sites provide representation of rural O_3 over the wider geographic areas of south-east England and northern UK, respectively. The O_3 exposures associated with health and vegetation impacts were quantified, respectively, by the SOMO10 and SOMO35 metrics, and by the flux-based POD_Y metrics for wheat, potato, beech and Scots pine. Statistical analyses of measured O_3 and NO_x concentrations was supplemented by analyses of meteorological data and NO_x emissions along air-mass back trajectories.

The findings highlight the differing responses of impact metrics to the decreasing contribution of regional O_3 episodes in determining O_3 concentrations at Harwell between 1990 and 2013, associated with European NO_x emission reductions. An improvement in human health-relevant O_3 exposure observed when calculated by SOMO35, which decreased significantly, was not observed when quantified by SOMO10. The decrease in SOMO35 is driven by decreases in regionally-produced O_3 which makes a larger contribution to SOMO35 than to SOMO10. For the O_3 vegetation impacts at Harwell, no significant trend was observed for the POD_Y metrics of the four species, in contrast to the decreasing trend in vegetation-relevant O_3 exposure perceived when calculated using the crop AOT40 metric. The decreases in regional O_3 production have not decreased POD_Y as climatic and plant conditions reduced stomatal conductance and uptake of O_3 during regional O_3 production.

Ozone concentrations at Auchencorth (2007-2013) were more influenced by hemispheric background concentrations than at Harwell. For health-related O_3 exposures this resulted in lower SOMO35 but similar SOMO10 compared with Harwell; for vegetation POD_Y values, this resulted in greater impacts at Auchencorth for vegetation types with lower exceedance ("Y") thresholds and longer growing seasons (i.e. beech and Scots pine). Additionally, during periods influenced by regional O_3 production, a greater prevalence of plant conditions which enhance O_3 uptake (such as higher soil water potential) at Auchencorth compared to Harwell resulted in exacerbation of vegetation impacts at Auchencorth, despite being further from O_3 precursor emissions sources. .

These analyses indicate that quantifications of future improvement in health-relevant O_3 exposure achievable from pan-European O_3 mitigation strategies is highly dependent on the

choice of O_3 concentration cut-off threshold, and reduction in potential health impact associated with more modest O_3 concentrations requires reductions in O_3 precursors on a larger (hemispheric) spatial scale. Additionally, while further reduction in regional O_3 is more likely to decrease O_3 vegetation impacts within the spatial domains of Auchencorth compared to Harwell, larger reductions in vegetation impact could be achieved across the UK from reduction of hemispheric background O_3 concentrations.

1 Introduction

As part of the European Monitoring and Evaluation Program (EMEP) monitoring network, the UK operates two level II 'supersites' at Harwell (80 km west of London, Figure 1) and Auchencorth (17 km south of Edinburgh, Figure 1) (Torseth et al., 2012). The utility of the supersite concept as part of a strategy to address air quality research issues through concurrent measurements of a suite of atmospheric constituents has recently been reinforced (Kuhlbusch et al., 2014). The distinct impacts of one of the constituents measured at Harwell and Auchencorth, ground-level ozone (O_3), on human health and vegetation have been widely studied (REVIHAAP, 2013;RoTAP, 2012), but changes in the recommended metrics by which O_3 exposure relevant to these impacts is quantified (see below) necessitates new analyses of supersite measurement data.

The analyses in this study are based on the chemical climatology concept introduced by chemist Robert Angus Smith in *Air and rain: The beginnings of a chemical climatology* (Angus Smith, 1872). A chemical climatology approach comprises three elements (Malley et al., 2014a): (i) an 'impact' of the atmospheric composition, often characterised through a metric; (ii) the 'state' of relevant atmospheric composition variation (temporal, spatial and covariance) producing instances of the impact; (iii) the 'drivers' of this state, which could include meteorology, source proximity and emission profiles. A chemical climate has temporal boundaries (time period) and spatial boundaries (geographical extent); where there is identification of a significant change in the impact, resulting from significant change to the drivers and state, then these may be classified as different phases of the chemical climate.

In this study the six steps in the construction of a chemical climate described in Figure 2, and outlined in Malley et al (2014a) were applied to characterise the exposure of ground-level O_3 concentrations measured at Harwell and Auchencorth relevant to human health and four vegetation types. The O_3 measured at these sites has been shown to be representative of rural

O_3 concentrations in the larger geographical areas of south-east England and northern UK, respectively (Malley et al., 2014b).

Ozone exposure relevant to health impacts is quantified using the SOMO10 and SOMO35 metrics, which are the annual sums of daily maximum running 8-h average O_3 concentrations above 10 and 35 ppb thresholds, respectively. These metrics are in line with the recent World Health Organisation Review of evidence on health aspects of air pollution (REVIHAAP, 2013) report which recommends quantifying acute O_3 health impacts using both these measures of daily O_3 concentration and across the full year. In earlier syntheses of human health effects of O_3, importance was attached to the peak O_3 concentrations (WHO, 2006). The recent REVIHAAP synthesis shows important O_3 effects on human health down to very small concentrations, and a suggestion that there is no specific threshold for effects. The inclusion of SOMO10 reflects this recent synthesis. To quantify vegetation impacts of O_3, the species-specific metric of phytotoxic O_3 dose above a threshold flux Y (POD_Y) is used (LRTAP Convention, 2010). This parameter represents the modelled accumulated stomatal uptake of O_3 over a fixed time period based on hourly variations in climate (temperature (T), vapour pressure deficit (VPD), photosynthetically active radiation (PAR)), soil moisture (soil water potential (SWP) or plant available water (PAW)), O_3 and plant phenology (Emberson et al., 2000). Stomatal flux metrics are increasingly used to assess O_3 vegetation impacts, as they more accurately reflect the spatial pattern of O_3 damage across Europe compared with concentration-based metrics such as AOT40 (Mills et al., 2011b;RoTAP, 2012). Statistical analyses of O_3 and NO_x variation provide characterisation of the 'state' of atmospheric composition at the two sites for the different impacts, while analysis of meteorology, air mass history and NO_x emissions provide insight into the relevant 'drivers' of the chemical climates.

The focus of this study is characterisation of the variation in O_3 impacts with time at Harwell, and spatially between Harwell and Auchencorth, and of the contributions of regional and hemispheric O_3-modifying processes in determining each impact. Hemispheric background O_3 concentrations are defined here as O_3 formed from anthropogenic and natural precursor emissions outside of Europe (Derwent et al., 2013). Superimposed on this, regional net O_3 production or loss derives from the balance of processes such as emissions, deposition and meteorological conditions occurring on a regional scale. Photochemical reactions between NO_x and volatile organic compounds (VOCs) emitted in Europe produces O_3 regionally, but high NO_x environments (regionally and locally) limit O_3 formation (Jenkin, 2008;Munir et al., 2013). Spatial and temporal variation of these processes in the UK context have been discussed previously (AQEG, 2009). Studies have also quantified both human health (EMEP, 2014;Stedman and Kent, 2008;Gauss et al., 2014;Guerreiro et al., 2014) and vegetation O_3 impacts (Mills et al., 2011a;RoTAP, 2012) within the spatial domain of each supersite. However, consideration of both impacts at each site using a common chemical climatology approach links the impacts studies with the analyses of temporal and spatial O_3 variation, and allows identification of differences and similarities in the drivers of each impact which inform the development of co-beneficial O_3 mitigation strategies.

An important aspect of this study is to also compare impacts quantified through the updated metrics with previously used metrics. For the health impact the contrast is between health-relevant exposure quantified by SOMO10 and SOMO35 compared with that quantified using the higher thresholds of the WHO guideline (50 ppb) and the EU target value (60 ppb) (Derwent et al., 2013;EEA, 2014b). For the vegetation impact the contrast is between the POD_Y metric and the concentration-based crop AOT40 metric, the sum of hourly O_3 concentrations above 40 ppb during daylight hours during the growing season (Coyle et al., 2002;Klingberg et al., 2014;Jenkin, 2014). In addition, comparison is made between POD_Y calculated using on-site measured O_3 and meteorological data (used in this study and previously (Karlsson et al., 2007)) and analyses which have used gridded modelled O_3 and meteorological data to calculate POD_y (Emberson et al., 2007;Klingberg et al., 2011;Mills et al., 2011a;Mills et al., 2011b;Simpson et al., 2007).

The ambition to integrate data (such as measured concentrations) with knowledge (such as the adverse impacts of O_3) to advance both science and policy is currently an area of intense research interest (Schmale et al., 2014;Abbatt et al., 2014;Kuhlbusch et al., 2014). This current work, using the chemical climatology concept, presents a clear methodology for achieving this and shows a simple categorisation for summarising information which could be more widely adopted.

2 Methods

A chemical climate is based on an identified impact (Figure 2, Step 1), which is linked to atmospheric composition variation through a suitable metric (Step 2). For assessment of O_3 acute health impact, REVIHAAP (2013) recommends the use of all-year metrics based on the value by which the daily maximum 8-hour average O_3 concentration exceeds either 10 ppb or

35 ppb. The annual sum of the daily exceedances of these thresholds yields the SOMO10 and SOMO35 metrics respectively. The POD_Y metric for the vegetation chemical climates was calculated using the DO_3SE model version 3.0.5 (http://www.sei-international.org/do3se, Emberson et al. (2000)). POD_Y values were calculated for two crops (wheat and potato) and two forest trees (beech and Scots pine), accumulated across their respective growing seasons. The length of the growing seasons, and phenological limitation on stomatal conductance throughout the growing season were derived according to methods detailed in LRTAP Convention (2010). The growing seasons for wheat (late April – early August) and potato (late May – early September), were calculated by accumulated temperature and therefore varied inter-annually based on meteorological conditions. For beech, the growing season was calculated using a latitude model (19/04-20/10 at Harwell, 26/04-10/10 at Auchencorth). The Scots pine growing season was the full year.

The DO_3SE model calculates the stomatal flux for each species using parameterisations which quantify the sensitivity of each species to modification of stomatal conductance due to the effects of phenology, O_3, PAR, T, VPD and soil moisture (SWP for potato, beech and Scots pine and PAW for wheat) (LRTAP Convention, 2010). For this study, the DO_3SE model used as input hourly measured O_3 concentrations at Harwell and Auchencorth, and the following hourly meteorological data from the Met Office stations closest to each monitoring site: wind speed, rainfall, vapour pressure deficit, temperature, global radiation and pressure (UK Meteorological Office, 2012). For Harwell, the station at Benson (SRC ID: 613), 13 km distance, provided all meteorological data except global radiation which was obtained from Bracknell (SRC ID: 838, 1990-2002) and Rothamsted (SRC ID: 471, 2003-2013). For Auchencorth, all meteorological data were obtained from the station at Gogarbank (SRC ID: 19260), 14 km distance. All archived data from these stations undergoes documented quality control procedures (http://badc.nerc.ac.uk/data/ukmo-midas/ukmo_guide.html). The DO_3SE model calculated hourly O_3 concentrations at the top of the canopy and stomatal conductance for each vegetation type (LRTAP Convention, 2010;Emberson et al., 2000). SWP and PAW were calculated in the DO_3SE model using the measured meteorological data based on the Penman-Monteith model of evapotranspiration (Bueker et al., 2012). In addition to meteorological conditions, the evaporation of moisture from soil is dependent on the hydraulic properties of the soil texture. Statistics were therefore calculated for four different soil textures, sandy loam (soil texture classification = coarse), silt loam (medium coarse), loam (medium) and clay loam (fine). The properties of these soil textures are detailed in Bueker et al. (2012).

POD_Y was accumulated when this stomatal flux was above a plant-specific threshold flux set at 6 nmol m^{-2} s^{-1} for crops and 1 nmol m^{-2} s^{-1} for forest trees. Response functions were applied to wheat, potato and beech to convert POD_Y into grain yield, tuber weight and whole-tree biomass reduction estimates respectively (Mills et al., 2011c). As the representative coniferous species in the 'Atlantic central Europe' geographic zone (LRTAP Convention, 2010), Scots pine was included despite no published response function, with increasing POD_Y assumed to indicate increasing potential damage. In addition, the crop-specific AOT40 metric for May to July was calculated (Fuhrer et al., 1997) to allow for comparison with previous studies that used AOT40 to estimate the impact of O_3 on crops (e.g. Derwent et al., 2013;Jenkin, 2014).

The spatial domain (Figure 2, Step 3) in this analysis was the area of representivity of each monitoring site. In the context of European O_3 variation evaluated across all EMEP sites measuring O_3, Harwell was shown to be representative of rural sites within 120 km of London, and Auchencorth representative of rural locations in a larger domain including the rest of the UK (Malley et al., 2014b). The temporal domain investigated was 1990-2013 for Harwell (NO_x data available from 1996) and 2007-2013 for Auchencorth. The NO_x and O_3 measurements were co-located at Harwell, but the NO_x data for analyses at Auchencorth were obtained from Bush (UK-AIR ID: UKA00128), 8 km from Auchencorth. The suitability of Bush as a proxy site for Auchencorth has been outlined previously, and O_3 variation was found to be similar at both sites (Malley et al., 2014b). The chemical data were downloaded from the UK-Air data repository (http://uk-air.defra.gov.uk) and the Automatic Urban and Rural Network (AURN) reports provide further details on these measurements (Eaton and Stacey, 2012).

A minimum data capture of 75% across the year for SOMO10/35 calculations, and across the relevant growing season for POD_Y and AOT40 calculations, was imposed for inclusion in the summary statistics. This resulted only in the exclusion of statistics at Harwell for potato in 1995 and Scots pine in 1993. As data capture was generally very high, no adjustment of summary statistics for missing data was applied. At Harwell, average annual data capture for 1990-2013 was 94%. The lowest annual data capture was 76% (1993). When the missing hourly O_3 data were estimated through linear interpolation, 1993 SOMO35 and SOMO10 increased by no more than 2% compared with no interpolation. For the four vegetation types, the 1990-2013 average data capture during the respective growing seasons at Harwell was between 92 and 94%. Sensitivity to missing O_3 and meteorological data during the years of lowest data capture (above 75%) for wheat (1994, 75%), potato (1993, 80%), beech (1995, 82%) and pine (2007, 81%) was also evaluated through linear interpolation. POD_Y values were 19%, 19% and 18% higher for wheat, beech and pine, respectively, compared with no linear interpolation, and 6% lower for potato. These sensitivities illustrate an estimate of the greatest extent of impact metrics not included due to missing data. For the majority of years biases will be much smaller, as data capture was substantially higher. As estimation of missing data introduces new sources of uncertainty, the impacts calculated using measured data only are considered here.

The state (Figure 2, Step 4) of the human health chemical climates was characterised using the following statistics for the SOMO10 and SOMO35 metrics: the number of accumulation days (ADs), i.e. days on which the maximum 8-hour O_3 concentration exceeded 10 or 35 ppb; percentage contribution per season to annual number of ADs; the percentage contribution per season to SOMO10/35; the average diurnal amplitudes in O_3, NO and NO_2 concentrations on ADs and non-accumulation days (NADs); and the contributions from 13 daily maximum 8-h O_3 concentration bins (10 ppb to >70 ppb in 5 ppb groups) to SOMO10/35. The state for the vegetation chemical climates was characterised by the following statistics for the POD_Y metric for each vegetation type: the number of POD_Y accumulation days; the percentage monthly contributions to POD_Y across the growing season; the contributions from 15 hourly O_3 concentration bins (0 ppb to >70 ppb in 5 ppb groups) to POD_Y; and the average diurnal amplitudes of O_3, NO and NO_2 on ADs and NADs. For the AOT40 metric, the contributions from May, June and July were calculated as well as the average diurnal amplitudes in May, June and July of O_3, NO and NO_2.

Three potential drivers of the state (Step 5) were investigated. First, the effect of temperature was investigated using data from Benson (SRC ID: 613), 13 km from Harwell, and Gogarbank (SRC ID: 19260), 14 km from Auchencorth (UK Meteorological Office, 2012). The mean daily temperature on ADs and NADs for SOMO10/35 and POD_Y were compared. Monthly averaged temperatures during the AOT40 growing season were calculated. Secondly, the association of the state (Step 4) with air-mass history was investigated by grouping back trajectories based on the similarity of their pathway. The proportion of trajectories arriving from each group during SOMO10/35 and POD_Y ADs and NADs, and over the AOT40 growing season, was then compared. Pre-calculated 4-day HYSPLIT air-mass back trajectories arriving at 3 hour intervals (2920 trajectories per year) (Draxler and Rolph, 2013;Carslaw and Ropkins, 2013;R Core Development Team, 2008) were grouped using Ward's linkage hierarchical cluster analysis which has been shown through simulations to perform effectively (Mangiameli et al., 1996). The similarity between trajectories was quantified using the measure of their 'angle' from the receptor (Equation 1):

$$d_{1,2} = \frac{1}{n}\sum_{i=1}^{n} cos^{-1}\left(0.5\frac{A_i+B_i+C_i}{\sqrt{A_iB_i}}\right) \tag{1}$$

where

$$A_i = (X_1(i) - X_0)^2 + (Y_1(i) - Y_0)^2$$

$$B_i = (X_2(i) - X_0)^2 + (Y_2(i) - Y_0)^2$$

$$C_i = (X_2(i) - X_1(i))^2 + (Y_2(i) - Y_1(i))^2$$

$d_{1,2}$ is the variance between trajectory 1 and trajectory 2, X_0 and Y_0 are the latitude and longitude coordinates of the origin of the back trajectory (i.e. the supersite), and X_1, Y_1, and X_2, Y_2 are the coordinates of back trajectories 1 and 2, respectively, at a common time point i along the trajectory. In Ward's method each object (back trajectory) initially constitutes its own cluster. At each step, the two clusters are merged that give the smallest increase in total within-cluster variance. This process is repeated until all trajectories are located in one cluster (Kaufman and Rousseeuw, 1990). The summary dendrogram was then 'cut' to produce a set of four clusters in which the back trajectories were predominantly 'westerly', 'easterly', 'northerly' and 'southerly'.

Thirdly, the 2920 4-day back trajectories arriving each year were combined with reported gridded NO_x emissions to investigate the contribution of NO_x emissions as a chemical climate driver. Each 1 h time point along a trajectory was associated with the relevant 0.5° × 0.5° grid square NO_x emissions reported by EMEP (Mareckova et al., 2013;Simpson et al., 2012). This grid encompasses the region 30.25°N to 75.25°N and 29.75°W to 60.25°E. The associated annual NO_x gridded emissions were adjusted using month, day of week and hour of day time factors (Simpson et al., 2012) to obtain an estimate of the hourly NO_x emissions during the hour in which the trajectory passed over the grid cell. The 96 hourly emissions estimates for each trajectory were summed, and averaged across the 8 trajectories arriving each day, producing a daily average trajectory NO_x emissions estimate which was compared on SOMO10/35 and POD_Y ADs and NADs. The monthly average trajectory NO_x emissions estimate was calculated for the May-July AOT40 growing season.

The chemical climate statistics derived were compared between Harwell and Auchencorth for evidence of different spatial phases in the O_3 impacts (Figure 2, Step 6). Evidence for a different temporal phase in the O_3 impact chemical climate at Harwell was investigated by Theil-Sen trend analysis of the 24-year time series of chemical climate statistics. This non-parametric test selects the median of all the slopes between pairs of points in a time series as the estimate of the trend, and calculates statistical significance using bootstrap re-sampling (Carslaw and Ropkins, 2013). The 7-year dataset from Auchencorth was of insufficient duration to evaluate significant changes in either the health or vegetation impacts.

The terminology spring, summer, autumn and winter refer to the 3-month periods Mar-Apr-May, Jun-Jul-Aug, Sep-Oct-Nov and Dec-Jan-Feb, respectively.

3 Results and Discussion

The chemical climate statistics derived for the O_3 human health and vegetation impacts at Harwell and Auchencorth are presented as datasheets in Supplementary Information Tables S1-S12. For Harwell, the statistics are averaged across six time periods (1990-1993, 1994-1997, 1998-2001, 2002-2005, 2006-2009, 2010-2013). These tables have a lot of statistics and exemplify a resource which could be replicated and collated for different impacts, locations and time periods to identify key linkages between chemical climates and aid in the development of more holistically-considered mitigation strategies. The main features which support the key conclusions from the human health and vegetation O_3 chemical climates at the UK supersites are presented in Figures 3-14 and discussed in the following subsections.

3.1 O_3 human health impact chemical climates

The detailed statistics describing the O_3 human health chemical climates at Harwell and Auchencorth are presented in Tables S1 and S2, respectively. This section presents two analyses of the impact, state and drivers of the chemical climatology framework (Figure 2, steps 1-5); specifically, changes in chemical climate phase (Figure 2, Step 6) temporally at Harwell between 1990 and 2013 (Section 3.1.1) and spatially between Auchencorth and Harwell (Section 3.1.2).

3.1.1 Long-term changes at Harwell

When characterised by the SOMO35 metric, the O_3 exposure associated with human health impact at Harwell decreased significantly between 1990-2013 (Figure 3), with a median trend of –2.2% y^{-1} (p = 0.001). The annual number of SOMO35 accumulation days (ADs) did not vary significantly during this period, averaging 148 ± 28 days y^{-1}. In contrast, when characterised by the SOMO10 metric, O_3 exposure associated with human health impact at Harwell showed no statistically significant trend (1990-2013 mean (±sd) = 8329 ± 802 ppb.d) (Figure 3). However, the annual number of SOMO10 ADs has increased significantly with a median trend of +1.7 days y^{-1} (p = 0.01). In the more recent years, the additional ADs occurred in winter, and SOMO10 was accumulated on almost every day of the year (Table S1).

The majority of SOMO35 accumulation at Harwell occurred in spring and summer (Figure 4). Between 1990 and 2013 the spring contribution to SOMO35 increased significantly (+1.1% y^{-1}, p = 0.01), whilst the summer contribution decreased significantly (–1.2% y^{-1}, p = 0.01). The spring and summer contributions to SOMO35 values were considerably larger, and showed larger inter-annual variation, compared with those for SOMO10 (Figure 4). Between 1990 and 2013 there was a significant decrease in contribution to SOMO10 during summer (trend –0.4% y^{-1}, p = 0.01) and a significant increase during winter (+0.3% y^{-1}, p = 0.001).

Figure 5 shows the contributions from thirteen 5-ppb daily maximum 8-h O_3 concentration bins to SOMO10 and SOMO35 at Harwell. The majority of SOMO10 was accumulated on days when the O_3 concentration was between 25 and 45 ppb (Figure 5a). Contributions to SOMO10 from days with the highest concentrations (60-70 ppb and >70 ppb) decreased significantly between 1990 and 2013 (–0.2 and –0.4 % y^{-1} respectively), while contributions from more moderate O_3 concentrations (20-30 ppb and 40-50 ppb) increased significantly (+0.3% y^{-1} and +0.2% y^{-1} respectively). Ozone concentrations between 10 and 35 ppb, i.e. included in SOMO10 but not in SOMO35, contributed on average 40 ± 8% across the whole 24-year period. The contribution to SOMO35 from the higher concentration bins was larger than for SOMO10, but also decreased significantly (Figure 5b): the 1990-2013 trends in SOMO35 contributions from O_3 concentrations between 60-70 ppb and >70 ppb were –0.4 and –1.4 % y^{-1} respectively. There were significant increases in contributions to SOMO35 from concentrations between 35 and 50 ppb (trends in the range +0.4 to +1.5% y^{-1}). At Harwell the amplitude of the diurnal O_3 cycle was consistently greater (by 7-18 ppb) on SOMO35 ADs compared with SOMO35 NADs (Table S1), while the diurnal NO and NO_2

cycles were substantially lower on ADs than on NADs. Figure 6 shows that the mean diurnal amplitudes of O_3, NO_2 and NO on SOMO35 ADs decreased significantly between 1990 and 2013 (trends of −1.8% y^{-1}, −2.8% y^{-1}, −3.6% y^{-1}, respectively). There was also a significant decrease in mean diurnal cycle amplitudes of O_3, NO_2 and NO on SOMO10 ADs (trends of −1.4, −2.6, and −3.9% y^{-1}, respectively, NO_x data only from 1996). Trends of decreasing diurnal amplitudes were also observed on SOMO35 NADs (note that SOMO10 NADs were rare, and in 2010-2013 there were essentially no SOMO10 NADs).

The largest change in the O_3 human health chemical climate drivers between 1990 and 2013 at Harwell was the decrease in the estimated daily averaged NO_x emissions along the air-mass back trajectories (Figure 7). For SOMO35 ADs and NADs, the decreases were −3.1% y^{-1} and −3.0% y^{-1} respectively, while the decrease on SOMO10 ADs was −2.9% y^{-1} (all p = 0.001). For SOMO10 and SOMO35, temperatures on NADs were lower than on ADs. For SOMO35, the average temperature was 2.3 ± 1.5 °C higher on ADs than on NADs between 2010-2013, smaller than the corresponding differential of 3.9 ± 1.3 °C between 1990 and 1993. The median trend in this temperature differential was −2.5% y^{-1} (p = 0.001). The proportion of air-mass back trajectories classified into the four geographic groupings through cluster analysis did not vary significantly between ADs and NADs for SOMO35, or across the whole 1990-2013 period. In 2003, the effects of long-term changes in the emissions drivers were temporarily offset and SOMO10 and SOMO35 values were elevated (Figure 3). This was due to the 'heat-wave' period experienced across south-east England during summer that year. The elevated temperatures enhanced O_3 concentrations by leading to greater biogenic VOC emissions and increased reactivity of VOCs with OH, and to reduced O_3 dry deposition (Lee et al., 2006;Vieno et al., 2010).

The trends and differences in the statistics presented for the SOMO10 and SOMO35 metrics for 1990-2013 at Harwell reveal changes in the relative importance to O_3 concentrations of hemispheric, regional and local-scale processes in determining the health-relevant O_3 exposure at Harwell. Hemispheric background levels of O_3 over Europe feature a pronounced spring maximum and summer minimum (Derwent et al., 2013;Parrish et al., 2013). Hence during spring the SOMO35 threshold is exceeded on the majority of days. Derwent et al. (2013) analysed O_3 concentrations in non-European influenced air masses and found an increasing trend up to 2008, most strongly observed in winter and spring, followed by a levelling off and decrease. Wilson et al. (2012) also calculated a significant positive trend between 1996 and 2005 in monthly 5th percentile O_3 concentrations, taken as a measure of background concentrations, at 82 out of 158 European monitoring sites, including the majority of sites in the UK. This increase in hemispheric background concentrations has led to the increases in the number of winter SOMO10 ADs and in the spring contribution to SOMO35.

Regional O_3 production is greatest in summer when solar intensity and temperatures are highest, so the contribution to the O_3 exposure associated with the health impact during summer is predominantly of European origin (Jenkin, 2008). Autumn and winter have far fewer SOMO35 ADs because of lower hemispheric background levels and lower solar intensity for regional production; however, the consistent exceedance of 10 ppb during autumn and winter leads to a significant contribution to SOMO10 (approximately 40% in 2010-2013 (Table S1)). The decrease in summer contribution to SOMO35 results from reduced regionally-produced O_3 episodes. This is evidenced by the reduced contribution from the highest O_3 concentration days, the decreased amplitude of diurnal O_3 variation during SOMO35 and SOMO10 ADs and the decreased temperature difference between SOMO35 AD and NADs (regionally-generated O_3 exhibits a pronounced diurnal cycle due to its photochemical production and is therefore determined to a greater extent by European meteorological conditions than is hemispheric background O_3). Jenkin (2008) and Munir et al. (2013) likewise attributed long-term decreases in high percentile O_3 concentrations at UK monitoring sites to reduced regional photochemical O_3 episodes, and increases in lower percentile concentrations to increased hemispheric background.

The decrease in regional O_3 production is due to the decreasing trend in precursor emissions affecting Harwell (Figure 7). The European Environment Agency (EEA) estimate that, across the EU28 countries, NO_x emissions have decreased by 51% between 1990 and 2012 and volatile organic compound (VOC) emissions have decreased by 60% (EEA, 2014a). Unlike SOMO35, the SOMO10 metric did not decline between 1990-2013 because of the lower contribution to SOMO10 from the highest O_3 concentrations, which derive from regional photochemical episodes. SOMO10 was therefore less sensitive to decreases in the magnitude of these episodes, and the decrease was offset by an increase in contribution from 20-30 ppb daily maximum 8-hour ADs, which were not included in SOMO35.

In summary, whether it is concluded there has been a decline or no decline in O_3 exposure associated with human health impact between 1990 and 2013 at Harwell differs according to the choice of a 35 ppb or 10 ppb threshold, both of which are recommended in the recent WHO review (REVIHAAP, 2013). Although the absolute health impact apportioned to O_3 is sensitive to the choice of threshold (Stedman and Kent, 2008;Heal et al., 2013), the analyses presented here have shown that, irrespective of whether a 35 or 10 ppb threshold is selected, the extent, timing and severity of the human health impact of O_3 is increasingly driven by more frequent, modest exceedances of the respective threshold, rather than short-lived extreme episodic exceedances.

3.1.2 Spatial differences between Auchencorth and Harwell (2007-2013)

In the comparison between Auchencorth (representative of much of the rural west and north of the UK) and Harwell (representative of SE England), annual mean and 75th percentile O_3 concentrations were greater at Auchencorth between 2007 and 2013, while maximum values were substantially greater at Harwell (Tables S1 and S2). Between 2007 and 2013, the average SOMO35 was 14% lower at Auchencorth, while the average SOMO10 was 7% higher compared with Harwell. The proportion of SOMO10 accumulated in spring was similar at both sites, but the proportion accumulated in summer was on average 5.3 ± 2.9% lower at Auchencorth. The contribution to SOMO35 from spring was greater at Auchencorth, but smaller for summer compared with Harwell (Figure 4). Auchencorth also had a smaller contribution from days with >60 ppb daily maximum 8-hour O_3 concentrations (Table S2). Mean amplitudes of diurnal O_3 variation on SOMO10 and SOMO35 ADs were also smaller at Auchencorth than at Harwell (see Figure 6 for the data relating to SOMO35 ADs). In addition, the difference in mean amplitudes of diurnal O_3, NO_2 and NO variation on SOMO10/35 ADs and NADs was smaller at Auchencorth than at Harwell. For example, diurnal O_3 amplitude was 2.2-4.5 ppb greater on SOMO35 ADs than on NADs at Auchencorth (Table S2), which was smaller than the 5.6-8.2 ppb differential at Harwell between 2007 and 2013 (Table S1).

The estimated daily averaged NO_x emissions along the air-mass back trajectories were substantially lower at Auchencorth than at Harwell (Figure 7) and generally lower (13 ± 9% on average in 2007-2013) on SOMO35 ADs compared with NADs. The temperature difference between SOMO35 ADs and NADs at Auchencorth was less than at Harwell, ranging between 1.7 °C higher on average on ADs in 2010 to 1.4 °C lower on ADs in 2013. Elevated SOMO10 (6% above 2007-2013 average) and SOMO35 (67%) values in 2008 at Auchencorth (as also reported by Gauss et al. (2014) using the EMEP/MSC-W model) resulted from an increased contribution from days with maximum 8-h concentrations above

50 ppb (12% and 36% contributions to SOMO10 and SOMO35 respectively). In addition, 28% of trajectories were grouped in an 'easterly' cluster on SOMO35 ADs in 2008, compared with 13% on NADs. Patterns were similar in 2009, 2012 and 2013, but without the elevated SOMO35 compared to 2008. The larger O_3 and NO_2 diurnal amplitudes on SOMO10 and SOMO35 ADs in 2008, and the elevated temperatures on SOMO35 ADs (Table S2) suggests regional O_3 production was a substantially stronger driver of SOMO35 in 2008 compared to other years at Auchencorth.

The chemical climate state and driver statistics for Auchencorth indicate that O_3 concentrations at this location are less modified from the hemispheric background than at Harwell, consistent with spatial patterns reported in Jenkin (2008). The larger contribution from spring to SOMO35 at Auchencorth compared to Harwell shows that the hemispheric spring maximum in O_3 produces the majority of SOMO35, and the lower contribution from high O_3 concentration ADs indicates lower influence from regional photochemical O_3 production. Since SOMO10 is determined to a lesser extent by high O_3 concentration ADs, this explains why calculated SOMO35 are lower at Auchencorth, yet SOMO10 values are similar at Auchencorth and Harwell.

3.1.3 Comparison between SOMO10/SOMO35 and higher threshold metrics

In spite of these spatial differences between the SOMO10 and SOMO35 metrics, both provide a substantially different picture of the extent (proportion of year over which impact metric is accumulated), timing (particular periods when impact metric is accumulated) and severity (magnitude of impact metric) of human health relevant O_3 exposure at Harwell and Auchencorth compared with use of higher threshold metrics such as the WHO air quality guideline (50 ppb) or the EU target value (60 ppb). For example, in 2013, the extent of exceedance of the 60 ppb EU target value across the UK was only 19 days (at least 1 of 81 UK sites exceeding threshold), and the timing of these exceedances was mainly in summer (EEA, 2014b). In contrast, at Harwell in 2013, there were 356 and 130 ADs for SOMO10 and SOMO35 respectively, of which only 27% and 28% was accumulated in summer. In respect of severity, at Harwell in 2010-2013, on average 91% and 66% of SOMO10 and SOMO35 respectively was accumulated on days with maximum 8-h O_3 concentrations below the WHO guideline of 50 ppb, compared to 76% and 38% in 1990-1993 (Table S1). At Auchencorth, an even larger proportion of SOMO10 and SOMO35 were accumulated below 50 ppb, on average 96% and 84% respectively during the 2007-2013 monitoring period (Table S2).

The overall impression from these statistics showing a decline in exposure to concentrations in excess of 35 ppb is that the threat to human health has declined between 1990 and 2013 in south-east England. The comments from the EEA (2014b) on the very few episodes in excess of 50 or 60 ppb in 2013 are consistent with this view. However, the recent REVIHAAP (2013) synthesis shows that the lower percentiles of O_3 are also important and it is hard to define a precise threshold below which O_3 is not harmful. Thus the dose of O_3 to humans through respiration may be the more important guide to the potential threat, and as the SOMO10 (and the mean values) have changed little with time, the suggested improvement in air quality from the EEA may be more apparent than real. An important policy implication of these trends is the degree to which local, regional or global policies are required to decrease the threat to human health from O_3. In the case of exposures to O_3 in excess of 60 ppb, controls at the European and national scales can be effective, as the measurements demonstrate. However, if the mean or lower percentiles are important, as suggested in recent syntheses, then controls at much larger (hemispheric) scales are required.

3.2 O_3 vegetation impact chemical climates

The detailed statistics describing the impacts of O_3 on crops at Harwell and Auchencorth, as derived using the POD_Y metric are presented in Tables S3 and S4 for potato, Tables S5 and S6 for wheat, and as derived using the generic crop AOT40 metric for a May-July growing season in Tables S7 and S8. The statistics for the POD_Y metric for forest trees are presented in Table S9 and S10 for beech, and Tables S11 and S12 for Scots pine. The POD_Y statistics presented in Tables S5-S12, and Figures 8-13 were calculated for the loam (medium) soil texture (Bueker et al., 2012). The representativeness of the conclusions derived from the interpretation of these statistics to other soil textures is discussed in Section 3.2.1 and 3.2.2. This section presents two analyses of the impact, state and drivers of the chemical climatology framework (Figure 2, steps 1-5); specifically, changes in chemical climate phase (Figure 2, Step 6) temporally at Harwell between 1990 and 2013 (Section 3.2.1) and spatially between Auchencorth and Harwell (Section 3.2.2).

3.2.1 Long-term changes in vegetation impact at Harwell (1990-2013)

Figure 8 shows the impact of O_3 on vegetation at Harwell, as quantified by the relevant POD_Y and response (grain yield for wheat, tuber weight for potato and biomass reduction for beech). The 1990-2013 average POD_Y values calculated using sandy loam (coarse), silt loam (medium coarse), loam (medium) and clay loam (fine) soil texture properties are shown in Table 1. The ratio between the largest and smallest average POD_Y due to differences in soil moisture for the different soil textures was 1.57 (wheat), 1.32 (potato), 1.14 (beech) and 1.10 (Scots pine), but the annual pattern of POD_Y accumulation was consistent across the four soil textures. The statistics in the following sections are those calculated for the loam soil texture, unless otherwise stated, which has intermediate hydraulic properties compared with the three other soil textures.

For crops, there has not been a statistically significant change in POD_Y between 1990 and 2013, across all soil textures. Using the critical levels for adverse vegetation damage agreed by the UN Convention on Long Range Transboundary Air Pollution (LRTAP) (Mills et al., 2011c), O_3 has a greater impact on wheat than potato at Harwell, with 13 of the 24 years exceeding the 5% yield reduction critical level for wheat, compared to 6 years exceeding the 5% tuber weight reduction critical level for potato. Mills et al (2011a), using modelled O_3 and meteorological data to assess the impact of O_3 on vegetation across the UK in 2006 and 2008, also reported a smaller impact on potato than wheat, due to the lower sensitivity of potato to O_3.

The majority of POD_Y accumulation for potato and wheat occurred in June (Tables S3 and S5). Between 1990 and 2013 there were significant decreases in diurnal O_3, NO_2 and NO amplitudes on June ADs (Figure 9, Tables S3 and S5). The median trend in diurnal O_3 amplitude on June ADs was –2.0% y^{-1} and –2.4% y^{-1} for potato and wheat respectively (p = 0.001), and, in the latter period (2010-2013), the difference in diurnal O_3 amplitude between June ADs and NADs was small (Tables S3 and S5). Figure 10 shows the percentage of POD_Y accumulated during different measured hourly O_3 concentration ranges. There were significant decreasing trends in the contribution from the highest concentration bins (65-70 ppb and >70 ppb) for potato (–0.4 to –1.4 % y^{-1}), and from the 55-60 and 65-70 ppb concentrations bins for wheat. In contrast, there were increasing trends in POD_Y contribution from the 25-45 ppb O_3 concentration bins for potato (+0.1 to +0.8% y^{-1}) and from the 30-45 ppb concentration bins for wheat (+0.5 to +1.1% y^{-1}). These trends were due to a decreasing frequency of hours with O_3 concentrations in the range 55 to >70 ppb during the growing seasons of potato (–3.0 to –4.3% y^{-1}) and wheat (–2.1 to –4.8% y^{-1}) and increasing frequency of hourly O_3 concentrations in the range 25-45 ppb (wheat) and 20-35 ppb (potato). For both crops, the estimated back-trajectory NO_x emissions on ADs decreased significantly in the period 1990-2013 for each month of the growing season (Figure 9 shows this decrease for ADs in June), with trends ranging from −2.5 to −4.3% y^{-1}. Other drivers such as temperature, global radiation and back-trajectory pathway did not change significantly between 1990 and 2013 (Tables S3 and S5).

For beech and Scots pine, there was no significant trend in POD_Y between 1990 and 2013 across all soil types (Figure 8). The average POD_Y for beech (Table 1) was four times the critical level (Mills et al., 2011c). Beech and Scots pine PODy values were substantially higher than for the crops, due to a lower threshold for exceedance, a longer growing season and other differences in the stomatal conductance response to T, PAR, VPD and SWP. The average beech POD_Y value calculated here is comparable with the estimate for beech POD_Y modelled by Simpson et al. (2007) for the south east of England (8-16 mmol m^{-2}), but both values were higher than the values estimated in Emberson et al. (2007) for three European climate regions (not including UK) in 1997.

The low 1 nmol m^{-2} s^{-1} threshold for POD_Y accumulation for beech and Scots pine was exceeded during the majority of days during the respective growing seasons. The major contributions by month to POD_Y were consistently May and June for beech, and April, May and June for Scots pine (Tables S9 and S11). During 1990-2013 diurnal O_3 amplitude decreased significantly on beech and Scots pine ADs between May and September, with median monthly AD trends between −1.5% and −2.3% y^{-1} for beech, and −1.3% and −2.4% y^{-1} for Scots pine. Across the 24 year period there was a more consistent, major contribution to POD_Y during hourly O_3 concentrations in the range 25-50 ppb compared with wheat and potato, especially for Scots pine (Figure 10c and 10d). For beech and Scots pine, the trends in contribution from different concentration bins were smaller compared with crops. Decreasing trends in POD_Y contribution were significant for concentration bins between 50 and >70 ppb (–0.1 to –0.4 % y^{-1} for beech and –0.1 to –0.2 % y^{-1} for Scots pine), and significant increasing trends in more moderate concentration bins (25-40 ppb) were only apparent for beech. During the growing season of each tree, the frequency of high O_3 concentrations (55 to >70 ppb) decreased significantly (–2.5 to –5.3% y^{-1} for both trees), and there was an increase in the frequency of concentrations between 25-35 ppb (+1.4 to +2.2% y^{-1} for both trees). Karlsson et al. (2007) calculated a similar result for Norway Spruce in Sweden, where between 2002-2004 approximately 80% of POD_Y was accumulated during O_3 concentrations between 30 and 50 ppb. The estimated NO_x emissions into the air-mass trajectories also decreased significantly during beech and Scots pine ADs, with median monthly trends ranging from −3.2 to −3.6% y^{-1} for beech, and −1.9 to −3.7% y^{-1} for Scots pine.

The significant trends in state (pollutant diurnal variation and concentration bin contributions) and drivers (trajectory emissions estimates) for the four vegetation types (Figure 9 and Tables S3, S5, S9 and S11) indicate an increase in the relative importance of hemispheric background O_3 concentrations in determining POD_Y. Despite this change, POD_Y values have not decreased, in contrast to SOMO35 for which decreased contribution from high O_3 concentrations (produced during regional O_3 episodes) resulted in a decreasing trend. This was due to non-O_3 factors such as stomatal response to VPD and soil moisture which also determine the severity of a vegetation impact by limiting the O_3 flux during high O_3 concentration episodes, reducing the sensitivity of POD_Y values to decreases in regional O_3 production. For example, during the potato growing season the median stomatal conductance during hours with O_3 concentrations in the ranges 60-65, 65-70 and >70 ppb were 86, 90 and 65 mmol m^{-2} s^{-1} respectively (median across 1990-2013). These are significantly lower than the maximum stomatal conductance for potato of 750 mmol m^{-2} s^{-1} (LRTAP Convention, 2010), and similar to the median stomatal conductances calculated during more moderate O_3 concentrations, such as 35-40 ppb (54 mmol m^{-2} s^{-1}), 40-45 ppb (68 mmol m^{-2} s^{-1}) and 45-50 ppb (87 mmol m^{-2} s^{-1}).

Soil water potential (SWP) is a soil texture dependent determinant of potato stomatal conductance in the DO_3SE model, which decreases when SWP is lower than −0.5 MPa (LRTAP Convention, 2010;Bueker et al., 2012). The 1990-2013 average SWP during hours when O_3 concentrations at Harwell were in the concentration ranges 60-65 ppb, 65-70 ppb and >70 ppb were −1.50 ± 1.32 MPa, −1.14 ± 0.93 MPa and −1.10 ± 0.90 MPa respectively for the clay loam (fine) soil texture. The average SWP during these O_3 concentration ranges were lower, and even more limiting for the other three soil textures. These are substantially lower than the average SWP for the O_3 concentration ranges between 25 and 50 ppb, all of which are above the −0.5 MPa cut-off except 45-50 ppb for sandy loam, silt loam and loam soil textures (average SWP of −0.65, −0.52 and −0.58 MPa respectively). Across all soil textures, reduction in the frequency of elevated O_3 concentrations produced during regional photochemical episodes has therefore not reduced POD_Y, as these elevated O_3 concentrations coincided with other factors (e.g. SWP) which limit stomatal conductance and hence any potential increase in O_3 accumulation resulting from increased O_3 concentrations. Decreasing regional O_3 production resulted in the largest change in concentration bin contributions for potato POD_Y (Figure 10b). This is due to a later growing season compared with wheat, and a shorter accumulation period and higher maximum stomatal conductance compared with forest trees (150 and 180 mmol m^2 s^{-1} for beech and Scots pine respectively compared to 750 mmol m^2 s^{-1} for potato), limiting the O_3 flux during high O_3 episodes.

These non-O_3 factors, such as SWP, also determine the annual pattern of POD_Y accumulation. For example, between 2010 and 2013 at Harwell, the average SWP on potato ADs in June was −0.11 MPa, compared to −0.72 MPa on NADs (loam soil texture). Hence in June, O_3 concentrations were sufficient that, when plant conditions were favourable, accumulation of POD_Y occurred. In July, SWP was substantially higher due to increased temperatures (2010-2013 average SWP on potato ADs was −1.02 MPa). This, combined with decreasingly favourable potato and wheat phenology, reduced potato and wheat stomatal conductance, leading to a smaller contribution to total POD_Y in July compared to June. Higher O_3 concentrations were therefore needed to accumulate POD_Y; these occurred during regional photochemical O_3 production, hence the larger difference between diurnal O_3 amplitude on AD and NADs in July compared with June for the two crops.

For beech and Scots pine, the proportion of POD_Y accumulated in May and June was higher than in July and August, despite no change in phenology used in the DO_3SE model from May-August, and exceedance of the 1 nmol m^{-2} s^{-1} threshold on the majority of days. For beech, reduction in stomatal conductance occurs when SWP is lower than −0.8 MPa (LRTAP Convention, 2010). Between 2010 and 2013, across the four soil textures, on average 0% and 0-9% of hourly SWP values in May and June, respectively, were below this value, compared with 23-51% and 18-31% in July and August respectively. The effect of SWP on stomatal conductance begins at –0.7 MPa for Scots pine, and therefore has a larger limiting effect. SWP was also found to be one of the most important limiting factors in determining the impact of O_3 on forests across Europe (Emberson et al., 2007). Clay loam had the highest SWP of the four soil textures, and therefore the lowest limitation to stomatal conductance, followed by silt loam, loam and sandy loam. However, the variation in soil moisture between different soil textures due to differences in the extent of evaporation is sufficiently small that the lack of long-term trend in POD_Y and annual pattern of accumulation is consistent across the soil textures.

3.2.2 Spatial differences between Auchencorth and Harwell (2007-2013)

The 2007-2013 average POD_Y calculated for the four soil textures is shown in Table 1, and the variation between soil textures is less than at Harwell. The ratio between the largest and smallest average POD_Y due to differences in soil moisture for the different soil textures was 1.24 (wheat), 1.15 (potato), 1.02 (beech) and 1.02 (Scots pine). The pattern of accumulation, and spatial differences between Harwell and Auchencorth, were consistent across soil textures. Annual POD_Y for potato at Auchencorth (Table S4) were consistently lower than at Harwell, while, for wheat, POD_Y were higher at Auchencorth (Table S6) for 3 of the 7 years. The LRTAP critical level for impact (Mills et al., 2011c) was only exceeded at this site in 2008 for wheat (5.04% yield reduction). These observations, determined using measured O_3 and meteorological data, are consistent with the spatial patterns identified by Mills et al. (2011a) in which modelled O_3 and meteorological variables were used to model POD_Y in 10 km × 10 km grids across the UK. However, the calculated 2008 tuber weight reduction of 1.4% for potato at Auchencorth is higher than the 0% reduction estimated for the grids containing Auchencorth. Simpson et al. (2007) also modelled wheat POD_Y across Europe for 2000, and calculated POD_Y in south-east Scotland of 0.5-1 mmol m^{-2}, and in south-east England of 1-3 mmol m^{-2}, which are similar to those determined here using the measurement data at Harwell and Auchencorth. In general, diurnal amplitudes of O_3, NO_2 and NO and back-trajectory NO_x emissions estimates were lower at Auchencorth (shown in Figure 11b for wheat and potato POD_Y ADs in June), which indicates a greater importance of hemispheric background concentrations in determining the O_3 impact at Auchencorth on wheat and potato.

Periods with elevated regional O_3 influence at Auchencorth can lead to a larger effect on POD_Y compared with Harwell. For example, in 2008 across all soil textures, July contributed 0.47 mmol m^{-2} (36% total) to wheat POD_Y (Figure 12a). In this month, O_3 concentrations at Auchencorth had a significant regional photochemical contribution, evidenced by elevated diurnal O_3 and NO_2 variation and 71% higher back-trajectory NO_x emissions on ADs compared to the 2007-2013 average (Figure 12b). POD_Y in July 2011 at Auchencorth was also influenced by regional O_3 production. Diurnal O_3 amplitude in July 2011 was 6 ppb higher on ADs than on NADs and global radiation during ADs was 26% higher than the AD average. July 2011 contributed 80% of the annual wheat POD_Y at Auchencorth across all soil textures. At Harwell in July 2008, wheat POD_Y was less than half the Auchencorth value, and in July 2011, there was no POD_Y accumulation, despite elevated regional O_3 influence in both cases. These two examples demonstrate that elevated regional photochemical O_3 production can have a larger crop impact, characterised through POD_{Y}, in south-east Scotland than in south-east England, despite being further from major sources of O_3 precursor emissions. The meteorological conditions conducive to regional photochemical O_3 production (higher temperature and global radiation) at Harwell resulted in unfavourable conditions for high O_3 stomatal conductance in crops compared with Auchencorth. The median daytime O_3 stomatal conductance at Harwell was 58 mmol m^{-2} s^{-1} and 63 mmol m^{-2} s^{-1} in July 2008 and 2011 respectively for loam soil texture, compared to 94 mmol m^{-2} s^{-1} and 95 mmol m^{-2} s^{-1} at Auchencorth. Average SWP in July 2008 and 2011 was –0.03 MPa and –0.02 MPa respectively at Auchencorth, and –0.63 MPa and –1.17 MPa at Harwell. In addition lower temperatures at Auchencorth result in a longer accumulated temperature growing season. In July 2008 and 2011, the phenological limitation on wheat stomatal conductance was similar for the first three weeks of the month at both sites, but in the final week diverged and was substantially more limiting at Harwell at the end of July (40% and 50% lower in 2008 and 2011, respectively), also resulting in less favourable conditions for POD_Y accumulation in south-east England.

Between 2007 and 2013 across the soil textures, Scots pine and beech POD_Y were on average 27-37% and 5-19%% higher at Auchencorth compared to Harwell (Table 1 and Figure 13a). These larger values were due to larger contributions from July and August at Auchencorth (Tables S10 and S12). In these months, higher temperatures at Harwell produced conditions which reduced stomatal conductance. For example, in 2007-2013 at Harwell for loam soil texture, SWP was on average 59% higher in July and 82% higher in August than at Auchencorth.

Elevated regional photochemical O_3 production also had varying impacts on forest trees at the two sites. In May 2008 across all soil textures, accumulated POD_Y was elevated at Auchencorth for both Scots pine and beech (Figure 13b). Larger diurnal O_3 variation (28% higher than the 2007-2013 average) and back-trajectory NO_x emissions (53% higher) during May 2008 indicate regional photochemical O_3 production made a significant contribution to measured O_3 concentrations at Auchencorth (Figure 13c). Despite larger increases in these variables at Harwell, the accumulated POD_Y in May 2008 was 14% and 29% less than at Auchencorth for beech and Scots pine, respectively across all soil textures (Figure 13b), and the frequency of hours with high POD_Y accumulation was lower at Harwell. For example, the maximum hourly POD_Y accumulated at Harwell and Auchencorth in May 2008 were 0.027

mmol m^{-2} and 0.033 mmol m^{-2} respectively and there were 21 fewer hours when hourly POD_Y accumulated was above 0.02 mmol m^{-2} compared with Auchencorth. Hence the conditions during this regional O_3 episode at Harwell, e.g. a 12% increase in monthly average temperature, also produced less favourable plant conditions for POD_Y accumulation.

3.2.3 Comparison between POD_Y and AOT40

The chemical climates based on the AOT40 metric (Tables S7 and S8) were derived for the crop-based AOT40 definition and are therefore most comparable with the wheat and potato POD_Y chemical climates. At Harwell, there was a significant long-term decrease in AOT40 from an average of 6533 ppb.h in 1990-1993 to an average of 2623 ppb.h in 2010-2013 (trend: −3.6% y^{-1}, $p = 0.001$, Figure 14, Table S7). This decrease in AOT40 is in contrast to the trends in wheat and potato POD_Y at Harwell, which showed no significant trend across the 24 year period (Figure 8a). However, the AOT40 climate showed similar decreases in diurnal pollutant amplitudes and back-trajectory NO_x emissions estimates compared with the crop POD_Y climates, indicating increased importance of hemispheric background concentrations. This is in line with Derwent et al. (2013) which reported an increase between 1989-2012 in AOT40 when selecting hemispheric background air arriving at Mace Head, Ireland. AOT40 at Auchencorth was lower than at Harwell, and the magnitude of the difference was much larger than for POD_Y. This was similar to the spatial differences in Jenkin (2014), where estimated regional background AOT40 was twice as large at Harwell compared to a rural site in central Scotland (EMEP site GB0033R: Bush).

The spatial difference between sites was less for POD_Y because AOT40 does not account for modification of stomatal conductance, especially during summer months when SWP at Harwell can be low. Hence the average contribution from July in 2010-2013 to AOT40 was 35%, but only 3% for wheat POD_Y (Tables S5 and S7). Conversely, the contribution from July to AOT40 at Auchencorth is lower than the contribution to wheat and potato POD_Y (Tables S6 and S8), indicating that O_3 concentrations below the 40 ppb threshold determine the wheat and potato POD_Y to a large extent during this month. The limitations of the fixed growing season in the AOT40 concept have been detailed previously (RoTAP, 2012;Coyle et al., 2003), including the observation that there can be significant impact on vegetation below the 40 ppb threshold. For forest trees, Gauss et al. (2014) reported forest-based AOT40 across the UK from 2007-2012 to be between 5 and 50% lower than that calculated in 2000. In addition Klingberg et al. (2014) found a much smaller decline in forest-specific POD_Y than AOT40 between 1960 and 2100 using modelled O_3 and meteorological data at 14 sites across Europe.

In summary, the crop-based AOT40 trend at Harwell showed an improvement in O_3 crop impact which is not shown when the interaction between plant and O_3 climates are modelled using biologically more relevant POD_Y metric.

4 Conclusions

A chemical climatology framework was applied to characterise O_3 exposure associated with human health and vegetation impacts using measured data at the Harwell and Auchencorth UK EMEP supersites. These sites have been shown to be representative of rural O_3 over the wider geographic areas of south-east England and northern UK, respectively.

At Harwell, each chemical climate analysis indicated a decrease over the period 1990-2013 in the relative importance of regional photochemical O_3 production, associated with NO_x emissions reductions, and increasing relative importance of hemispheric background concentrations. However trends in the human health and vegetation metrics associated with these changes were different.

As quantified by the SOMO35 metric, the human health-relevant O_3 exposure at Harwell decreased significantly over the period 1990-2013 (–2.2% y^{-1}), while quantification using the SOMO10 metric showed no trend due to its lower dependence on the highest O_3 concentrations, which have decreased due to declining regional photochemical production. Hence the choice of these two O_3 concentration thresholds, which are both recommended by WHO REVIHAAP for health impact assessments, determines both the perceived annual pattern of health burden and whether there has been improvement in time. The policy significance of these findings is important since the regional policies adopted to date, of controls on NO_x and VOC emissions in Europe, have been effective in reducing peak concentrations and exposure. The growth in these emissions elsewhere has increased the importance of background contribution to O_3 exposure in the UK. The effective controls for background O_3 would be controls at hemispheric scales on O_3 precursors, and in methane emissions especially.

The POD_Y metrics used to quantify the impact of O_3 on vegetation showed no change over the period 1990-2013 at Harwell for wheat and potato crops, and beech and Scots pine trees, in contrast to a decreasing trend in potential impact if quantified by the crop AOT40 metric. The contrast highlights the need to model vegetation impacts using the biologically more relevant POD_Y metrics. The potential reductions in vegetation impact (i.e. POD_Y), due to decreases in regional photochemical O_3 production decreases (as reflected in the decrease in crop AOT40 at Harwell), did not occur due to the other factors that reduce plant stomatal conductance and hence accumulated O_3 uptake (e.g. changing plant phenology and low soil water potential). Thus the long-term decrease in regional O_3 production evident at Harwell led to a lower beneficial effect on POD_Y than on SOMO35.

The chemical climates indicate a greater influence of hemispheric background concentrations at Auchencorth compared to Harwell (for the period 2007-2013). SOMO10 values were similar at both sites, but SOMO35 was lower at Auchencorth. POD_Y values were larger for vegetation species with longer growing seasons and lower thresholds for exceedance compared to Harwell (i.e. for beech and Scots pine). In addition, more favourable plant conditions (higher SWP, longer accumulated temperature derived growing season) during periods of elevated regional O_3 production resulted in exacerbation of vegetation impacts at Auchencorth compared to Harwell. Hence the potential for O_3 vegetation impact reduction from future reductions in regional O_3 is greater at Auchencorth than at Harwell, despite being further from the major sources of O_3 precursors. However, the policies required to substantially reduce exposure of vegetation in the UK to damage from O_3, like those for human health, are measures that reduce the background O_3 concentrations, hence the need for hemispheric control measures on O_3 precursors.

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Table 1: Average ± SD wheat, potato, beech and Scots pin POD_Y calculated for 4 different soil textures (see Bueker et al. (2012) for a description of their hydraulic properties) over the monitoring periods at Harwell and Auchencorth.

Harwell 1990-2013 average	**Sandy loam (coarse)**	**Silt loam (medium coarse)**	**Loam (medium)**	**Clay loam (fine)**
Wheat POD_Y (mmol m^{-2}) (grain yield % reduction)	1.21 ± 1.07 (4.61%)	1.75 ± 1.19 (6.64%)	1.51 ± 1.14 (5.72%)	1.90 ± 1.19 (7.22%)
Potato POD_Y (mmol m^{-2}) (tuber yield % reduction)	2.35 ± 1.27 (3.03%)	3.10 ± 1.42 (3.99%)	2.64 ± 1.32 (3.40%)	3.10 ± 1.46 (4.00%)
Beech POD_Y (mmol m^{-2}) (biomass % reduction)	14.0 ± 3.7 (15.4%)	16.0 ± 3.5 (17.6%)	14.7 ± 3.7 (16.2%)	16.1 ± 3.4 (17.7%)
Pine POD_Y (mmol m^{-2})	26.2 ± 5.5	28.7 ± 5.3	27.0 ± 5.6	28.8 ± 5.3
Auchencorth 2007-2013 average				
Wheat POD_Y (mmol m^{-2}) (grain yield % reduction)	0.85 ± 0.45 (3.23%)	1.01 ± 0.38 (3.86%)	0.96 ± 0.39 (3.65%)	1.05 ± 0.37 (3.99%)
Potato POD_Y (mmol m^{-2}) (tuber yield % reduction)	0.95 ± 0.41 (1.22%)	1.08 ± 0.46 (1.39%)	0.99 ± 0.41 (1.28%)	1.09 ± 0.47 (1.40%)
Beech POD_Y (mmol m^{-2}) (biomass % reduction)	16.6 ± 1.6 (18.3%)	16.9 ± 1.2 (18.6%)	16.7 ± 1.5 (18.4%)	16.9 ± 1.2 (18.6%)
Pine POD_Y (mmol m^{-2})	35.9 ± 3.6	36.5 ± 2.7	36.2 ± 3.3	36.6 ± 2.7

Figure 1: Map of the United Kingdom and Ireland showing the location of the two UK EMEP supersites (purple circles) at Auchencorth and Harwell, as well as the location of the UK Met Office stations from which meteorological data was used (green circles).

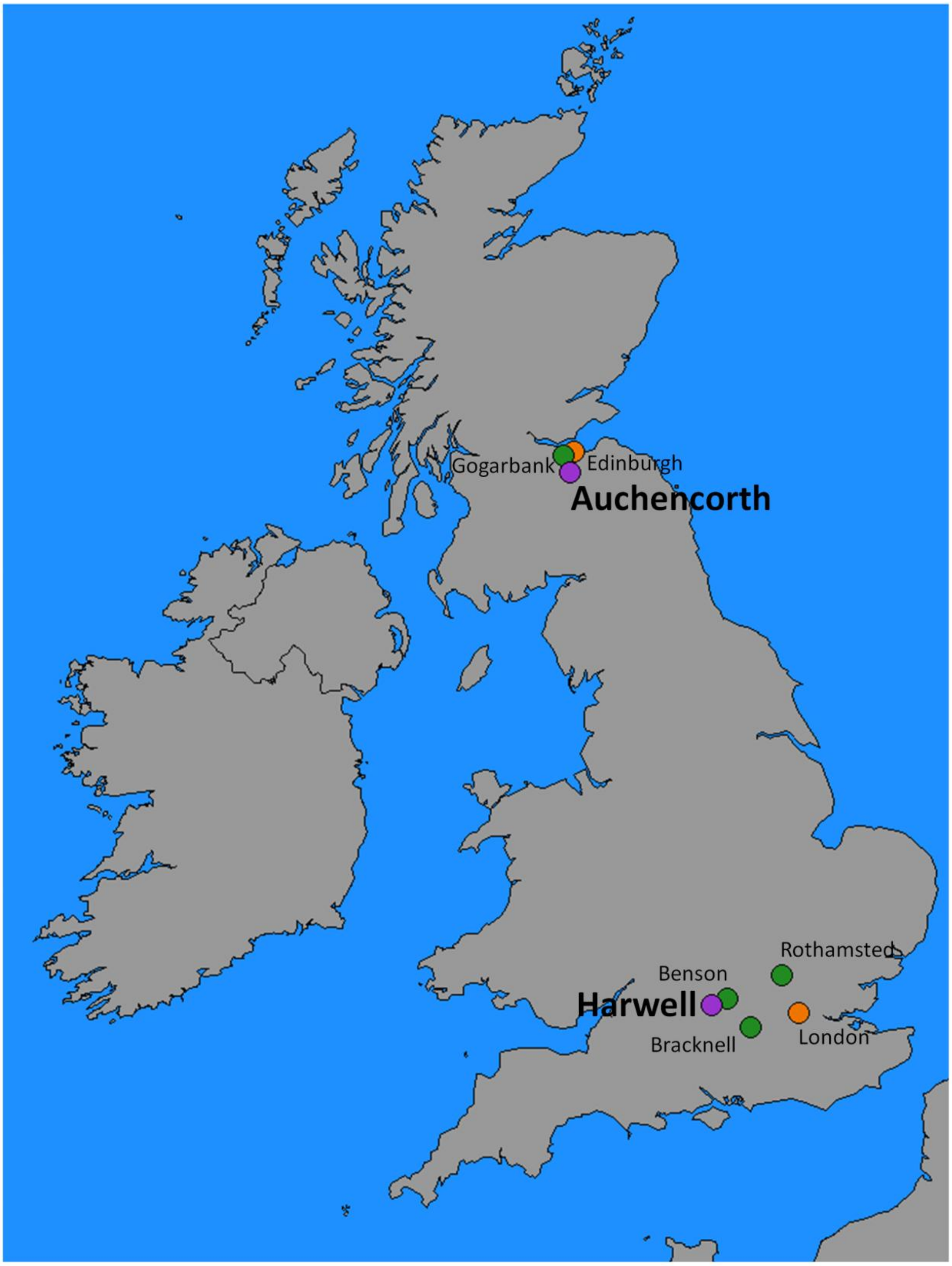

Figure 2: Practical steps for derivation of a chemical climate. The impact of premature mortality associated with short-term exposure to O_3 is used as an example. Text in the chemical climate datasheets are coloured the same as the step which gave rise to the statistic. The detail of application of these 6 steps to the focus of this study is described in Section 2.

Step 1: Identify the impact. Associations between short-term exposure to O_3 and premature mortality.

↓

Step 2: Establish the metric. Daily maximum 8-hour running mean O_3 concentrations, above a threshold of 10 or 35 ppb, over the full year.

↓

Step 3: Define temporal and spatial boundaries to the chemical climate. Examples: a single receptor site, a geographic region, a season, a 20-year period, etc.

↓

Step 4: Describe and summarise the state. For example, determine relevant temporal and spatial patterns and variations of O_3 concentrations greater than 10 and 35 ppb. Assessment of diurnal and seasonal O_3 variation is necessary, including covariance with NO_x.

↓

Step 5: Identify the drivers. Use statistical and other source apportionment methods. For example, assess relationships between exceedances and combinations of meteorological conditions, including importance of local, regional and hemispheric influences on O_3 (& precursors) during exceedances. Source activities may also be identified using multivariate methods, chemical transport models, etc.

↓

Step 6: Phase identification. Note boundaries demarcating significant change to impact, state and drivers. Different phases may be identified during steps 2 – 5 or through independent application of steps 2 – 5 for different spatial/temporal periods, followed by collation into a single chemical climate. For example, different phases of O_3 health impact may arise for different time periods (e.g. different 5-year periods) and/or space (e.g. north-west vs Mediterranean Europe, Europe vs Asia).

Figure 3: Human health relevant exposure to O_3 at Harwell (1990-2013) and Auchencorth (2007-2013), as characterised by the SOMO10 and SOMO35 metrics.

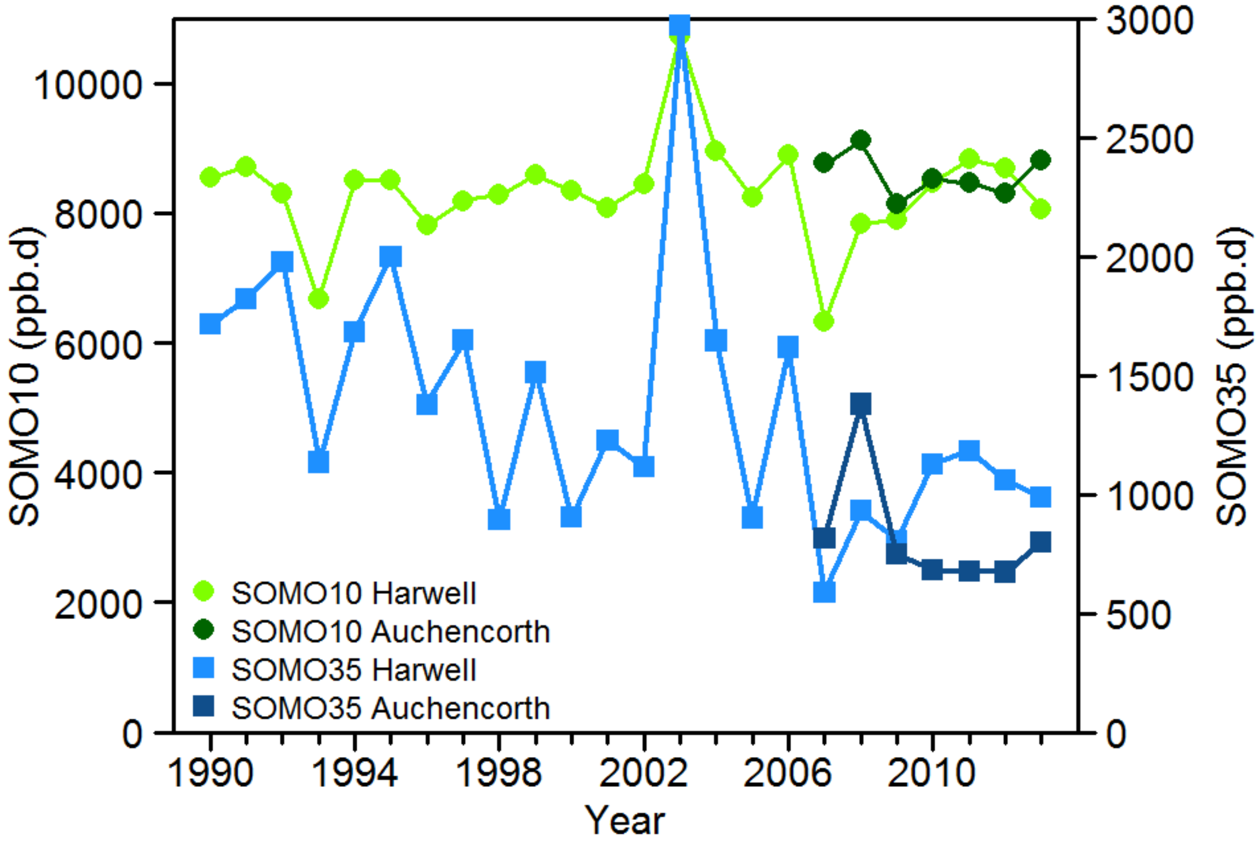

Figure 4: Relative annual contributions from spring (MAM) and summer (JJA) to (a) SOMO10 and (b) SOMO35.

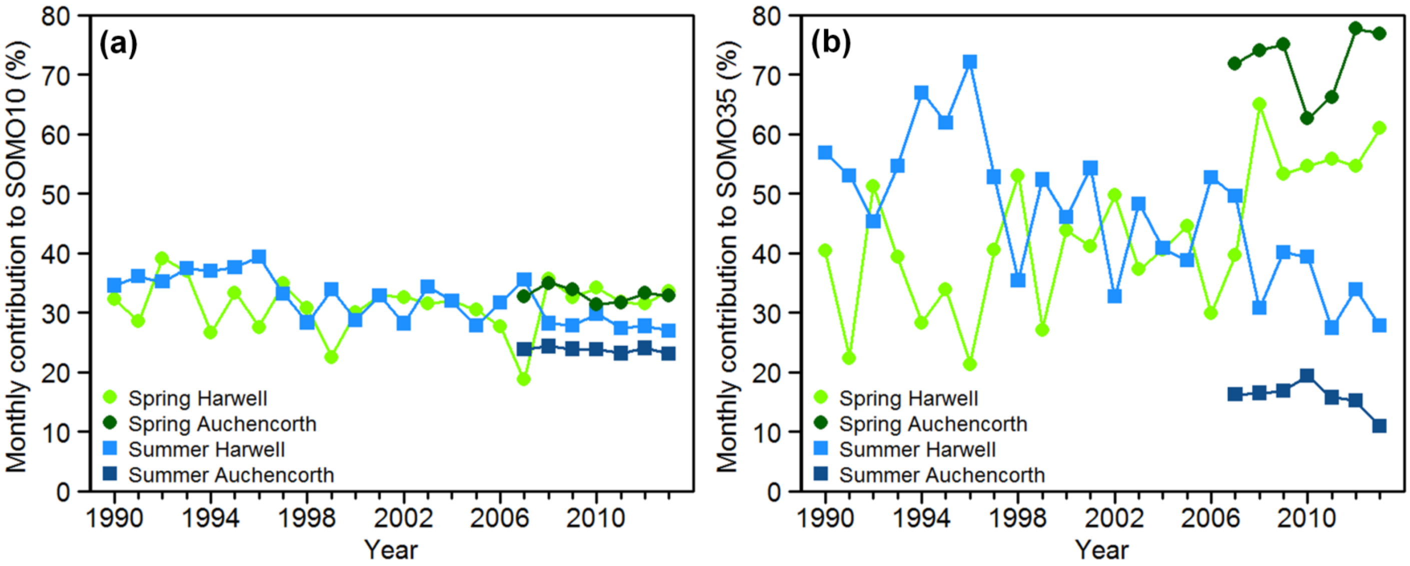

Figure 5: Relative annual contributions to (a) SOMO10 and (b) SOMO35 at Harwell from different O_3 concentration bins. Concentrations are separated into thirteen 5 ppb bins spanning daily maximum 8-h mean O_3 concentrations between 10 ppb and >70ppb. Note: these concentration bins are contributing to a decreasing long-term trend in SOMO35 and to a constant trend in SOMO10, as illustrated in Figure 2.

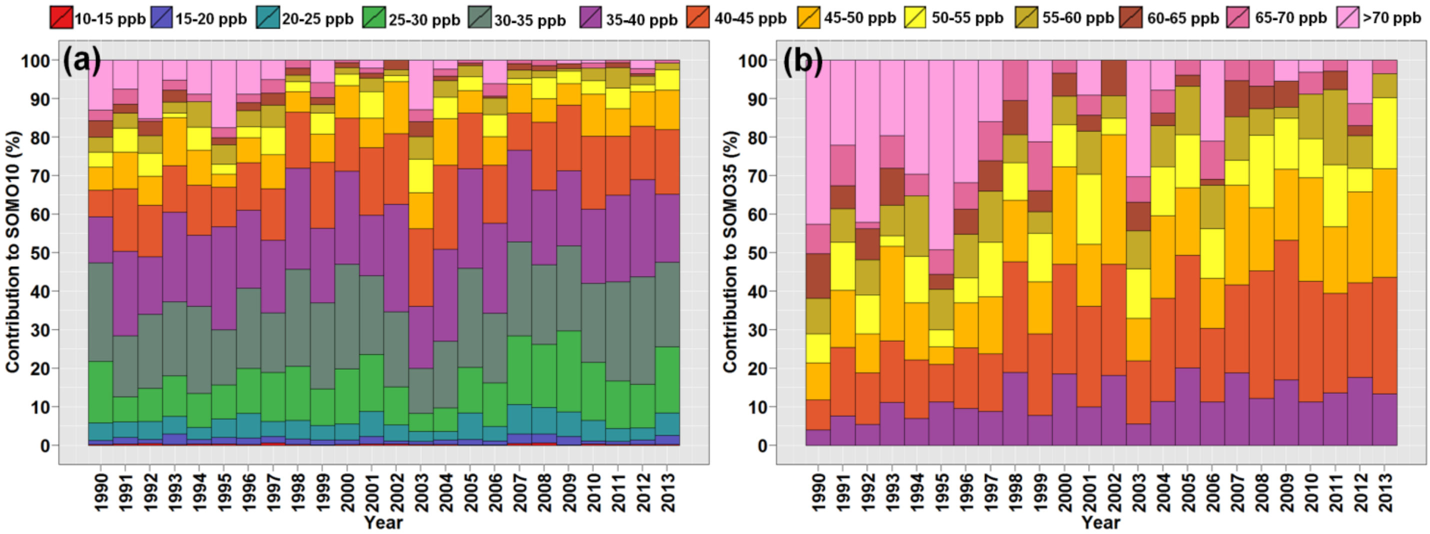

Figure 6: Amplitude of the diurnal O_3, NO_2 and NO cycles at Harwell and Auchencorth during SOMO35 accumulation days (ADs).

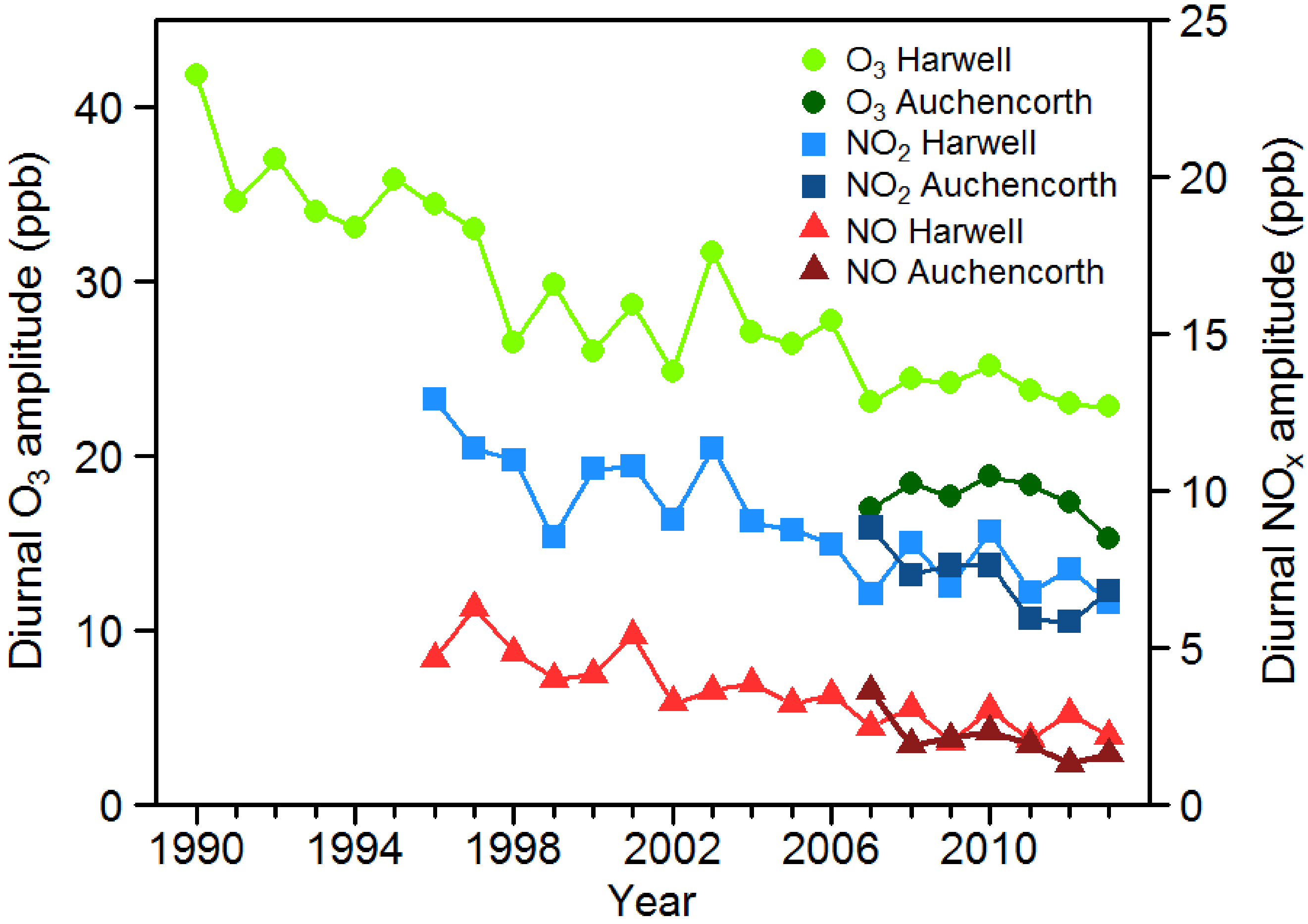

Figure 7: Estimate of the hourly European NO_x emissions emitted from the EMEP 0.5° grids over which 96-h back trajectories passed prior to arrival at Harwell and Auchencorth for SOMO35 accumulation days (ADs) and non-accumulation days (NADs).

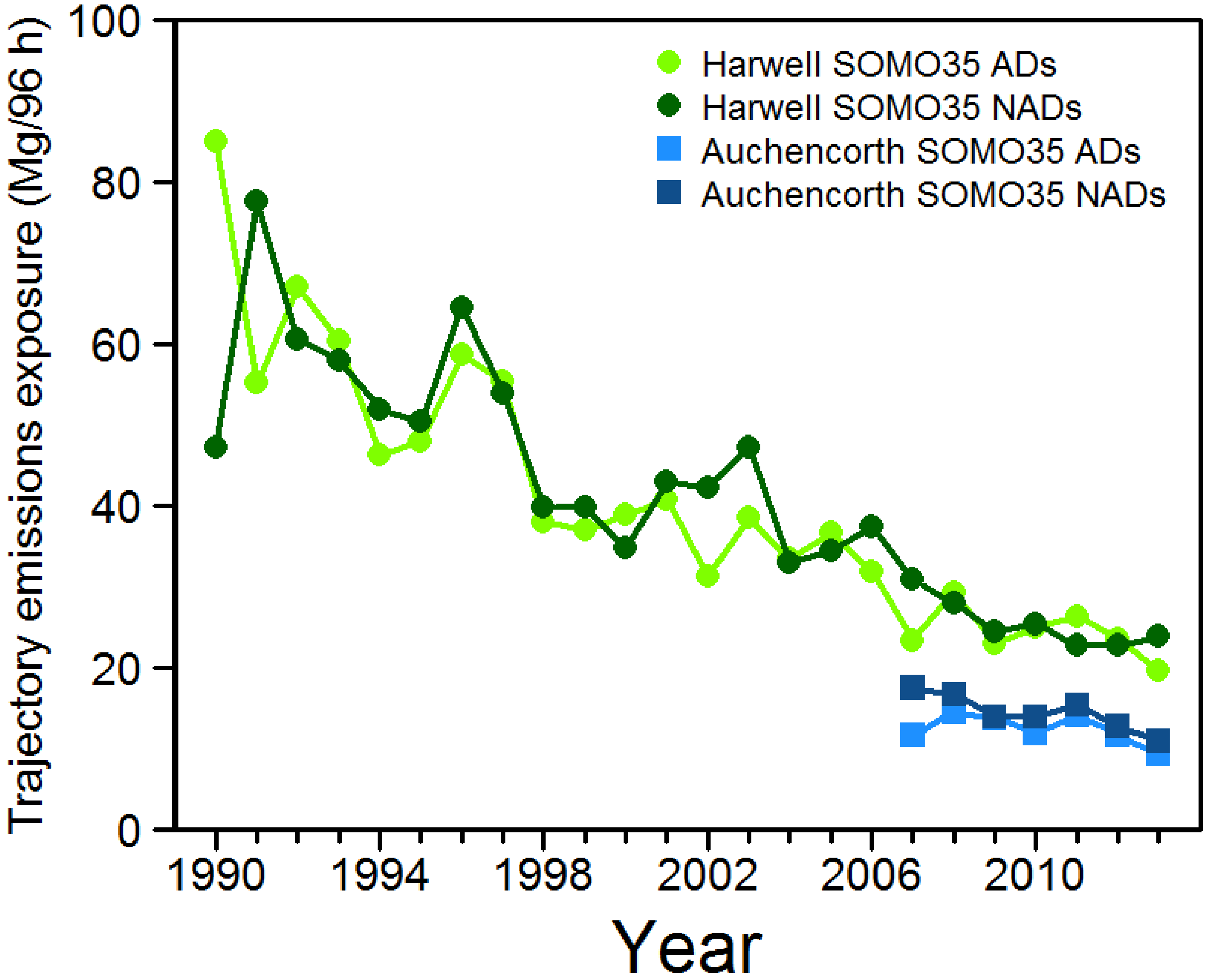

Figure 8: Impact of O_3 characterised by the POD_Y metric (and associated response) for (a) wheat (grain yield reduction) and potato (tuber weight reduction), and (b) beech (biomass reduction) and Scots pine at Harwell between 1990 and 2013.

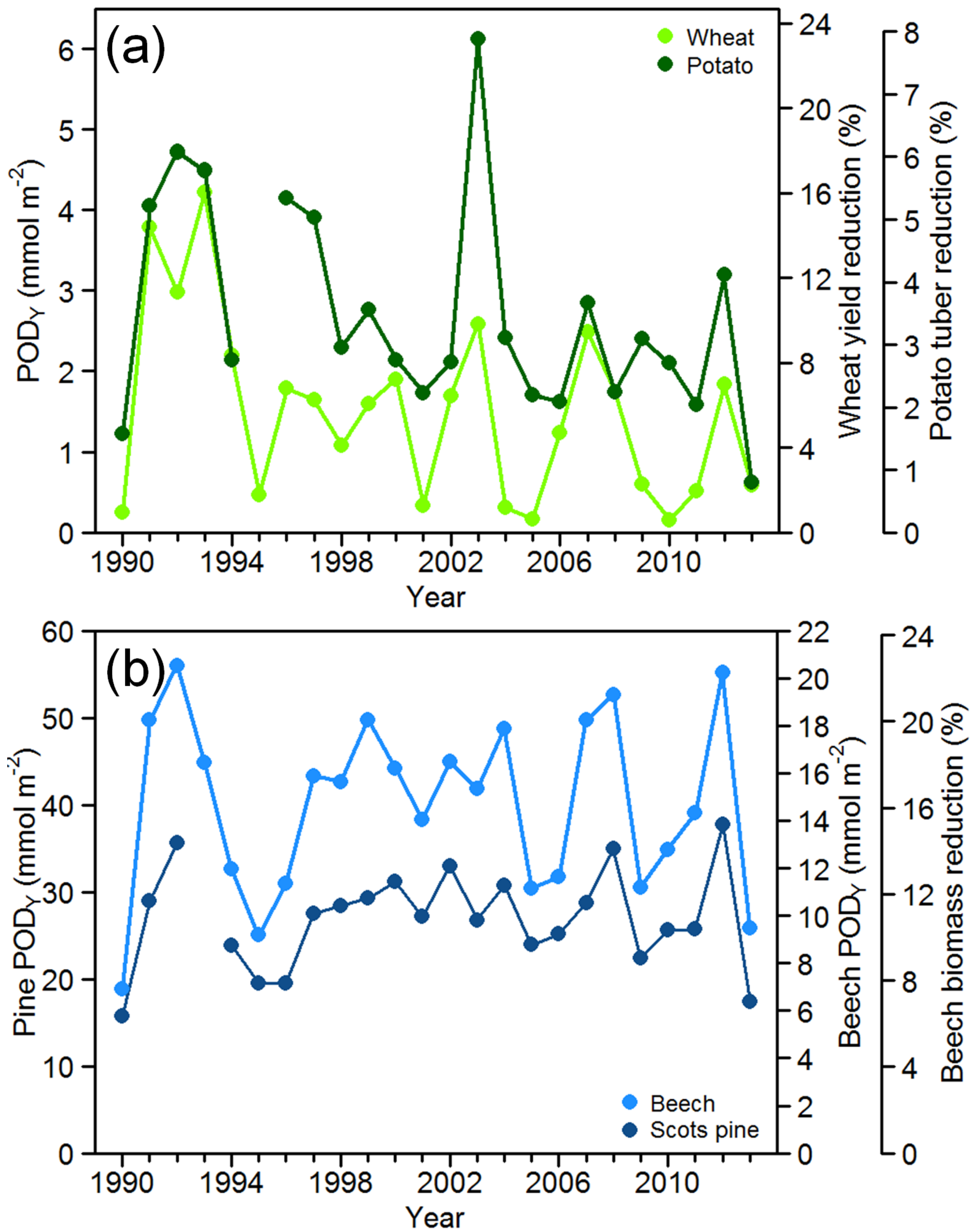

Figure 9: Amplitude of the diurnal O_3 cycle at Harwell during June POD_Y accumulation days for wheat and potato. and hourly European NO_x emissions estimate for the EMEP 0.5° grids over which 96-h back trajectories passed prior to arrival at Harwell during June POD_Y accumulation days for wheat and potato.

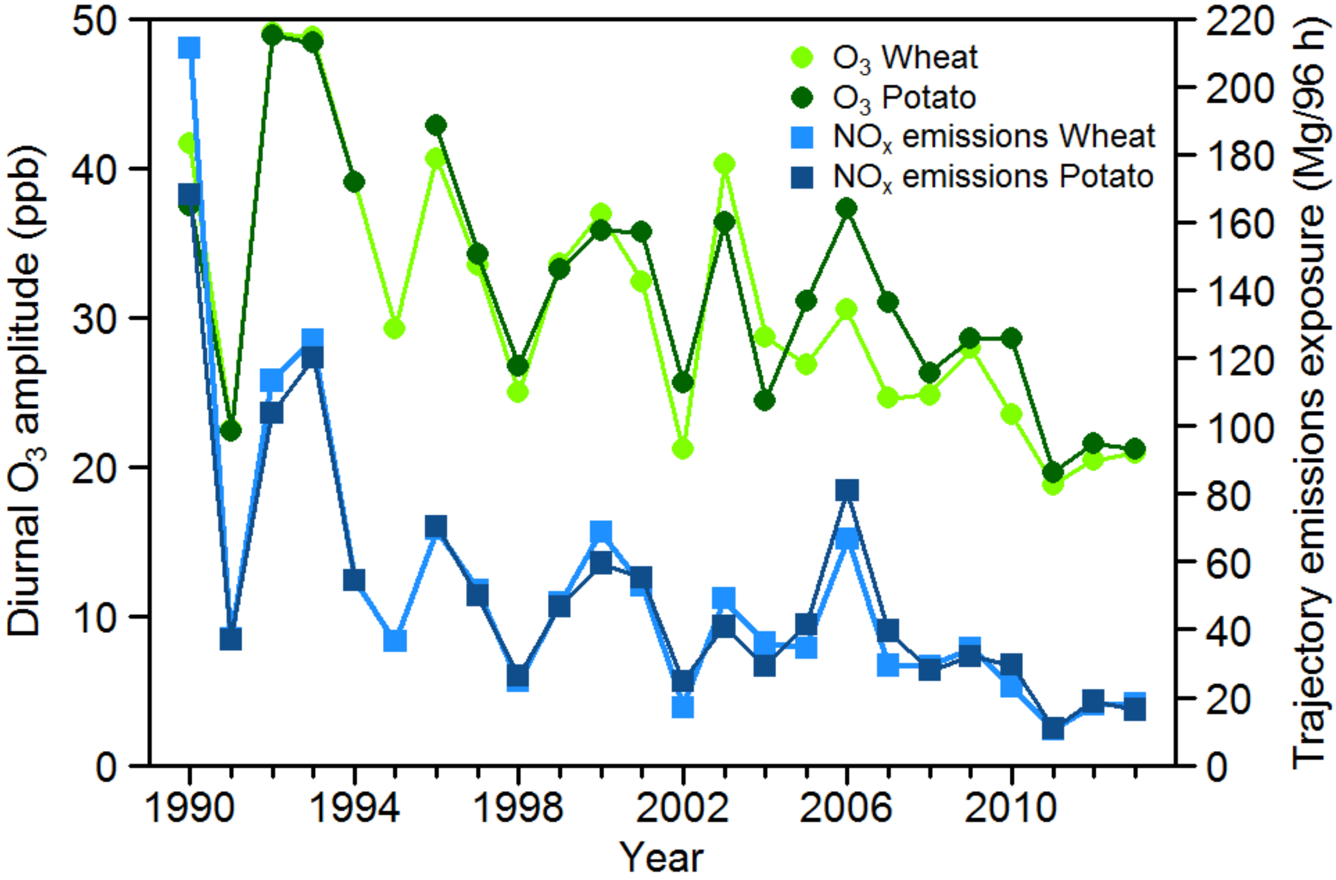

Figure 10: Relative annual contributions to (a) wheat POD_Y, (b) potato POD_Y, (c) beech POD_Y and (d) Scots pine POD_Y at Harwell from different O_3 concentration bins. Concentrations are separated into fifteen 5 ppb groups spanning hourly O_3 concentrations between 0 ppb and >70ppb. Note: these concentration bins are contributing to constant trends in POD_Y for each vegetation type – see figure 7.

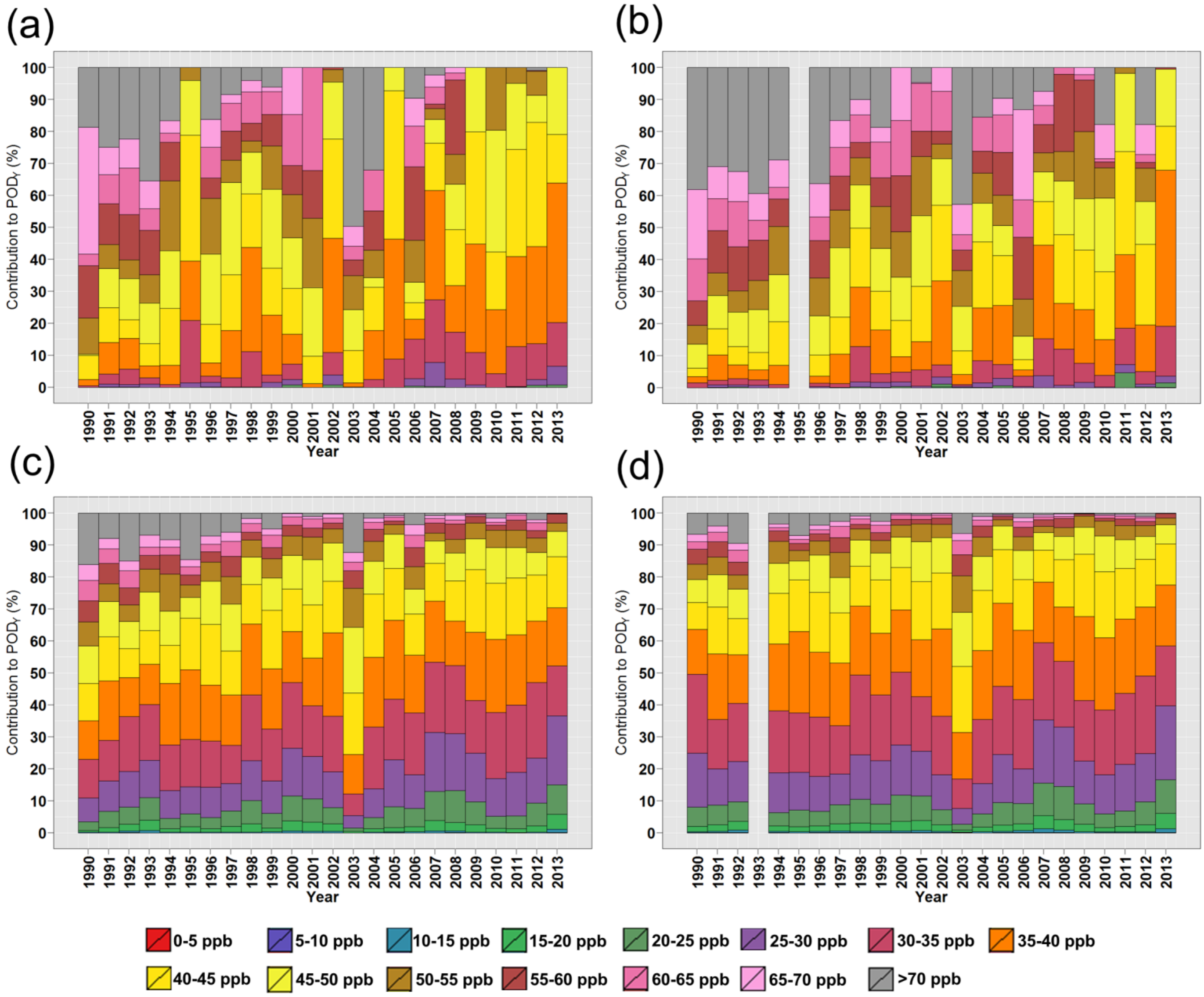

Figure 11: Comparison of O_3 vegetation impact chemical climates for wheat and potato 2007-2013. (a) Annual POD_Y for wheat and potato, (b) Diurnal O_3 amplitude during June accumulation days (ADs) at Harwell and Auchencorth, and trajectory NO_x emissions estimates at Harwell and Auchencorth.

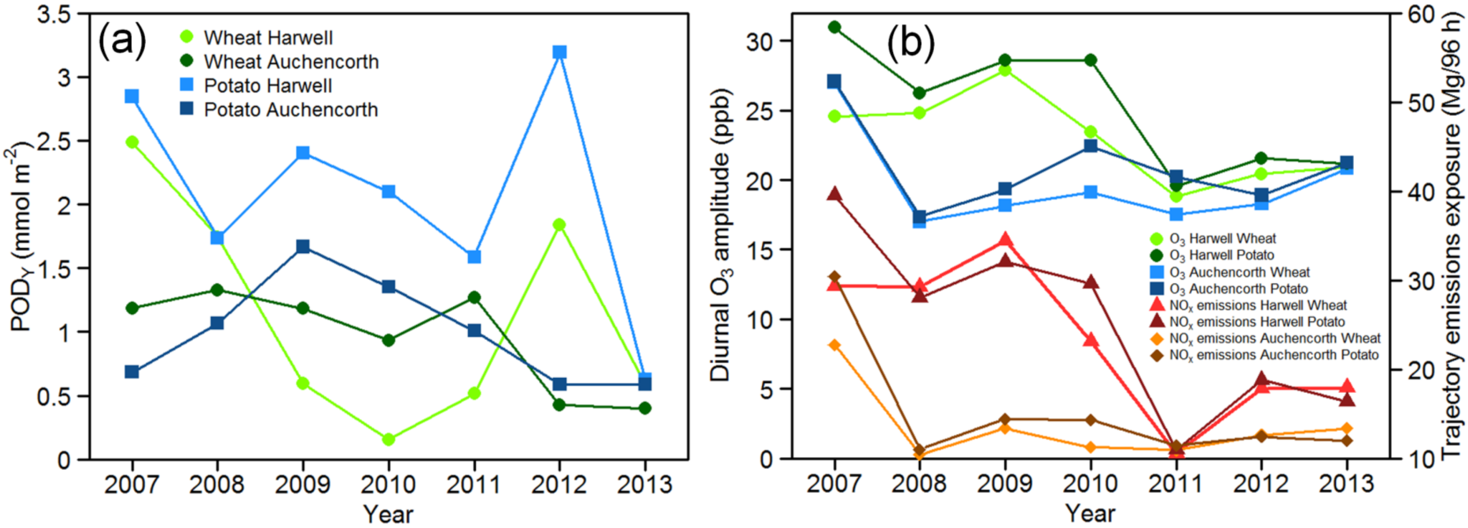

Figure 12: (a) Wheat POD_Y accumulated during July at Harwell and at Auchencorth, 2007-13. (b) Diurnal cycle amplitude of O_3 and NO_2, and back-trajectory NO_x emissions estimates during wheat accumulation days (ADs) in July at Harwell and at Auchencorth, 2007-13.

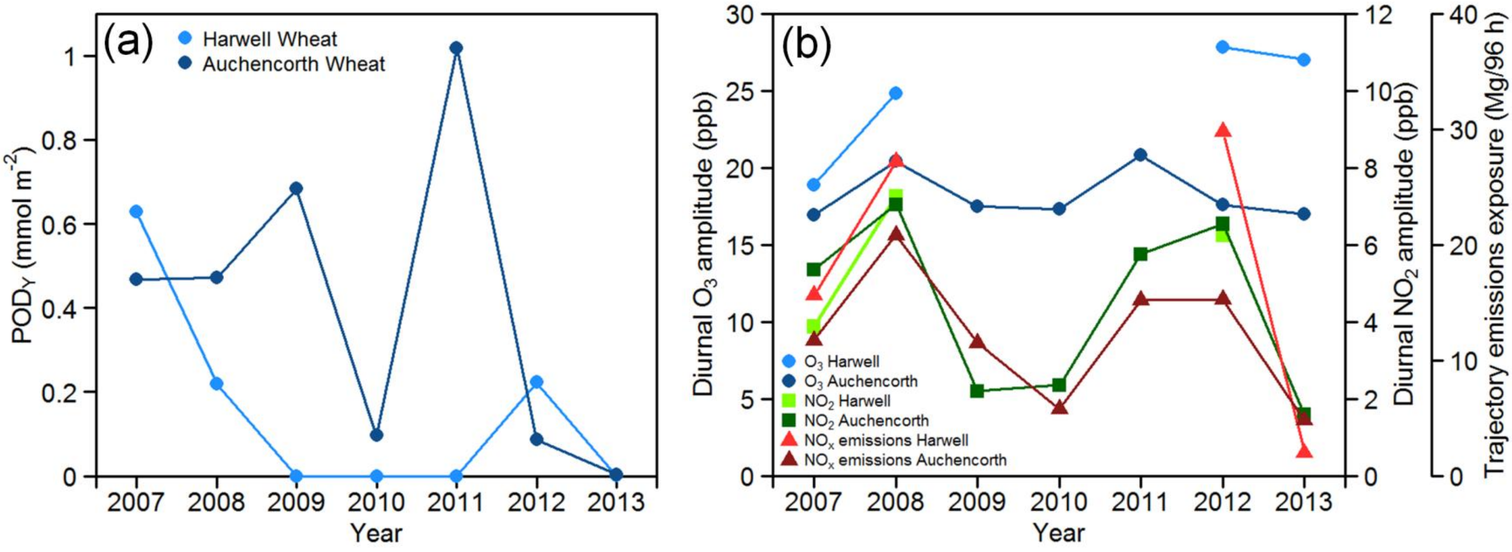

Figure 13: Comparison of O_3 vegetation impact chemical climates for beech and Scots pine 2007-2013 at Harwell and Auchencorth. (a) Annual POD_Y for beech and Scots pine. (b) POD_Y accumulated in May for beech and Scots pine. (c) May monthly average diurnal amplitude of O_3 and NO_2, and back-trajectory NO_x emissions estimates.

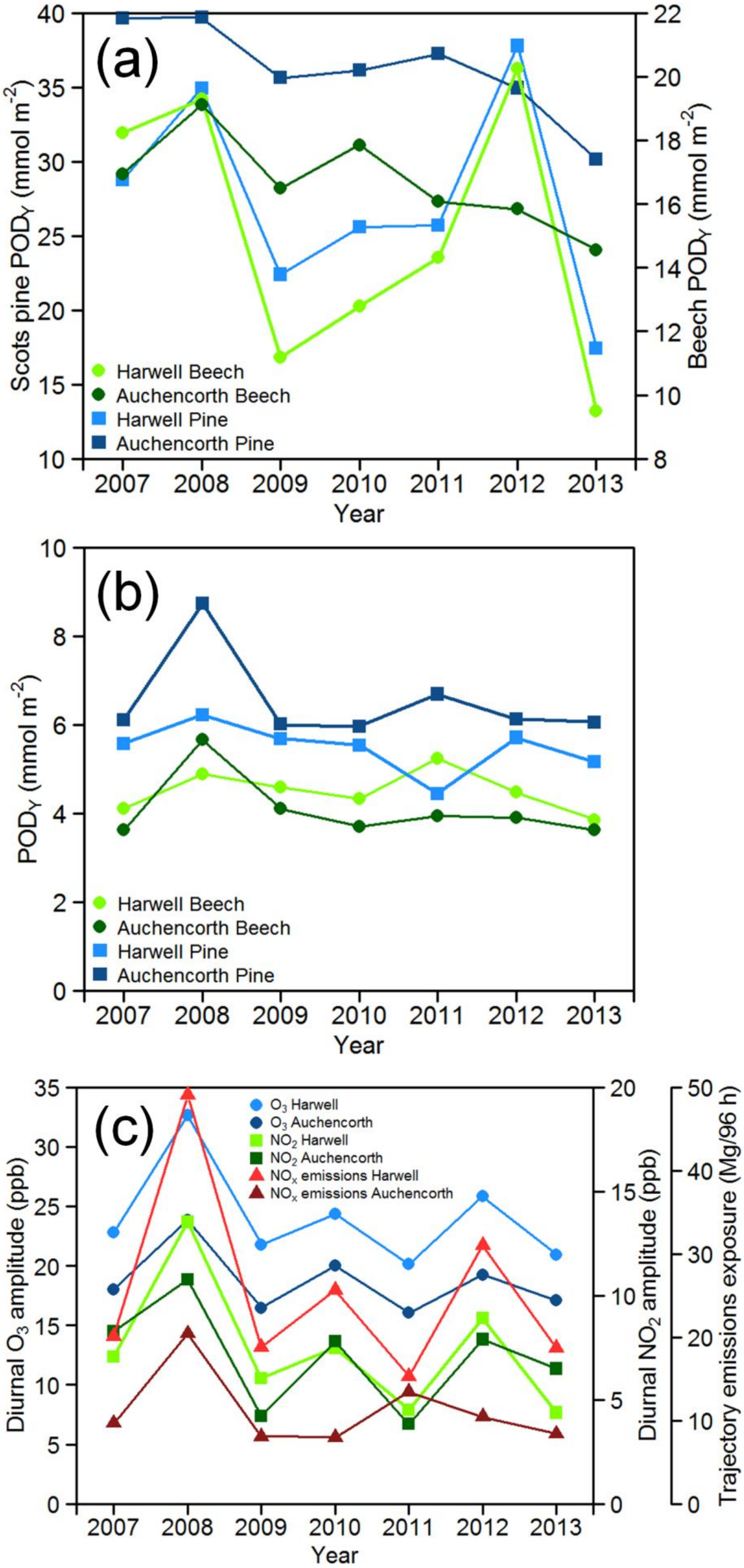

Figure 14: Crop-relevant AOT40 (calculated between May and July) at Harwell for the period 1990 to 2013. The Theil-Sen trend estimate of median trend (shown in red) is –3.6 % y^{-1} (p = 0.001).