Response to reviewers

Atmos. Chem. Phys. Discuss., 15, 1869-1914, 2015**: "Trends and drivers of ozone human health and vegetation impact metrics from UK EMEP supersite measurements (1990-2013)" by Malley et al.**

We thank the reviewers for their time spent reviewing our manuscript and for their recommendations for publication after attention to some revisions. Below we respond to each comment individually and indicate the revisions we have made to the manuscript. Reviewers' comments are in italics, additional tables and figures are located at the end of the response. Page and line numbers below refer to the original version of the paper published on ACPD.

Reviewer #1:

This paper presents a detailed analysis of the changes over a 20 year time period in key indices used to assess health and vegetation impacts of ozone at the Harwell EMEP supersite in the south of the UK, including an important evaluation of the role of regional precursor emission control and changes in hemispheric background levels. This is supplemented by a comparison with values of the same indices over more recent years at a second supersite in Scotland. The very detailed analysis of trends in both health and vegetation indices, and by implication impacts, at Harwell clearly demonstrates the different trends in the various indices, and highlights the effect of considering different threshold indices. The paper also very nicely identifies the importance of hemispheric background concentrations and regional ozone production as underlying drivers of change. Both health and vegetation impacts of ozone are of global importance and hence these are important messages of wider importance for assessment of the future benefits of different measures to reduce these ozone impacts. I therefore recommend publication. However, I have a number of comments about the framing and detail of the paper which I suggest the authors consider before final publication.

Specific comments

Reviewer 1 comment: *The wording of the first para of the abstract implies that data from both sites was important in identifying trends in impact indices and their drivers, but in fact only the time-series from Harwell is long enough to allow analysis of trends. Given that the authors themselves identify (p6, l31) that Harwell is only representative of rural sites within 120km of London, this does place a constraint on the wider relevance of their findings. More discussion of the limitation that this places on wider conclusions about trends and drivers throughout the UK and other parts of NW Europe would be useful.*

Response: We acknowledge that the use of the term 'trends' in the first paragraph of the abstract was not sufficiently defined. While long-term temporal trends were only quantified at Harwell, this paper also reports on spatial trends in O_3 health and vegetation impacts across the UK through its comparison between Harwell and Auchencorth. The first sentence of the Abstract has therefore been changed as follows to emphasise that 'trends' refers to both spatial and temporal trends:

Changed text: "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."

The second and third paragraphs of the Abstract make it clear that the Harwell dataset was used to assess long-term temporal trends, and Auchencorth was used for comparison with Harwell over a shorter (2007-2013 time period).

We have been very clear in defining the geographical representativeness of the sites by reference to previous work that placed these two UK sites in a European context according to measured O_3 variation (Malley et al., 2014). As Harwell is representative of south-east England, the motivation for the spatial comparison between Harwell and Auchencorth (representative of the remainder of the rural UK (Malley et al., 2014)) was to evaluate how the state and drivers of O_3 impacts identified at Harwell compared with the remainder of the UK. While the study period is shorter at Auchencorth, the spatial comparison highlights important policy relevant conclusions about the differences in ozone impact accumulation across the UK. These are emphasised in both the Abstract and Conclusions, which state that, in general, O_3 impacts are determined to a greater extent by hemispheric background concentrations at Auchencorth than at Harwell; and that therefore, across the whole UK, reduction in hemispheric background concentrations is required for substantial improvement. An important exception is during regional O_3 episodes, when elevated POD_Y is accumulated at Auchencorth compared to Harwell; hence vegetation impacts at Auchencorth would improve to a larger degree than at Harwell from regional O_3 precursor emissions reductions. Again, this contrast between O_3 impacts in south-east England and the remainder of the UK is noted in the abstract and conclusions.

Reviewer 1 comment: *The chemical climatology idea is a key conceptual element of the introduction of the paper. However, it subsequently only provides a template for the detailed annexes, and it provides little of the framework for the body of the text and data analysis. Either this element should provide a stronger framework throughout the paper, or it should be omitted, as the key messages of the paper are not really connected to this concept and would be equally valid without it.*

Response: The focus of the Results and Discussion section is on what is learned through the application of the chemical climate approach (impact, state and drivers) on the spatio-temporal changes in the conditions producing O_3 impacts. The presentation and discussion of the material in the Results and Discussion is divided into sub-sections that map onto the chemical climatology framework. The human health (Section 3.1) and vegetation (Section 3.2) sections are further divided into two subsections which consider separately changes in temporal chemical climate phase at Harwell between 1990 and 2013 (Sections 3.1.1 and 3.2.1 for health and vegetation respectively), and spatial changes in chemical climate phase between Harwell and Auchencorth (Sections 3.1.2 and 3.2.2). As the reviewer notes, our Introduction and Methods sections already contain detailed explanation of how the chemical climatology framework was used, including citation to another publication, to which the reader can refer. However, to emphasise more the chemical climatology framework used in the derivation of the results and discussion statistics (but yet retain focus in these sections on the key findings, as recommended in a further comment below), the following two explanatory sentences have now been added to the start of Sections 3.1 and 3.2.

Additional text:

> P. 1879 ln 23: "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)."
>
> P. 1886 ln 24: "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)."

Reviewer 1 comment: *The manuscript is long and feels repetitious in places, and it would benefit from a stronger focus on the key findings of the study, rather than describing every piece of data. There are several ways in which this could be achieved; one suggestion from me would be to integrate the different elements implied within Fig 1 for all health and vegetation indices, e.g. from states, through trends, to drivers and phases in turn, with results and discussion integrated in both cases.*

Response: As outlined above, the Results and Discussion is structured to emphasise the investigation of different chemical climate phases within the chemical climatology framework. The collation of health and vegetation impacts (i.e. collation of multiple chemical climates) into a single section would dilute this emphasis on the chemical climatology framework used to derive the statistics. Nevertheless, in recognition of comments on length made by both reviewers, we have undertaken some further editing and restructuring, and deleted some repetitious text, to produce a revised manuscript with better focus on the key findings. The most significant changes are summarised below:

- Section 3.1.3 Comparison between SOMO10/SOMO35 and higher threshold metrics: A new section (3.1.3) has been created to compare SOMO10 and SOMO35 with other commonly used metrics such as the EU target value (60 ppb threshold) and the WHO guideline value (50 ppb). Text describing contributions to SOMO10 and SOMO35 from high O_3 concentrations, and comparison with higher threshold metrics (EU target value (60 ppb) and WHO guideline (50 ppb), has been moved from Sections 3.1.1 and 3.1.2 to Section 3.1.3. The effect is to focus Sections 3.1.1 and 3.1.2 on the description and interpretation of temporal and spatial changes, respectively, in the chemical climate statistics and in the contribution to health impact from regional and hemispheric O_3. However, important information about the comparability between SOMO10/35 and other commonly used metrics is also retained. Addition of a new Table 1 (in response to a comment below), which contains average POD_Y across different soil textures, means that statement of these values in the text has been deleted. Specifically, deletion of the following:

P. 1887 ln 4: "For crops, there has not been a statistically significant change in PODY between 1990 and 2013. The 1990–2013 average (± SD) PODY 5 for potato was 2.7±1.3 mmol m^{-2}, which corresponds to a 3.4 % reduction in tuber weight. For wheat, the average PODY was 1.5 ± 1.1 mmol m^{-2} (equivalent to a 5.7 % average grain yield reduction)."

P. 1888 ln 10 "The average PODY for beech of 14.7±3.7 mmol m^{-2} 10 was four times the critical level (Mills et al., 2011c) and corresponds to a biomass reduction of 16. %. The average PODY for Scots pine was 27.0 ± 3.7 mmol m^{-2}."

In addressing a comment about repetition of statistics from figures and supplements from Reviewer #2, additional deletions are:

Section 3.1.2:P. 1884, line 2: The first paragraph has been deleted, as it contained no new information which couldn't be found in the figures and supplementary materials; the reader is directed to the additional information contained in the latter at the start of the next paragraph. The information from the last sentence of the paragraph has been incorporated into P. 1885 line 6:

Original text: "Elevated SOMO10 and SOMO35 values in 2008 (as also reported by Gauss et al. (2014a) 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)"

Amended text: "Elevated SOMO10 (6% above 2007-2013 average) and SOMO35 (67%) values in 2008 at Auchencorth (as also reported by Gauss et al. (2014a) 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)"

Section 3.2.2: P. 1891, line 12: The start of the paragraph has been amended to remove repetition of statistics from figures and supplementary materials.

Original text: "At Auchencorth, the 2007–2013 average tuber weight reduction for potato predicted by the calculated PODY (Fig. 10a) was 1.3 ± 0.5% (Table S4), and for wheat the average yield reduction was 3.7 ± 1.5% (Table S6). The LRTAP critical level for impact (Mills et al., 2011c) was only exceeded at this site in 2008 for wheat (5.04% yield reduction). Annual PODY for potato at Auchencorth were consistently lower than at Harwell, while, for wheat, PODY were higher at Auchencorth for 3 of the 7 years."

Amended text: "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., 2011) was only exceeded at this site in 2008 for wheat (5.04% yield reduction)."

P. 1893, line 5: The sentence specifying the exact greater proportion of beech and Scots pine POD_Y accumulated during July and August at Auchencorth has been deleted.

Reviewer 1 comment: *I would prefer to see key conclusions that are highlighted in the abstract and conclusions to be clearly supported in the body of the text. For example, 3.2.3 compares POD and AOT40 trends, but the latter are lost in supplementary material. Addition of AOT40 to the time trends in the main figures alongside the POD trends would provide much a clearer demonstration to the reader of this key finding. The authors also make reference to comparison with health guidelines based on 50ppb or 60ppb thresholds, and data to support an inferred difference in trends could usefully be presented.*

Response: We note that Reviewer #2 has commented that the information regarding comparison between SOMO10 and SOMO35 is there, but scattered across multiple sections. An additional section (3.1.3) has been added to more usefully present this comparison, and is partly derived from the relocation of statistics presented in other sections:

> **"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 (2014) 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."

A new Figure 14 has been added showing crop AOT40 between 1990 and 2013 at Harwell, and the Theil-Sen estimate of the trend. Reference to this figure has been added at P. 1894 ln 3, and reference to the POD_Y figure (8a) for comparison has been added at P1894 ln 5.

Reviewer 1 comment: *Soil moisture is an important limiting factor for stomatal ozone flux, but it is unclear to me from the paper how the SWP and PAW was determined for the two sites. No mention is made of direct measurements at the supersites or the met. sites, and so I assume this was done within the DO3SE model. However, if the values were modelled, this needs to be explained, and the important assumptions about soil characteristics that need to be made should be stated; were these different for the species to reflect the very different soil types on which they are likely to grow?. In passing, once this variable is included in any index it cannot be stated that a site is regionally representative, as soil characteristics may vary widely over short distances, and indeed are likely to be associated with different vegetation types. This limitation to the use of flux-based indices should be recognised in the paper.*

Response: Soil moisture (SWP and PAW) was modelled, based on the measured meteorological input data. The DO_3SE model can be run with four different soil textures that have different hydraulic properties that alter the extent of evaporation and hence SWP. The soil textures are sandy loam (soil texture classification = coarse), silt loam (medium coarse), loam (medium) and clay loam (fine). POD_Y was calculated using the loam (medium) soil texture in the original manuscript but in order to extend the conclusions of the analysis to other soil textures, statistics have now been calculated for all four soil types.

At Harwell, the magnitude of POD_Y varied between soil textures, but the pattern of accumulation was consistent. At Auchencorth, there was much less variation in POD_Y with soil texture than at Harwell, indicating soil moisture to have a less limiting influence. This additional analysis shows that the key conclusions from the derivation of these O_3 vegetation chemical climates were consistent across the four soil textures; namely that there was no trend in POD_Y for any vegetation type between 1990 and 2013 at Harwell and that this was due to non-O_3 factors (e.g. SWP) which reduce stomatal conductance during high O_3 episodes. Text has been changed as follows to emphasise that the conclusions from the paper are applicable across a range of soil textures:

- Table 1: To compare the sensitivity of POD_Y to soil texture at each site, a new table has been added which shows the average POD_Y of each vegetation type, for each soil texture, over the study periods at Harwell and Auchencorth. This has also resulted in the deletion of results sentences which duplicate information now found in Table 1. Specific deletions:

P. 1887 ln 5: "The 1990–2013 average (± SD) PODY 5 for potato was 2.7 ± 1.3 mmol m^{-2}, which corresponds to a 3.4 % reduction in tuber weight. For wheat, the average PODY was 1.5 ± 1.1 mmol m^{-2} (equivalent to a 5.7 % average grain yield reduction)."

P. 1888 ln 10:
Original text: "The average PODY for beech of 14.7 ± 3.7 mmol m^{-2} 10 was four times the critical level (Mills et al., 2011c) and corresponds to a biomass reduction of 16%. The average PODY for Scots pine was 27.0 ± 3.7 mmol m^{-2}. These PODY values are 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."

Amended Text: "The average POD_Y for beech (Table 1) was four times the critical level (Mills et al., 2011). 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."

Additional text:
P. 1874 ln 24: Addition of the following statement in the Methods that soil moisture was calculated from measured meteorological data within the DO_3SE model, and POD_Y was calculated for 4 soil textures.
"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)."

P. 1886 ln 24: Explanation that the statistics included in the figures and supplementary datasheets are for the loam soil texture.
"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 Sections 3.2.1 and 3.2.2."

P. 1887 ln 4: Introduction of Table 1 in the text.
"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."

- Discussion of the effect of soil moisture in limiting O_3 accumulation during high O_3 episodes has been modified as follows to state that this conclusion is consistent across different soil textures.

SWP during different concentration ranges have been changed to those calculated for clay loam soil texture. Clay loam had the highest SWP, i.e. lowest stomatal conductance limitation due to soil moisture, but during high O_3 concentrations, SWP was sufficiently low to limit stomatal conductance compared to more moderate O_3 concentrations. The limitation was even stronger for the other soil textures.

Amended paragraph: P. 1890 ln 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 (Bueker et al., 2012; LRTAP Convention, 2010). 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."

- P. 1891 ln 5: The proportion of hours when beech SWP was below the threshold for stomatal conductance limitation is now stated as the range for the different soil textures, and a summary sentence has been added to the end of the paragraph to emphasise consistency across soil textures.

Original text: "Between 2010 and 2013, on average 0 and 5 % of hourly SWP values in May and June, respectively, were below this value, compared with 38 and 28 % 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 10 the impact of O_3 on forests across Europe (Emberson et al., 2007)."

Amended text: "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."

- Insertion of text stating that variation in POD_Y between soil textures was less at Auchencorth, and the spatial difference between Auchencorth and Harwell were consistent across soil texture.

P. 1891 ln 12 "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."

- In the discussion of elevated POD_Y at Auchencorth during regional photochemical O_3 episodes, "across all soil textures" has been added at P. 1892 ln 5 and ln 13 and P. 1893 ln 12 and 18 to emphasise that the elevated POD_Y was calculated for all soil textures. To highlight the higher stomatal conductance at Auchencorth compared to Harwell, specific loam soil texture stomatal conductance values are used, and hence "for loam soil texture" has been added to P. 1892 ln 22 to make this clear.

- P. 1893 ln 3: The paragraph has been amended to reflect the range of percentage increases in beech and Scots pine POD_Y at Auchencorth compared to Harwell across the four soil textures.

Original text: "Between 2007 and 2013, Scots pine and beech PODY were on average 31% and 11% higher at Auchencorth compared to Harwell (Fig. 12a). These larger values were due to larger contributions from July and August at Auchencorth (Tables S10 and S12). On average, July and August contributed 7% and 5% more of the annual PODY at Auchencorth for beech (4% and 3% for Scots pine). In these months, higher temperatures at Harwell produced conditions which reduced stomatal conductance. For example, in 2007–2013 at Harwell, SWP was on average 59% higher in July and 82% higher in 10 August than at Auchencorth."

Amended text: "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."

Reviewer 1 comment: *There seem to be a range of different months used for analysis of trends and drivers for vegetation types. In particular, the results for trees should focus on a longer growing season compared to wheat and potato, for which only a limited period of crop development is considered. Furthermore, phenological timings which are under climatic control within DO3SE may also vary between years and show long-term trends, and this needs to be considered.*

Response: A range of different months were used for analysis according to the recommended methods by which the growing seasons were determined in LRTAP Convention (2010). LRTAP Convention (2010) is a mapping manual which sets out the most suitable method to calculate the impact of O_3 on vegetation, and hence is referenced throughout as the source of parameterisation. To make it clearer that this parameterisation extends to the calculation of the growing season, this has now been stated in the methods:

> P. 1874 ln 4: "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."

More information about the growing season is included in the response to comments by Reviewer #2.

Reviewer 1 comment: *The authors claim that the lack of trends in PODy variables is due to changes in nonozone factors, but there is no analysis of trends in the individual factors limiting stomatal conductance, or of conductance itself. On p18, they focus on differences between ozone concentration bins (over what period of the year is not specified) rather than trend analysis, and they also need to consider that SWP/PAW is a cumulative variable and its seasonal development may be linked directly to phonological changes.*

Response: Given that the calculation of stomatal conductance is derived in part by phenology and in part by the meteorological input data, analysis of trends in the non-O_3 factors would require trend analysis in these meteorological variables. The aim of this paper was to assess how O_3 impacts have responded to spatial and temporal changes to their state and drivers, rather than an analysis of climate change over the last 24 years.

In-depth trend analysis of meteorological variables would reduce the focus on the key O_3 findings of the paper, as requested in an earlier comment from this reviewer.

The focus on the POD_Y accumulated during different O_3 concentration bins (by definition within the growing season of the respective vegetation type) is highly relevant for policy, as it determines a) whether past efforts to control O_3 (and reduce the frequency of high O_3 episodes) has reduced POD_Y, and b) whether future mitigation strategies would be more effective in reducing vegetation impacts through control of high O_3 episodic concentrations, or more frequent, moderate concentrations. Having established that at Harwell there has been a shift to increasing contribution from moderate concentrations, and reduction in the frequency of elevated O_3 has not reduced POD_Y, other factors are considered to explain these trends. This structure maintains focus on key findings in relation to past and future O_3 impact mitigation. When considering the limiting effect of soil moisture on stomatal conductance, and hence on POD_Y, the 1990-2013 median SWP during different O_3 concentration bins is appropriate to demonstrate that high O_3 concentrations coincide with SWP that is substantially more limiting to stomatal conductance across the entirety of the 24 year period. For example (see P. 1890 ln 5 for the analysis to which this relates), between 1990 and 2002 (the first half of the Harwell study period), the average SWP during 60-65 ppb, 65-70 ppb and >70 ppb is lower than the median in 6, 7 and 6 of the 12 years respectively. That approximately half of the years in the first half of the study are below the median suggest that there has not been a trend in SWP of sufficient magnitude to prevent it from generally limiting stomatal conductance during high O_3 concentrations.

Reviewer 1 Technical corrections

Reviewer 1 comment: *Provide the full name the first time that any acronym is mentioned.*

Response: The full name of REVIHAAP has been added on first usage.

Reviewer 1 comment: *P5, l13. Don't you mean 'during the growing season', not annual?*

Response: The text has been amended in line with this recommendation.

Reviewer 1 comment: *P5, l16-17. I'm not clear where this comparison of measured and gridded modelling is presented.*

Response: Comparison between the POD_Y calculated in this study and those calculated previously using modelled input data is presented throughout the Results and Discussion. Specifically comparison is found at P. 1887 ln 11, P. 1888 ln 15, P. 1891 ln 10 and P. 1891 ln 17-26.

Reviewer 1 comment: *P6. L26. This May-July period is only a relevant comparison for wheat and potato, for the tree species a six-month accumulation period would be more relevant.*

Response: We have been consistent throughout the manuscript, including in the Methods when first described, in stating that the AOT40 calculated for comparison was that which is relevant for comparison with crops, i.e. wheat and potato. Contrasting trends between forest POD_Y and AOT40 is made through reference on P. 1894 ln 24 to forest-relevant AOT40 calculated previously (Gauss et al., 2014b) across the UK which has decreased in recent years compared to 2000, in contrast to the forest POD_Y values calculated in this study.

Reviewer 1 comment: *The ozone concentration bin diagrams might be clearer and easier for the reader to interpret with a smaller number of bins with cut-offs more clearly related to the key significant trends in the data.*

Response: We agree that a balance is required in the determination of concentration bin size between being small enough to capture trends at different concentration ranges, and being large enough to avoid so many bins that the resulting figure is difficult to interpret. For many of the impacts, there is a contrasting trend at Harwell in the contribution of moderate O_3 concentrations (increasing) and high O_3 concentrations (decreasing), and in between, there are a range of concentrations with no trend in contribution. The issue of aggregating concentrations to a smaller number of bins is that the distinction in these trends becomes blurred, and the point at which trends change is determined with ever decreasing precision. We evaluated that 5 ppb concentration ranges were the optimum bin size to compromise between precisely determining the trends in O_3 concentration distributions associated with impacts, and creating an interpretable figure.

Reviewer #2:

General comments

The authors have submitted an interesting manuscript focusing on trends and drivers of ozone concentrations and associated potential impacts on human health (SOMO35 and SOMO10) and vegetation (PODY and AOT40). The study is based on ozone measurements from two UK EMEP supersites, applying a chemical climatology framework. The results indicate that over the period 1990-2013 the relative importance of regional photochemical ozone production have decreased while the importance of hemispheric background concentrations have increased. However, the change in health and vegetation impact metrics differ depending on which metric and threshold is chosen.

Ozone is a key air pollutant and it is important to understand how much, and to which direction driving forces will affect ground-level ozone concentrations and their impacts on human health and vegetation. Thus the topic of this manuscript is highly relevant from a scientific and policy-related point of view. The study is comprehensive, well thought through and the manuscript is well written. I therefore suggest publication after minor revisions.

Specific comments

Reviewer 2 comment*: In the introduction and methodology section it is strongly emphasized that the study is based on a chemical climatology approach. When I read the manuscript I feel that this approach is somewhat lost in the result and discussion sections. To be consistent I suggest linking also the second part of the manuscript to the different steps deriving the chemical climate in a more clear way e.g. by more clearly describing different temporal and spatial phases in the chemical climate.*

Response: The same comment was made by Reviewer #1. Therefore please see above for our detailed response and actions on this comment.

Reviewer 2 comment: *The manuscript is long and especially the amount of text in the result section is heavy for many readers. Numbers that can be found in figures, previous sections or in the supplementary material is unnecessary to repeat and I suggest reducing e.g. the sections about the spatial differences between the two supersites (section 3.1.2 and 3.2.2). Also I think the manuscript could be improved by integrating results and discussion more.*

Response: Several repetitions of numbers found elsewhere within the manuscript and in figures have been omitted to reduce the length of the Results and Discussion section. As noted in the reviewer comment, these mainly occur in sections 3.1.2 and 3.2.2. The addition of the new Table 1 has also resulted in the deletion of text which now states that data are summarised in the new table. Specific actions and deletions to avoid repetition and reduce the length of the manuscript are detailed above in response to a similar comment by Reviewer #1.

The structure of each individual section is such that an overview of the chemical climate impact, state and drivers statistics is given first, in relation to the change in chemical climate phase being discussed (e.g. temporal at Harwell vs spatial between Auchencorth and Harwell). This structure, coupled with the changes resulting from the previous comment help to emphasise the steps in the chemical climatology framework used to undertake the analysis.

It is when these statistics are considered as a whole (i.e. the chemical climate) that insight is gained in terms of changing relative contribution from hemispheric vs regional processes. We think that the shortening of the results paragraphs as detailed above and in the response to a similar comment by Reviewer #1 helps to focus these paragraphs on communicating the key temporal and spatial trends in the statistics necessary to understand the discussion paragraphs that follow. In addition, text relating to the comparison of SOMO10/35 with the EU target values and WHO air quality guideline values has also been moved to a separate section (see below), and hence presentation of key statistical trends and discussion of their meaning have been moved into closer proximity.

Reviewer 2 comment: *Methods: A map with the two supersites would be appreciated. The ones in the supplementary material are very small.*

Response: A map has been added as Figure 2 showing the monitoring sites, and the Met Office stations from which meteorological data was used.

How come meteorology is not measures at the two supersites? Are the meteorological stations representative for the air quality supersites? Is soil moisture also measured?

Response: Meteorological measurements are made at the two supersites, but it was appropriate to use the UK Met Office station data which was more readily available and subject to documented quality control procedures (http://badc.nerc.ac.uk/data/ukmo-midas/ukmo_guide.html#2.1). It is noted that the on-site meteorology is available on request and is planned to be submitted to the Met Office WOW database in the near future.

The location of the Met Office stations are specified such that it is 'representative on a scale required for the station'. The meteorological stations used in this study all measure synoptic scale weather patterns, and therefore are contained within the category of Met Office station with the largest area of representativeness (up to tens of kilometres). The main stations used, Benson and Gogarbank, are 13 km and 14 km form Harwell and Auchencorth respectively, and were therefore considered to be representative of conditions at the supersites. Combining O_3 and meteorological data from different sites to calculate POD_Y has been done previously at EMEP sites in Sweden (Karlsson et al., 2007).

Harwell: Temperature, wind speed and wind direction are measured but data was only available back to 2005. As the full suite of meteorological parameters required to determine stomatal conductance were also not provided, it was considered more appropriate to use data from nearby stations.

Auchencorth: The full meteorological parameters required to derive stomatal conductance are measured. However Auchencorth is an ombotrophic bog, and not a site where the vegetation types would be directly grown. Hence it was more appropriate in the calculation of POD_Y to use meteorological data from the nearby Gogarbank station which has been located to maximise the representativeness of its observations, including areas within south-east Scotland where the vegetation types would be grown.

Reviewer 2 comment: *P. 1876, line 23: How can PODY decrease for potato after interpolation of missing data?*

Response: The time period over which potato POD_Y is accumulated is based on accumulated temperature after plant emergence (outlined in more detail below). When missing values are interpolated, the maximum accumulated temperature (and hence end of the growing season) is reached earlier. Whether an increase or decrease in POD_Y results from this change in growing season depends on whether the parameters excluded from the growing season or those interpolated produce conditions (O_3 concentration and those affecting stomatal conductance) more favourable for POD_Y accumulation. For 1993, the excluded time periods had conditions more conducive to POD_Y accumulation and hence after interpolation POD_Y decreased by 6%.

The key point of the comparison between interpolated and non-interpolated potato POD_Y is the magnitude of the difference, not the direction. This example had the largest number of missing values of any year (above the data capture threshold of 75%), and, after interpolation, the change in magnitude of POD_Y was small. This gives confidence that the POD_Y values calculated for the other years are not largely biased due to missing values.

Reviewer 2 comment: *Results and discussion: I find the comparison between different impact metrics very interesting and highly relevant in a policy context. The comparison between the vegetation impact metrics PODY and AOT40 is discussed in an own section (3.2.3) but for human health metrics the comparison with the WHO air quality guideline (50 ppb) and EU target value (60 ppb) is not as easy to find. Much information is there but spread out in different section. The manuscript would benefit if this information is assembled into one paragraph.*

Response: We agree that the manuscript would benefit if the results relevant to comparison between SOMO10/35 and higher threshold metrics were presented together. Hence a new section, '3.1.3 Comparison between SOMO10/SOMO35 and higher threshold metrics' has been added.

- The final section of 3.1.2, from P. 1885, ln24 has been moved to Section 3.1.3, as have sentences from P. 1880 line 26 and P. 1881 line 8, which show the proportion of SOMO10 and SOMO35 accumulated below the WHO air quality guideline (50 ppb).
- Additional text has been added for the corresponding values at Auchencorth.
- The new section is shown above in response to a comment by Reviewer #1 about the conclusions from comparison with higher threshold metrics being better highlighted in the main text.

Reviewer 2 comment: *P. 1879, line13-14: Why are these specific time periods chosen?*

Response: The purpose of the datasheets is to provide a summary of the chemical climate impact, state and drivers statistics. Including individual year statistics for Harwell would result in a datasheet with such a density of statistics that it would be difficult to draw useful information. Hence to reduce the number of statistics, they were averaged into 4-year blocks. The length of the averaging period was chosen as a balance between producing an average representative of the time period whilst avoiding the incorporation of any long-term trends.

Reviewer 2 comment: *Section 3.2.1: Has the timing and length of the growth period changed during the 24-year period? Please discuss if/how that could have influenced your results.*

In order for the calculations of POD_Y in this work to be comparable with those in previous studies, the timing and length of the growing season were all calculated based on the methods outlined in the LRTAP mapping manual (LRTAP Convention, 2010), and summarised individually below. Their application in this work can account for changes in the length and timing of the growing season resulting from long term changes in temperature, but does not account for changes in farming practices (e.g. sowing times for crops).

Wheat: POD_Y accumulation is based on accumulated temperature, and begins 200 °C.days before mid-anthesis, and ends 700 °C.days after. The wheat phenology function is at maximum between −200 °C.days and 100 °C.days, before decreasing.

Inter-annual variability and long-term changes in temperature are accounted for, and during each year the exact timing and length of the growing season changes. However, any changes in the timing of mid-anthesis, due to changes in sowing dates are not reflected. Changes in sowing dates could both increase and decrease POD_Y, and the exact change would be determined by the temperature, soil moisture, and radiation conditions during that particular year. For example, we conclude that during summertime O_3 episodes, plant conditions are often such that increased accumulation of O_3 due to higher concentrations is inhibited by reduced stomatal conductance. A trend towards earlier sowing dates would result in the POD_Y accumulation period occurring earlier in the year, which could increase POD_Y, due to the lower frequency of conditions which reduce stomatal conductance during the summer (e.g. low soil moisture), but could also decrease POD_Y due to lower temperatures earlier in the year which reduce stomatal conductance (zero conductance below 12 °C).

Any changes in the length and timing of the growing season will not change the main conclusions from the analysis. There has been a shift towards a larger contribution from hemispheric background concentrations in determining POD_Y compared to regional episodes, and this has not resulted in a decrease in vegetation impact because during regional O_3 episodes, stomatal conductance is often reduced, and hence additional O_3 accumulation cannot occur.

Potato: POD_Y accumulation is also based on accumulated temperature, and occurs for 1130 °C.days after plant emergence. It is recommended that day 146 (26th May/27th in a leap year), is used as the plant emergence date (LRTAP Convention, 2010). The phenology function increased until 330 °C.days before decreasing until the end of the growing season. The conclusions about using this accumulated temperature method for potato are the same as for wheat. Inter-annual variability and long-term changes in temperature are accounted for by changes in the phenology function, but changes in sowing date are not. A change in sow date could similarly result in an increase or decrease in POD_Y, depending on the particular plant conditions during the year.

Beech: POD_Y is accumulated across a fixed growing season, which is calculated using a latitude model. Long-term changes in temperature between 1990 and 2014 do not result in an extension or curtailment of the growing season, which would increase or decrease POD_Y respectively. LRTAP Convention (2010) concluded that the latitude model agreed well with ground observations from studies across Europe covering multiple years up to 2003.

Scots Pine: The growing season for Scots pine is determined by air temperature, and is accumulated throughout the year when temperature is above 0 °C. Changes to the growing season due to long-term changes in temperature are therefore reflected in the calculation of POD_Y.

Text has been added to the methods to give more information about the difference in growing season between the vegetation types:

> P. 1874 ln 4: "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."

Reviewer 2 Technical corrections:

Reviewer 2 comment: *P. 1871, line 19: write out the REVIHAAP acronym first time mentioned.*

Response: The text has been amended in line with this recommendation.

Reviewer 2 comment: *P. 1873, line16: space between NOx and*

Response: The space was omitted on conversion to the discussion paper format, and is present in the original manuscript.

Reviewer 2 comment: *P. 1877, line 19-21: difficult sentence, please rephrase. Can the paragraph about the trajectories be written more clearly?*

Response: We agree that this section could be better phrased. Text has been reordered to make it clearer earlier in the paragraph how air-mass back trajectories were used to link air-mass history to the state of the chemical climate, i.e. by grouping back trajectories based on their pathway and calculating the proportion of trajectories from each group during SOMO10/35 accumulation and non-accumulation days. The remainder of the paragraph contains specific detail of the clustering method used to achieve this.

> **Original text:** "Secondly, the association of the state with air-mass history was investigated using the 2920 4-day HYSPLIT air-mass back trajectories arriving every 3 hours at each site per year (Carslaw and Ropkins, 2013; Draxler and Rolph, 2013; R Core Development Team, 2008). The trajectories were grouped using Ward's linkage hierarchical cluster analysis, a clustering method that has been shown through simulations to perform effectively (Mangiameli et al., 1996)"
>
> **Amended text:** "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) were used (Carslaw and Ropkins, 2013; Draxler and Rolph, 2013; R Core Development Team, 2008), and grouped using Ward's linkage hierarchical cluster analysis which has been shown through simulations to perform effectively (Mangiameli et al., 1996)"

The final sentence of this paragraph (P. 1878, line 11) has been removed as it is now repetition of the first sentences of the amended text.

Reviewer 2 comment: *P. 1878, line 24: . . .ADs and NADs for SOMO10/35 and PODY?*

Response: Text has been amended to make clear that daily emissions estimates were compared on SOMO10/35 and POD_Y exceedances days.

> **Original text:** "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 ADs and NADs."
>
> **Amended text:** "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."

Reviewer 2 comment: *P. 1884, line 11: . . .representative of much of the rural west and north of the UK. . .*

Response: Text has been amended in line with the recommendation.

References used in response to reviewers:

Bueker, P., Morrissey, T., Briolat, A., Falk, R., Simpson, D., Tuovinen, J. P., Alonso, R., Barth, S., Baumgarten, M., Grulke, N., Karlsson, P. E., King, J., Lagergren, F., Matyssek, R., Nunn, A., Ogaya, R., Penuelas, J., Rhea, L., Schaub, M., Uddling, J., Werner, W., Emberson, L. D., 2012. DO3SE modelling of soil moisture to determine ozone flux to forest trees. Atmos. Chem. Phys. 12, 5537-5562.

Carslaw, D. C., Ropkins, K., 2013. openair: Open-source tools for the analysis of air pollution data. R package version 0.8-5.

Draxler, R. R., Rolph, G. D., 2013. HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

EEA, 2014. Overview of exceedances of EC ozone threshold values: April–September 2013. EEA technical report No 3/2014. European Environment Agency. http://www.eea.europa.eu/publications/air-pollution-by-ozone-across-1.

Emberson, L. D., Buker, P., Ashmore, M. R., 2007. Assessing the risk caused by ground level ozone to European forest trees: A case study in pine, beech and oak across different climate regions. Environ. Pollut. 147, 454-466.

Gauss, M., Semeena, V., Benedictow, A., Klein, H., 2014a. Transboundary air pollution by main pollutants (S, N, Ozone) and PM: The United Kingdom. MSC-W Data Note 1/2014. http://emep.int/publ/reports/2014/Country_Reports/report_GB.pdf.

Gauss, M., Semeena, V., Benedictow, A., Klein, H., 2014b. Transboundary air pollution by main pollutants (S, N, Ozone) and PM: The European Union. MSC-W Data Note 1/2014. http://emep.int/publ/reports/2014/Country_Reports/report_EU.pdf.

Karlsson, P. E., Tang, L., Sundberg, J., Chen, D., Lindskog, A., Pleijel, H., 2007. Increasing risk for negative ozone impacts on vegetation in northern Sweden. Environ. Pollut. 150, 96-106.

LRTAP Convention, 2010. In: Mills, G., et al. (Eds.). Chapter 3 of the LRTAP Convention Manual of Methodologies for Modelling and Mapping Effects of Air Pollution. Available at: http://icpvegetation.ceh.ac.uk/.

Malley, C. S., Braban, C. F., Heal, M. R., 2014. The application of hierarchical cluster analysis and non-negative matrix factorization to European atmospheric monitoring site classification. Atmos. Res. 138, 30-40.

Mangiameli, P., Chen, S. K., West, D., 1996. A comparison of SOM neural network and hierarchical clustering methods. Eur. J. Oper. Res. 93, 402-417.

Mills, G., Pleijel, H., Braun, S., Bueker, P., Bermejo, V., Calvo, E., Danielsson, H., Emberson, L., Gonzalez Fernandez, I., Gruenhage, L., Harmens, H., Hayes, F., Karlsson, P.-E., Simpson, D., 2011. New stomatal flux-based critical levels for ozone effects on vegetation. Atmos. Environ. 45, 5064-5068.

R Core Development Team, 2008. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL http://www.R-project.org.

REVIHAAP, 2013. Review of evidence on health aspects of air pollution – REVIHAAP Project technical report. World Health Organization (WHO) Regional Office for Europe, Bonn. http://www.euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf.

Marked-up version of revised manuscript:

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

Christopher S. Malley[1,2], Mathew R. Heal[1], Gina Mills[3] and Christine F. Braban[2]

[1] {School of Chemistry, University of Edinburgh, Edinburgh, UK}

[2] {NERC Centre for Ecology & Hydrology, Penicuik, UK}

[3] {NERC Centre for Ecology & Hydrology, Environment Centre Wales, Bangor, UK}

Correspondence to: C.S Malley (C.Malley@sms.ed.ac.uk)

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., ~~2014b~~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 ~~1~~2, and outlined in Malley et al (~~2014b~~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., ~~2014a~~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 ~~REVIHAAP~~ Review of evidence on health aspects of air pollution (REVIHAAP, 2013) ~~review~~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, ~~2014a~~2014b). For the vegetation impact the contrast is between the POD_Y metric and the concentration-based crop AOT40 metric, the ~~annual~~ 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 ~~1~~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 ~~1~~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., ~~2014a~~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., ~~2014a~~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~~, 1~~ 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 ~~using~~by grouping back trajectories based on the ~~2920~~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 ~~every~~at 3 ~~hours at each site~~hour intervals (2920 trajectories per year) (Draxler and Rolph, 2013;Carslaw and Ropkins, 2013;R Core Development Team, 2008)~~. The trajectories~~ were grouped using Ward's linkage hierarchical cluster analysis~~, a clustering method that~~ 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):

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

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'. ~~The proportion of air masses from each cluster on ADs and NADs was compared, as well as the proportion of trajectories from each cluster during the AOT40 growing season.~~

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 ~~1~~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 ~~2-12~~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 ~~2~~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 ~~2~~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 ~~3~~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 ~~3~~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 ~~4~~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 ~~4a~~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). ~~In 2010-2013, on average 91% of the SOMO10 was accumulated on days with maximum 8-h O_3 concentrations below the WHO air quality~~

~~guideline of 50 ppb, compared to 76% in 1990-1993 (Table S1).~~ 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 ~~4b~~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}). ~~ADs with O_3 concentrations below the WHO air quality guideline of 50 ppb contributed on average 66% to SOMO35 in 2010-2013 compared to 38% in 1990-1993 (Table S1).~~

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 ~~5~~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 ~~6~~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 ~~2~~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 ~~6~~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, ~~2014b~~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)

~~For the period 2007-2013, annual SOMO10 values at Auchencorth ranged between 8137 and 9111 ppb.d (Figure 2), and was accumulated on 360-366 days y^{-1} (Table S2). The largest seasonal contribution to SOMO10 was in spring (31-35%), with similar, smaller contributions in summer, autumn and winter (Figure 3). Annual SOMO35 values ranged between 673 and 1379 ppb.d, accumulated on 123-166 days y^{-1}. Spring contributed a greater proportion to SOMO35 (63-78%) and to SOMO35 ADs (53-64%) than this season contributed to SOMO10 and SOMO10 ADs; summer was the second largest seasonal contributor to both SOMO35 statistics. In 2008 SOMO10 and SOMO35 were elevated by 6% and 67% above their 2007-2013 averages.~~

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 ~~3~~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 ~~5~~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 ~~6~~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~~, timing and severity~~ (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, ~~EEA~~ 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 (~~2014a~~EEA, 2014b)~~ reported that only 19 days were recorded when at least 1 of the 81 UK sites had an exceedance of the 60 ppb EU target value and the majority of these days occurred in summer.~~. 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 (~~2014a~~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 ~~7~~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~~. The 1990-2013 average (± SD) POD_Y for potato was 2.7 ± 1.3 mmol m^{-2}, which corresponds to a 3.4% reduction in tuber weight. For wheat, the average POD_Y was 1.5 ± 1.1 mmol m^{-2} (equivalent to a 5.7% average grain yield reduction).~~, 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 ~~8~~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 ~~9~~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 ~~8~~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 ~~7~~8). The average POD_Y for beech ~~of 14.7 ± 3.7 mmol m^{-2}~~(Table 1) was four times the critical level (Mills et al., 2011c). Beech and ~~corresponds to a biomass reduction of 16.2%. The average POD_Y for~~ Scots pine ~~was 27.0 ± 3.7 mmol m^{-2}. These~~ PODy values ~~are~~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 ~~9c~~10c and ~~9d~~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 ~~8~~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.~~39 ± 0.93~~50 ± 1.32 MPa, −1.~~37~~14 ± 0.93 MPa and −1.~~75 ± 1.40~~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 ~~cutoff~~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 ~~± 0.32~~ MPa~~). Reduction~~ 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 ~~9b~~10b). This is due to a later growing season compared ~~to~~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. ~~Between~~ 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 ~~5~~0-9% of hourly SWP values in May and June, respectively, were below this value, compared with ~~38~~23-51% and ~~28~~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)

At Auchencorth, the 2007-2013 average tuber weight reduction for potato predicted by the calculated POD_Y (Figure 10a) was 1.3 ± 0.5% (Table S4), and for wheat the average yield reduction was 3.7 ± 1.5% (Table S6).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). Annual POD_Y for potato at Auchencorth were consistently lower than at Harwell, while, for wheat, POD_Y were higher at Auchencorth for 3 of the 7 years. 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 10b11b 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 11a12a). 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 11b12b). 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 ~~31~~27-37% and ~~11%~~5-19%% higher at Auchencorth compared to Harwell (Table 1 and Figure ~~12a~~13a). These larger values were due to larger contributions from July and August at Auchencorth (Tables S10 and S12). ~~On average, July and August contributed 7% and 5% more of the annual POD_Y at Auchencorth for beech (4% and 3% for Scots pine).~~ 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 ~~12b~~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 ~~12c~~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 ~~12b~~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.

Acknowledgements

C. S. Malley acknowledges the University of Edinburgh School of Chemistry, the NERC Centre for Ecology & Hydrology (NERC-CEH studentship funding project no. NEC04544) and the UK Department for Environment, Food and Rural Affairs (Defra, Grant no. AQ0647) for funding. Defra contractors Ricardo-AEA, Bureau Veritas and NERC Centre for Ecology

& Hydrology and their field teams are acknowledged for operating the UK EMEP Supersites. Particular acknowledgement goes to Dr Mhairi Coyle for valuable discussion regarding AOT40 calculation, and to Professor David Fowler for insightful discussion regarding POD_Y vegetation assessment and for helpful guidance on the policy relevance of this work .

References

Abbatt, J., George, C., Melamed, M., Monks, P., Pandis, S., and Rudich, Y.: New Directions: Fundamentals of atmospheric chemistry: Keeping a three-legged stool balanced, Atmos. Environ., 84, 390-391, 2014.

Angus Smith, R.: Air and Rain: The Beginnings of a Chemical Climatology, Longmans, Green and co., London, 1872.

AQEG: Ozone in the United Kingdom: Air Quality Expert Group, Defra Publications, London. http://www.defra.gov.uk/environment/quality/air/airquality/publications/ozone/documents/aqeg-ozone-report.pdf, 2009.

Bueker, P., Morrissey, T., Briolat, A., Falk, R., Simpson, D., Tuovinen, J. P., Alonso, R., Barth, S., Baumgarten, M., Grulke, N., Karlsson, P. E., King, J., Lagergren, F., Matyssek, R., Nunn, A., Ogaya, R., Penuelas, J., Rhea, L., Schaub, M., Uddling, J., Werner, W., and Emberson, L. D.: DO3SE modelling of soil moisture to determine ozone flux to forest trees, Atmos. Chem. Phys., 12, 5537-5562, 2012.

Carslaw, D. C., and Ropkins, K.: openair: Open-source tools for the analysis of air pollution data. R package version 0.8-5, 2013.

Coyle, M., Smith, R. I., Stedman, J. R., Weston, K. J., and Fowler, D.: Quantifying the spatial distribution of surface ozone concentration in the UK, Atmos. Environ., 36, 1013-1024, 2002.

Coyle, M., Fowler, D., and Ashmore, M.: New directions: Implications of increasing tropospheric background ozone concentrations for vegetation, Atmos. Environ., 37, 153-154, 2003.

Derwent, R., Manning, A., Simmonds, P., Gerard Spain, T., and O'Doherty, S.: Analysis and interpretation of 25 years of ozone observations at the Mace Head Atmospheric Research Station on the Atlantic Ocean coast of Ireland from 1987 to 2012, Atmos. Environ., 80, 361-368, 2013.

Draxler, R. R., and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD., 2013.

Eaton, S., and Stacey, B.: QA/QC Data Ratification Report for the Automatic Urban and Rural Network, October-December 2011, and Annual Report 2011. AEAT/ENV/R/3284 Issue 1. Contract Report to the Department for Environment, Food and Rural Affairs. AEA. http://uk-air.defra.gov.uk/assets/documents/reports/cat05/1207040912_AURN_2011_Q4_Issue_1.pdf, 2012.

EEA: EU emission inventory report 1990-2012 under the UNECE Convention on long-range transboundary air pollution (LRTAP). EEA technical report No 12/2014. European Environment Agency. http://www.eea.europa.eu/publications/eu-emission-inventory-report-lrtap, 2014a.

EEA: Overview of exceedances of EC ozone threshold values: April–September 2013. EEA technical report No 3/2014. European Environment Agency. http://www.eea.europa.eu/publications/air-pollution-by-ozone-across-1, 2014b.

Emberson, L. D., Ashmore, M. R., Cambridge, H. M., Simpson, D., and Tuovinen, J. P.: Modelling stomatal ozone flux across Europe, Environ. Pollut., 109, 403-413, 2000.

Emberson, L. D., Buker, P., and Ashmore, M. R.: Assessing the risk caused by ground level ozone to European forest trees: A case study in pine, beech and oak across different climate regions, Environ. Pollut., 147, 454-466, 2007.

EMEP: Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 1/2014. European Monitoring and Evaluation Programme. http://emep.int/publ/reports/2014/EMEP_Status_Report_1_2014.pdf, 2014.

Fuhrer, J., Skarby, L., and Ashmore, M. R.: Critical levels for ozone effects on vegetation in Europe, Environ. Pollut., 97, 91-106, 1997.

Gauss, M., Semeena, V., Benedictow, A., and Klein, H.: Transboundary air pollution by main pollutants (S, N, Ozone) and PM: The United Kingdom. MSC-W Data Note 1/2014. http://emep.int/publ/reports/2014/Country_Reports/report_GB.pdf, 2014.

Guerreiro, C. B. B., Foltescu, V., and de Leeuw, F.: Air quality status and trends in Europe, Atmos. Environ., 98, 376-384, 2014.

Heal, M. R., Heaviside, C., Doherty, R. M., Vieno, M., Stevenson, D. S., and Vardoulakis, S.: Health burdens of surface ozone in the UK for a range of future scenarios, Environ. Int., 61, 36-44, 2013.

Jenkin, M.: Investigation of an oxidant-based methodology for AOT40 exposure assessment in the UK, Atmos. Environ., 94, 332-340, 2014.

Jenkin, M. E.: Trends in ozone concentration distributions in the UK since 1990: Local, regional and global influences, Atmos. Environ., 42, 5434-5445, 2008.

Karlsson, P. E., Tang, L., Sundberg, J., Chen, D., Lindskog, A., and Pleijel, H.: Increasing risk for negative ozone impacts on vegetation in northern Sweden, Environ. Pollut., 150, 96-106, 2007.

Kaufman, L., and Rousseeuw, P. J.: Finding Groups in Data: An Introduction to ClusterAnalysis. Wiley, New York, Wiley, New York, 1990.

Klingberg, J., Engardt, M., Uddling, J., Karlsson, P. E., and Pleijel, H.: Ozone risk for vegetation in the future climate of Europe based on stomatal ozone uptake calculations, Tellus A, 63, 174-187, 2011.

Klingberg, J., Engardt, M., Karlsson, P. E., Langner, J., and Pleijel, H.: Declining ozone exposure of European vegetation under climate change and reduced precursor emissions, Biogeosciences, 11, 5269-5283, 2014.

Kuhlbusch, T., Quincey, P., Fuller, G., Kelly, F., Mudway, I., Viana, M., Querol, X., Alastuey, A., Katsouyanni, K., Weijers, E., Borowiak, A., Gehrig, R., Hueglin, C., Bruckmann, P., Favez, O., Sciare, J., Hoffmann, B., EspenYttri, K., Torseth, K., Sager, U., Asbach, C., and Quass, U.: New Directions: The future of European urban air quality monitoring, Atmos. Environ., 87, 258-260, 2014.

Lee, J. D., Lewis, A. C., Monks, P. S., Jacob, M., Hamilton, J. F., Hopkins, J. R., Watson, N. M., Saxton, J. E., Ennis, C., Carpenter, L. J., Carslaw, N., Fleming, Z., Bandy, B. J., Oram, D. E., Penkett, S. A., Slemr, J., Norton, E., Rickard, A. R., Whalley, L. K., Heard, D. E., Bloss, W. J., Gravestock, T., Smith, S. C., Stanton, J., Pilling, M. J., and Jenkin, M. E.: Ozone photochemistry and elevated isoprene during the UK heatwave of August 2003, Atmos. Environ., 40, 7598-7613, 2006.

LRTAP Convention: In: Mills, G., et al. (Eds.). Chapter 3 of the LRTAP Convention Manual of Methodologies for Modelling and Mapping Effects of Air Pollution. Available at: http://icpvegetation.ceh.ac.uk/. 2010.

Malley, C. S., Braban, C. F., and Heal, M. R.: New Directions: Chemical climatology and assessment of atmospheric composition impacts., Atmos. Environ., 87, 261-264, 2014a.

Malley, C. S., Braban, C. F., and Heal, M. R.: The application of hierarchical cluster analysis and non-negative matrix factorization to European atmospheric monitoring site classification., Atmos. Res., 138, 30-40, 2014b.

Mangiameli, P., Chen, S. K., and West, D.: A comparison of SOM neural network and hierarchical clustering methods, Eur. J. Oper. Res., 93, 402-417, 1996.

Mareckova, K., Wankmueller, R., Whiting, R., and Pinterits, M.: Review of emission data reported under the LRTAP Convention and NEC Directive, Stage 1 and 2 review, Review of emission inventories from shipping, Status of Gridded and LPS data, EEA and CEIP technical report, 1/2013, ISBN 978-3-99004-248-9. Available at: http://www.ceip.at/review-of-inventories/review-2013/, 2013.

Mills, G., Hayes, F., Norris, D., Hall, J., Coyle, M., Cambridge, H., Cinderby, S., Abbott, J., Cooke, S., and Murrells, T.: Impacts of Ozone Pollution on Food Security in the UK: a Case Study for Two Contrasting Years, 2006 and 2008. Defra contract AQ0816, London., 2011a.

Mills, G., Hayes, F., Simpson, D., Emberson, L., Norris, D., Harmens, H., and Bueker, P.: Evidence of widespread effects of ozone on crops and (semi-)natural vegetation in Europe (1990-2006) in relation to AOT40-and flux-based risk maps, Global Change Biol., 17, 592-613, 2011b.

Mills, G., Pleijel, H., Braun, S., Bueker, P., Bermejo, V., Calvo, E., Danielsson, H., Emberson, L., Gonzalez Fernandez, I., Gruenhage, L., Harmens, H., Hayes, F., Karlsson, P.-E., and Simpson, D.: New stomatal flux-based critical levels for ozone effects on vegetation, Atmos. Environ., 45, 5064-5068, 2011c.

Munir, S., Chen, H., and Ropkins, K.: Quantifying temporal trends in ground level ozone concentration in the UK, Sci. Total Environ., 458, 217-227, 2013.

Parrish, D. D., Law, K. S., Staehelin, J., Derwent, R., Cooper, O. R., Tanimoto, H., Volz-Thomas, A., Gilge, S., Scheel, H. E., Steinbacher, M., and Chan, E.: Lower tropospheric ozone at northern midlatitudes: Changing seasonal cycle, Geophys. Res. Lett., 40, 1631-1636, 2013.

R Core Development Team: R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, URL http://www.R-project.org., 2008.

REVIHAAP: Review of evidence on health aspects of air pollution – REVIHAAP Project technical report. World Health Organization (WHO) Regional Office for Europe, Bonn. http://www.euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf, 2013.

RoTAP: Review of Transboundary Air pollution: Acidification, Eutrophication, Ground Level Ozone and Heavy metals in the UK. Contract Report to the Department for Environment, Food and Rural Affairs. Centre for Ecology and Hydrology. http://www.rotap.ceh.ac.uk/sites/rotap.ceh.ac.uk/files/CEH%20RoTAP.pdf, 2012.

Schmale, J., van Aardenne, J., and von Schneidemesser, E.: New Directions: Support for integrated decision-making in air and climate policies – Development of a metrics-based information portal, Atmos. Environ., 90, 146-148, 2014.

Simpson, D., Ashmore, M. R., Emberson, L., and Tuovinen, J. P.: A comparison of two different approaches for mapping potential ozone damage to vegetation. A model study, Environ. Pollut., 146, 715-725, 2007.

Simpson, D., Benedictow, A., Berge, H., Bergstrom, R., Emberson, L. D., Fagerli, H., Flechard, C. R., Hayman, G. D., Gauss, M., Jonson, J. E., Jenkin, M. E., Nyiri, A., Richter, C., Semeena, V. S., Tsyro, S., Tuovinen, J. P., Valdebenito, A., and Wind, P.: The EMEP MSC-W chemical transport model - technical description, Atmos. Chem. Phys., 12, 7825-7865, 2012.

Stedman, J. R., and Kent, A. J.: An analysis of the spatial patterns of human health related surface ozone metrics across the UK in 1995, 2003 and 2005, Atmos. Environ., 42, 1702-1716, 2008.

Torseth, K., Aas, W., Breivik, K., Fjaeraa, A. M., Fiebig, M., Hjellbrekke, A. G., Myhre, C. L., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009, Atmos. Chem. Phys., 12, 5447-5481, 2012.

UK Meteorological Office: Met Office Integrated Data Archive System (MIDAS) Land and Marine Surface Stations Data (1853-current), [Internet]. NCAS British Atmospheric Data Centre, 2014. Available from http://badc.nerc.ac.uk/view/badc.nerc.ac.uk__ATOM__dataent_ukmo-midas, 2012.

Vieno, M., Dore, A. J., Stevenson, D. S., Doherty, R., Heal, M. R., Reis, S., Hallsworth, S., Tarrason, L., Wind, P., Fowler, D., Simpson, D., and Sutton, M. A.: Modelling surface ozone during the 2003 heat-wave in the UK, Atmos. Chem. Phys., 10, 7963-7978, 2010.

WHO: Air Quality Guidelines. Global update 2005. Particulate matter, ozone, nitrogen dioxide and sulfur dioxide., World Health Organisation Regional Office for Europe, Copenhagen. ISBN 92 890 2192
6. http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf?ua=1, 2006.

Wilson, R. C., Fleming, Z. L., Monks, P. S., Clain, G., Henne, S., Konovalov, I. B., Szopa, S., and Menut, L.: Have primary emission reduction measures reduced ozone across Europe? An analysis of European rural background ozone trends 1996-2005, Atmos. Chem. Phys., 12, 437-454, 2012.

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).

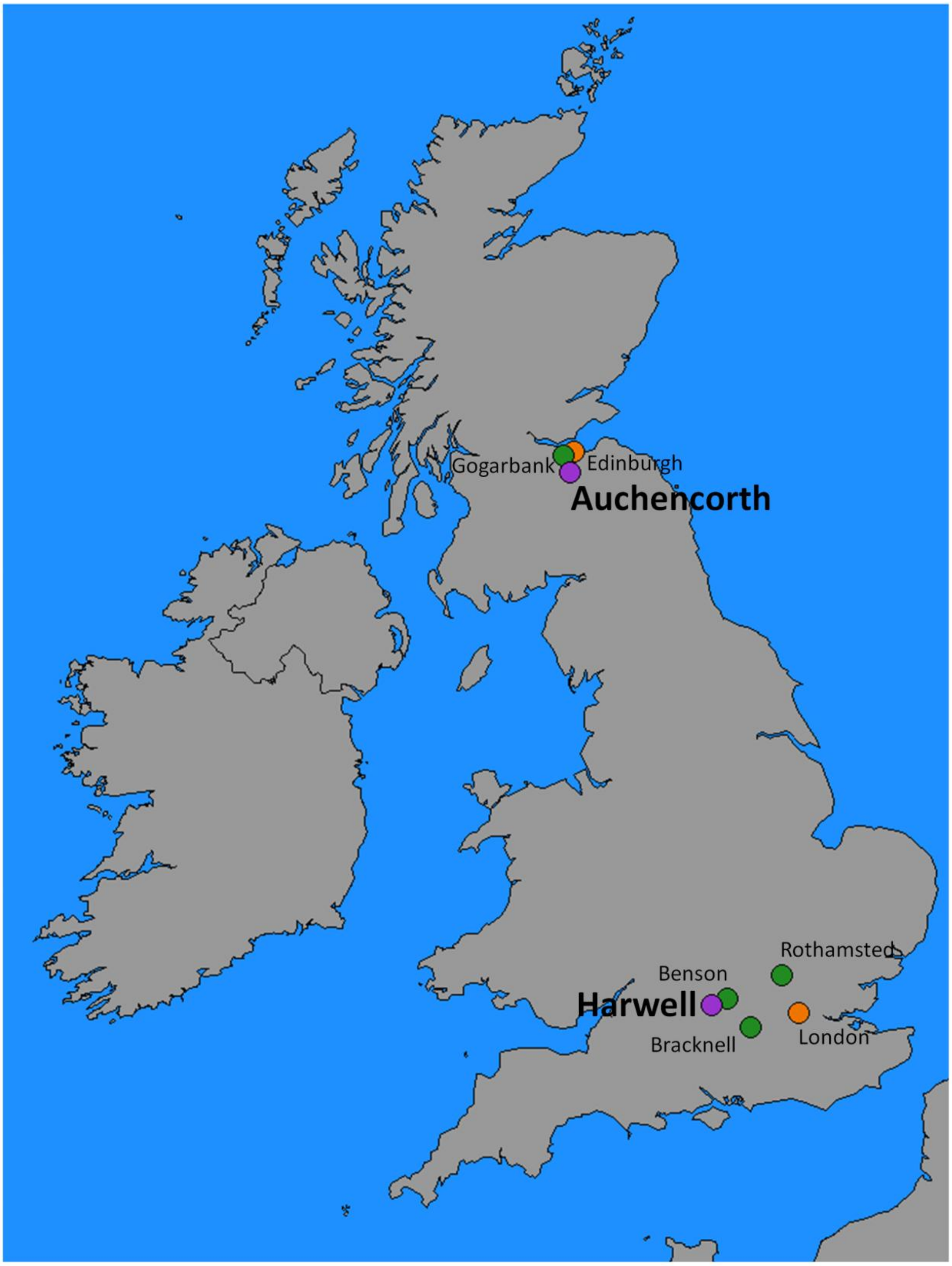

Figure 2: Practical steps for derivation of a chemical climate. The impact of premature mortality associated with short-term exposure to O_3 is used as an example. Text in the chemical climate datasheets are coloured the same as the step which gave rise to the statistic. The detail of application of 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 ~~2~~3: Human health relevant exposure to O_3 at Harwell (1990-2013) and Auchencorth (2007-2013), as characterised by the SOMO10 and SOMO35 metrics.

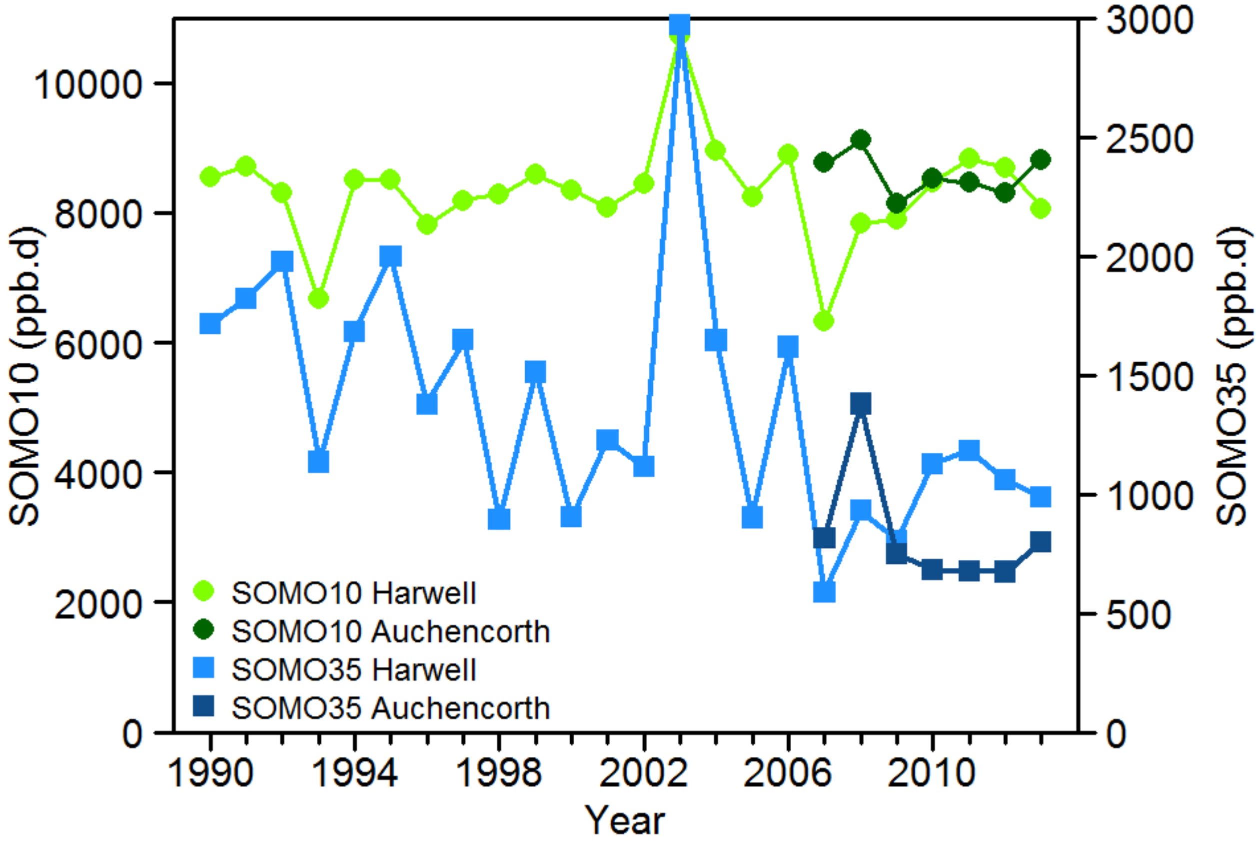

Figure ~~3~~4: Relative annual contributions from spring (MAM) and summer (JJA) to (a) SOMO10 and (b) SOMO35.

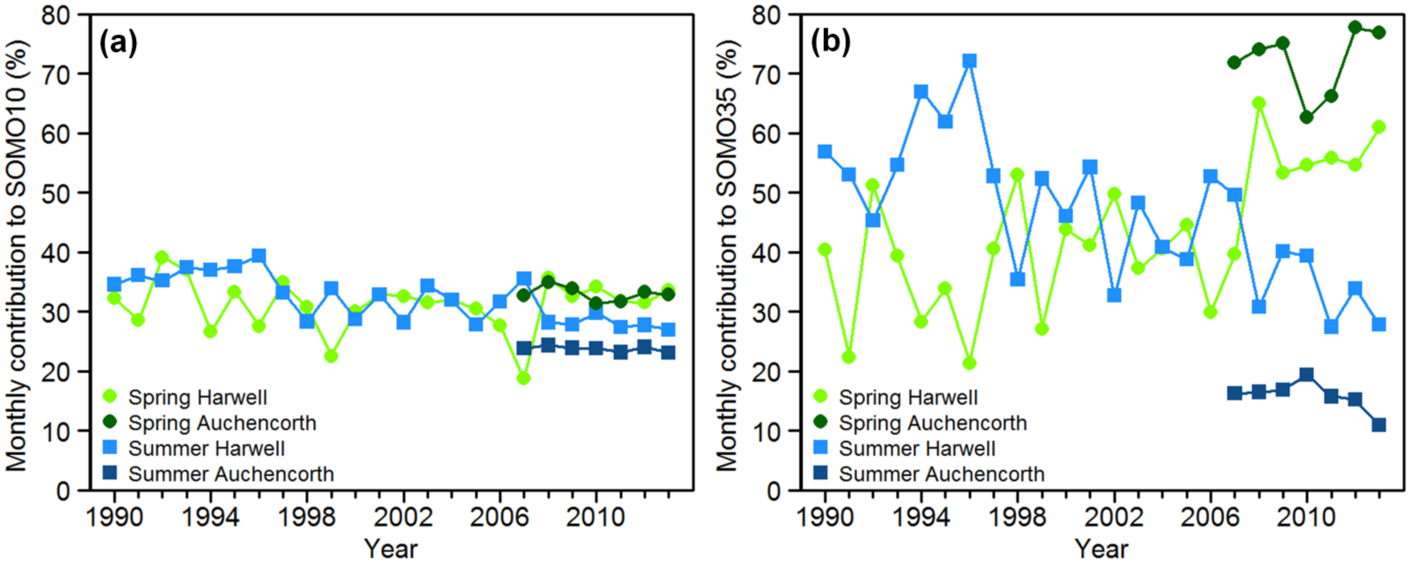

Figure 45: Relative annual contributions to (a) SOMO10 and (b) SOMO35 at Harwell from different O_3 concentration bins. Concentrations are separated into thirteen 5 ppb bins spanning daily maximum 8-h mean O_3 concentrations between 10 ppb and >70ppb. Note: these concentration bins are contributing to a decreasing long-term trend in SOMO35 and to a constant trend in SOMO10, as illustrated in Figure 2.

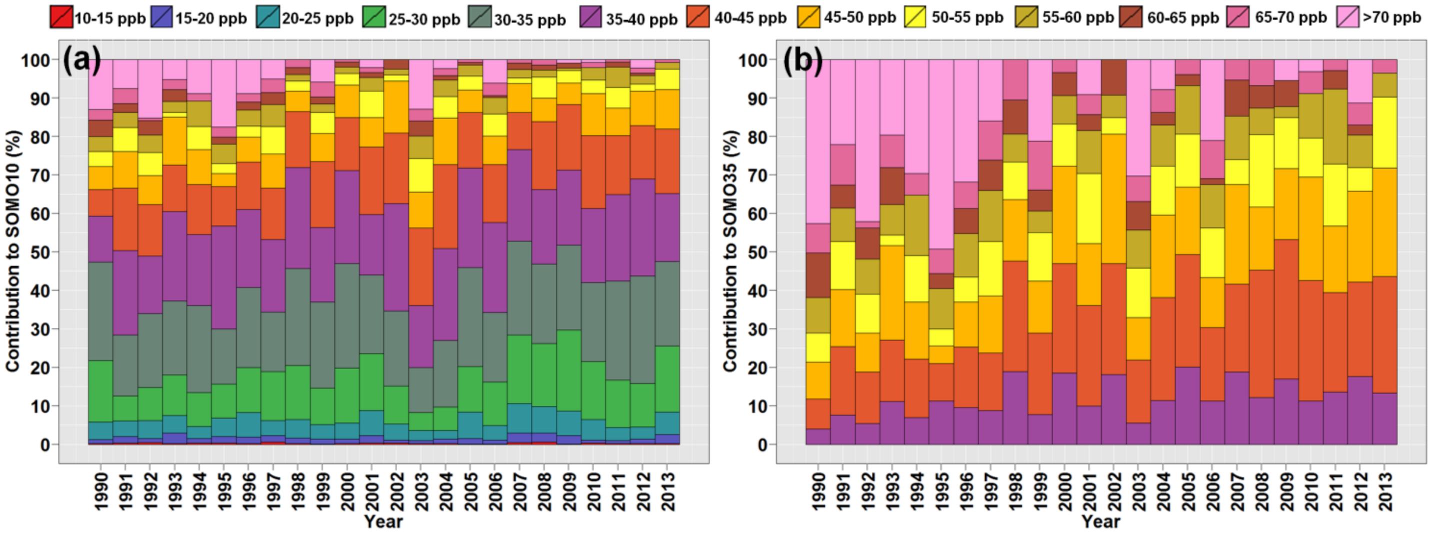

Figure ~~5~~6: Amplitude of the diurnal O_3, NO_2 and NO cycles at Harwell and Auchencorth during SOMO35 accumulation days (ADs).

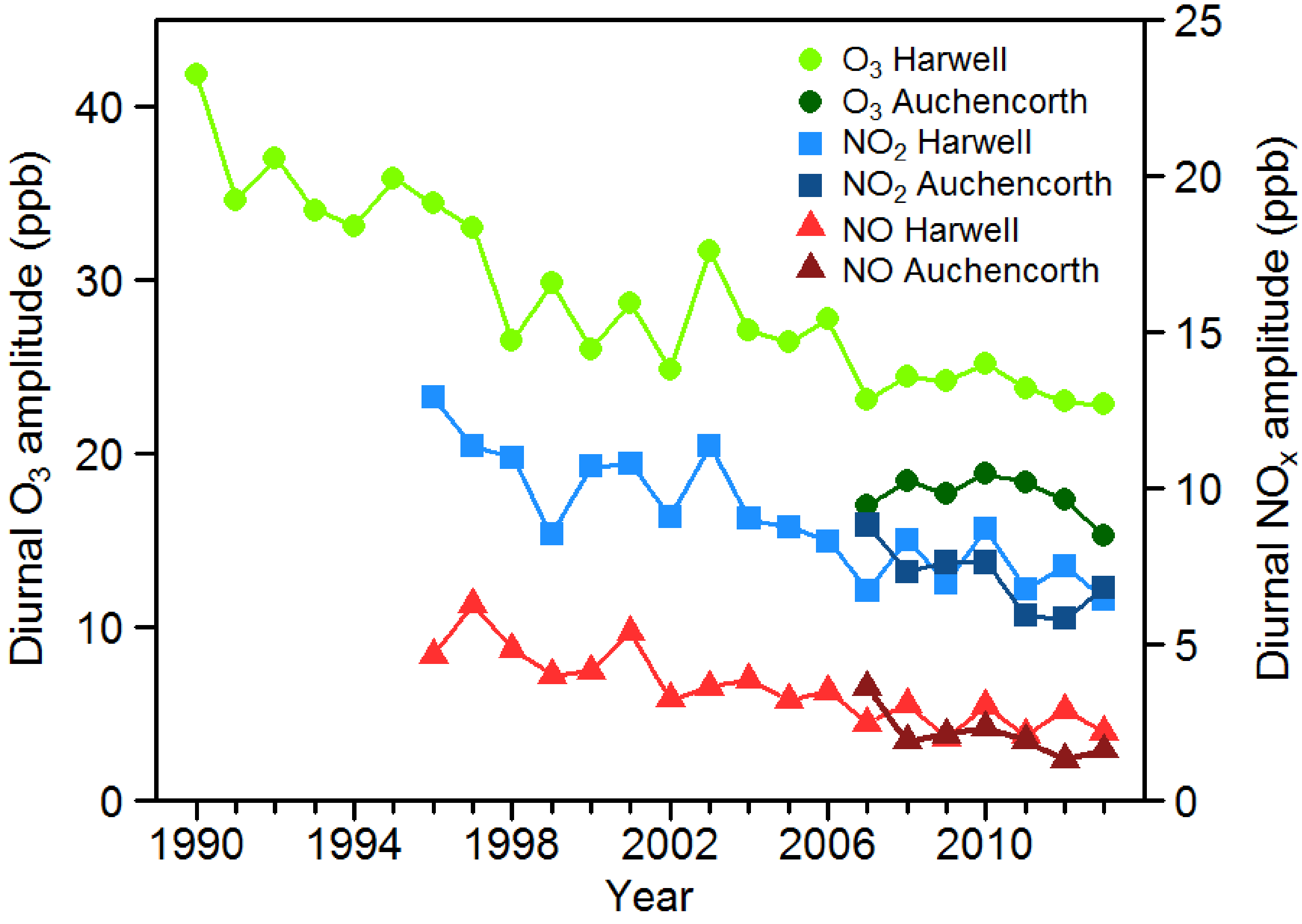

Figure 67: Estimate of the hourly European NO_x emissions emitted from the EMEP 0.5° grids over which 96-h back trajectories passed prior to arrival at Harwell and Auchencorth for SOMO35 accumulation days (ADs) and non-accumulation days (NADs).

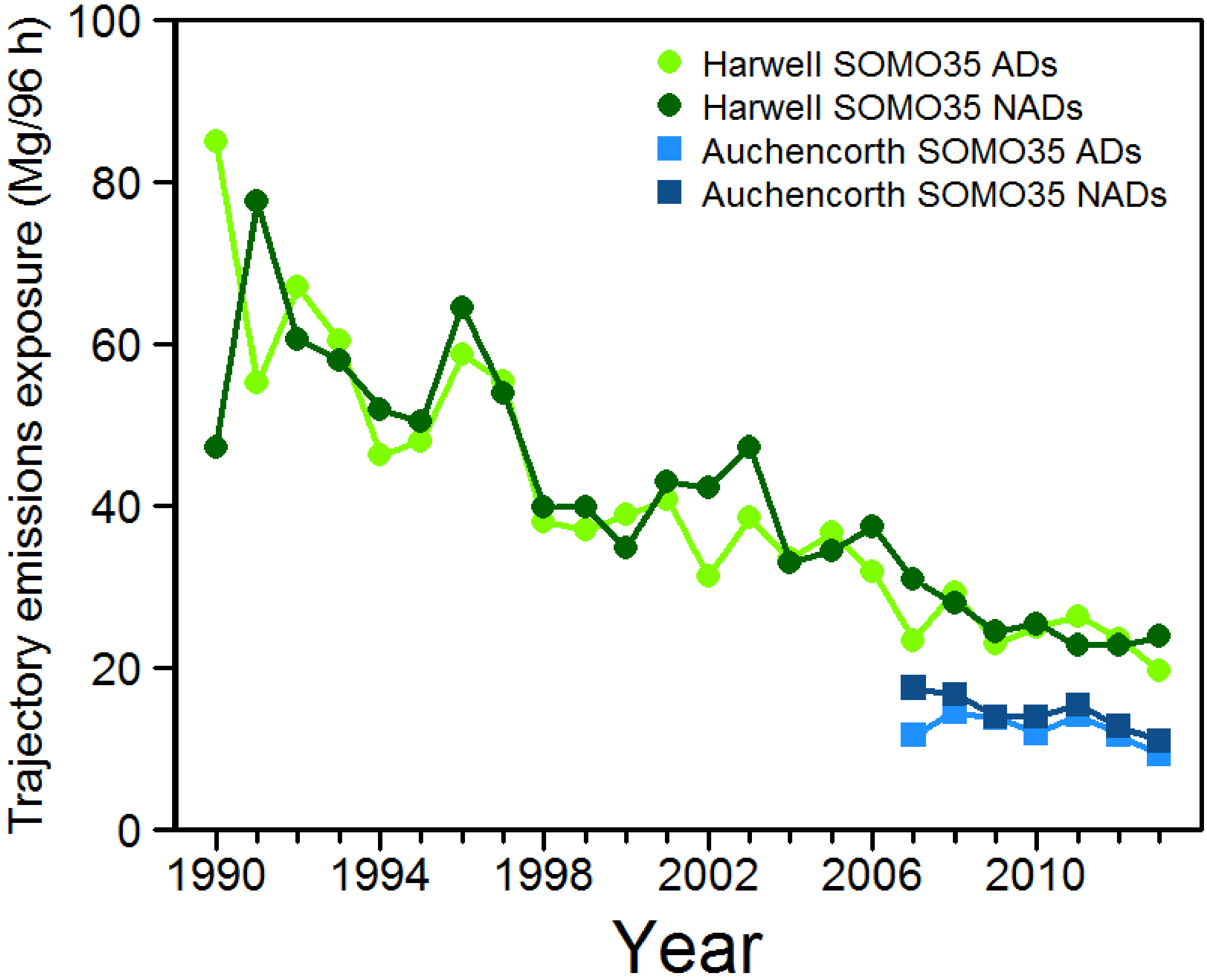

Figure ~~7~~8: Impact of O_3 characterised by the POD_Y metric (and associated response) for (a) wheat (grain yield reduction) and potato (tuber weight reduction), and (b) beech (biomass reduction) and Scots pine at Harwell between 1990 and 2013.

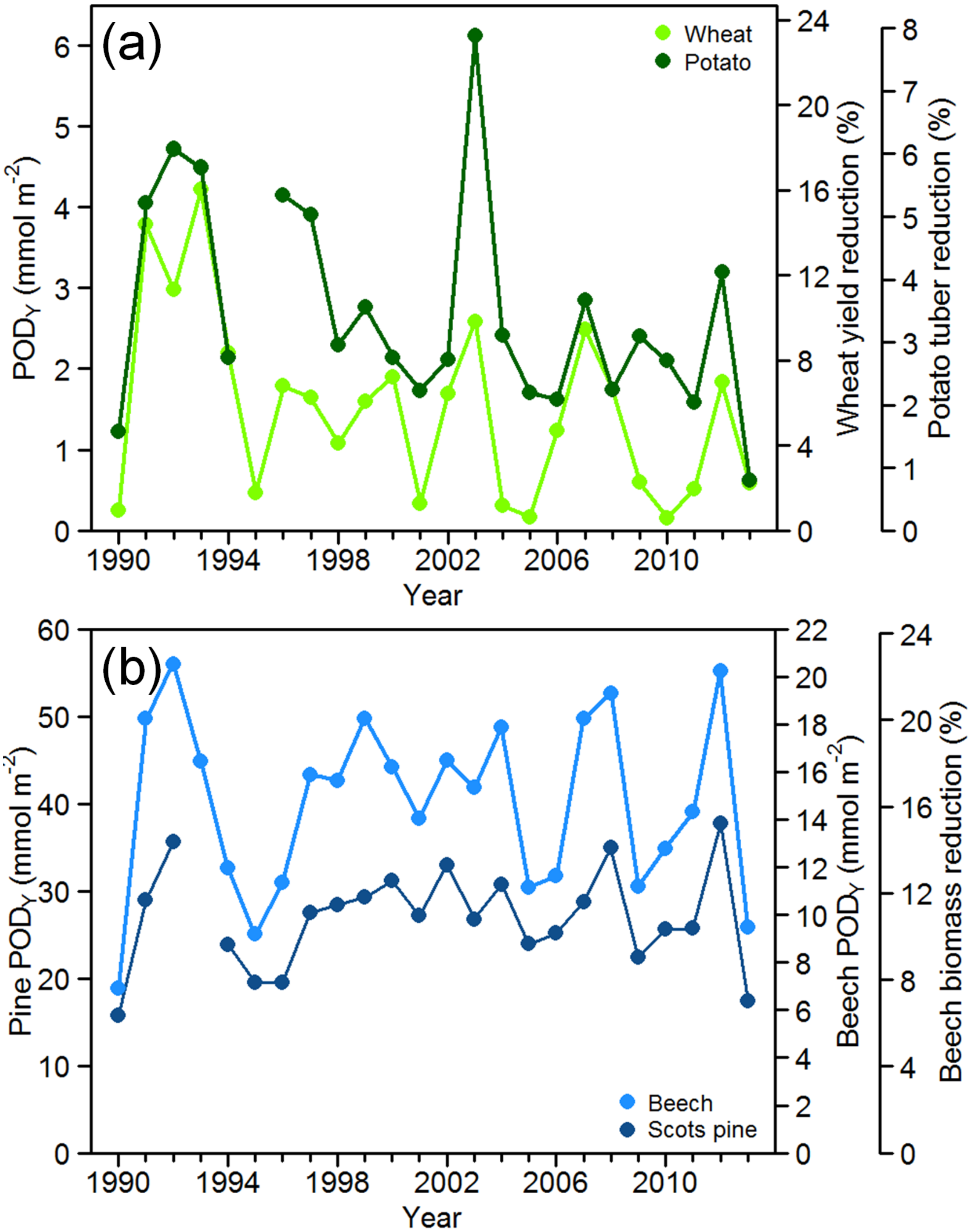

Figure ~~8~~9: Amplitude of the diurnal O_3 cycle at Harwell during June POD_Y accumulation days for wheat and potato. and hourly European NO_x emissions estimate for the EMEP 0.5° grids over which 96-h back trajectories passed prior to arrival at Harwell during June POD_Y accumulation days for wheat and potato.

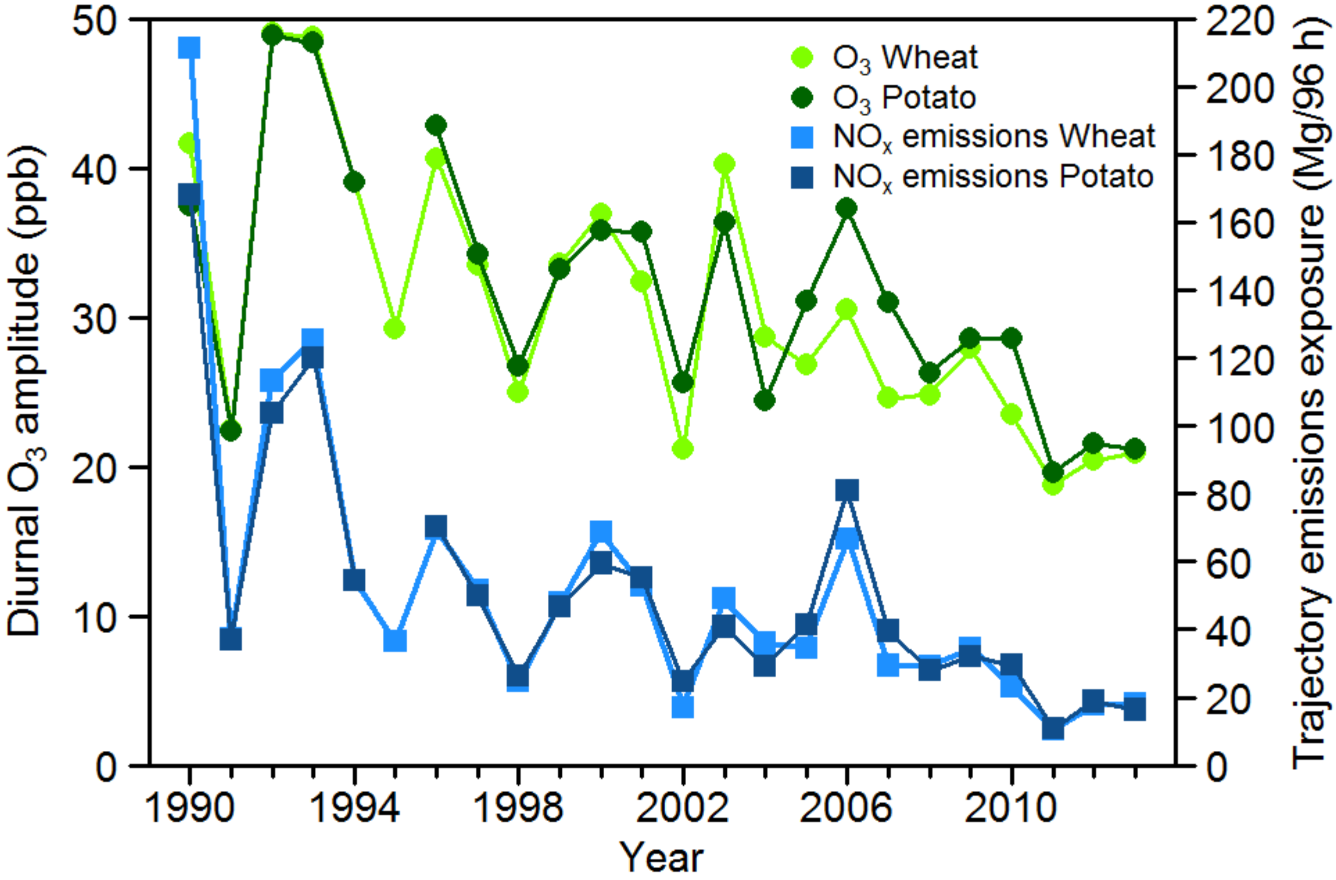

Figure ~~9~~10: Relative annual contributions to (a) wheat POD_Y, (b) potato POD_Y, (c) beech POD_Y and (d) Scots pine POD_Y at Harwell from different O_3 concentration bins. Concentrations are separated into fifteen 5 ppb groups spanning hourly O_3 concentrations between 0 ppb and >70ppb. Note: these concentration bins are contributing to constant trends in POD_Y for each vegetation type – see figure 7.

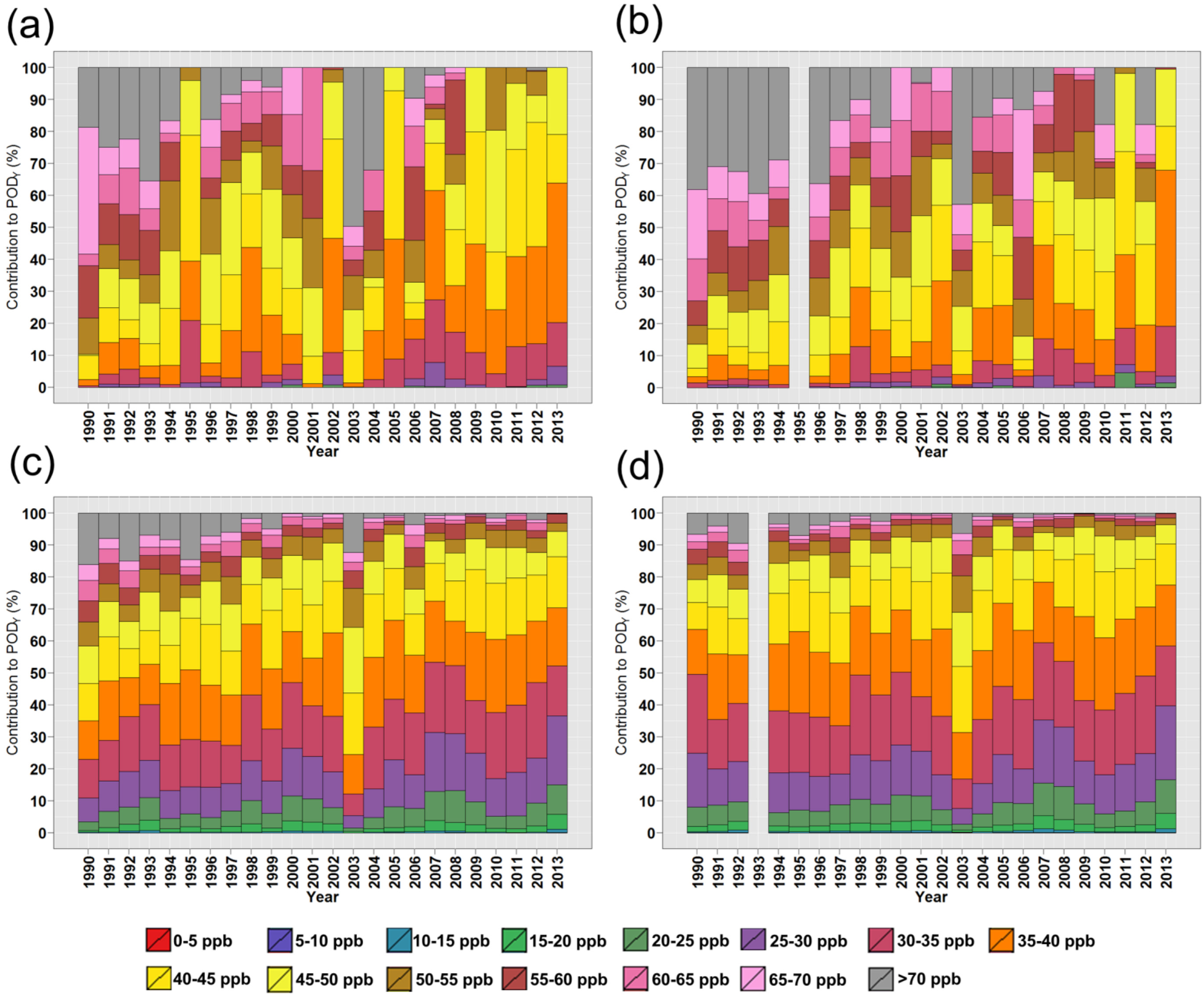

Figure ~~10~~11: Comparison of O_3 vegetation impact chemical climates for wheat and potato 2007-2013. (a) Annual POD_Y for wheat and potato, (b) Diurnal O_3 amplitude during June accumulation days (ADs) at Harwell and Auchencorth, and trajectory NO_x emissions estimates at Harwell and Auchencorth.

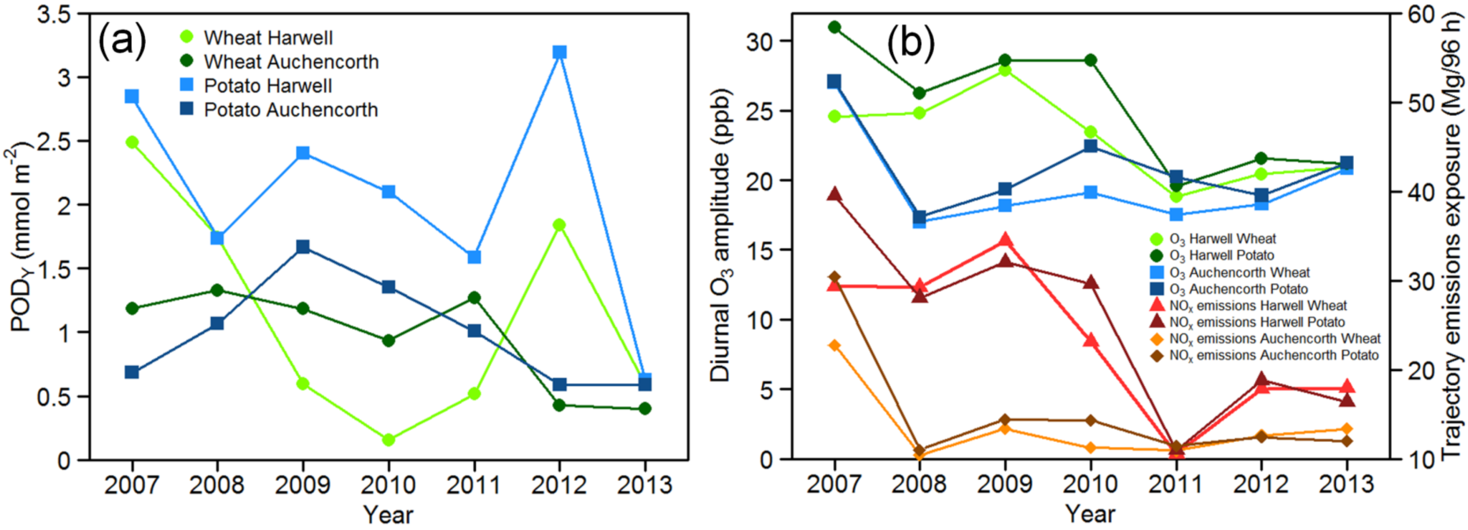

Figure ~~11~~12: (a) Wheat POD_Y accumulated during July at Harwell and at Auchencorth, 2007-13. (b) Diurnal cycle amplitude of O_3 and NO_2, and back-trajectory NO_x emissions estimates during wheat accumulation days (ADs) in July at Harwell and at Auchencorth, 2007-13.

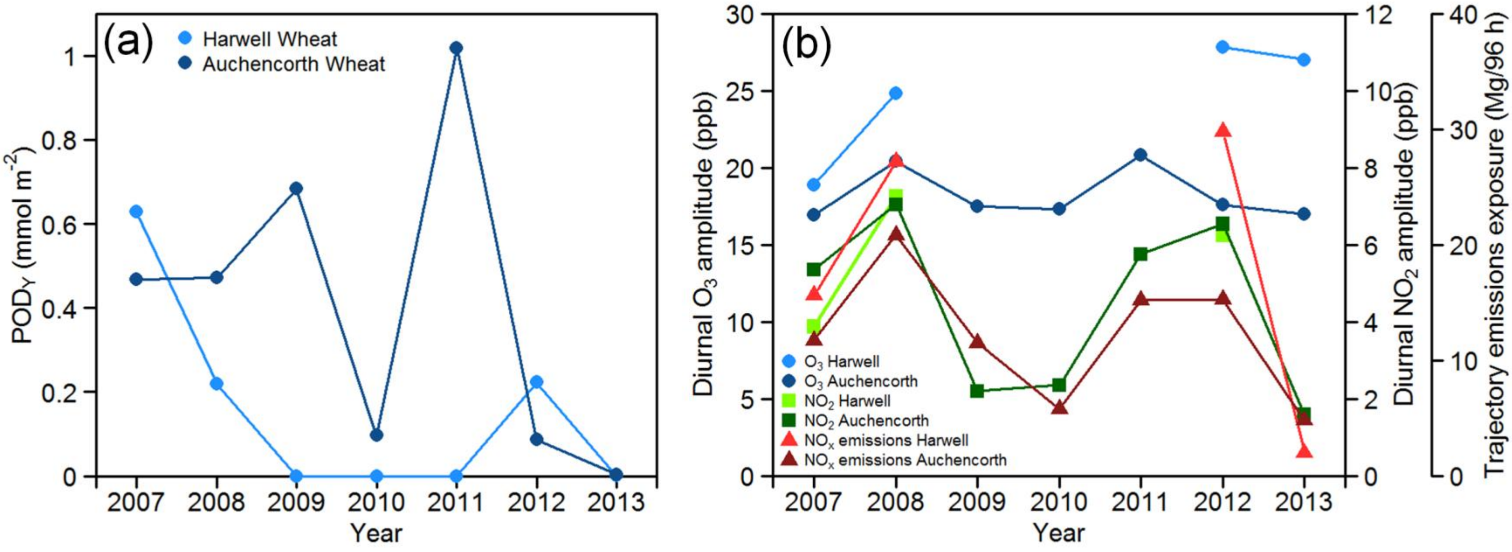

Figure ~~12~~13: Comparison of O_3 vegetation impact chemical climates for beech and Scots pine 2007-2013 at Harwell and Auchencorth. (a) Annual POD_Y for beech and Scots pine. (b) POD_Y accumulated in May for beech and Scots pine. (c) May monthly average diurnal amplitude of O_3 and NO_2, and back-trajectory NO_x emissions estimates.

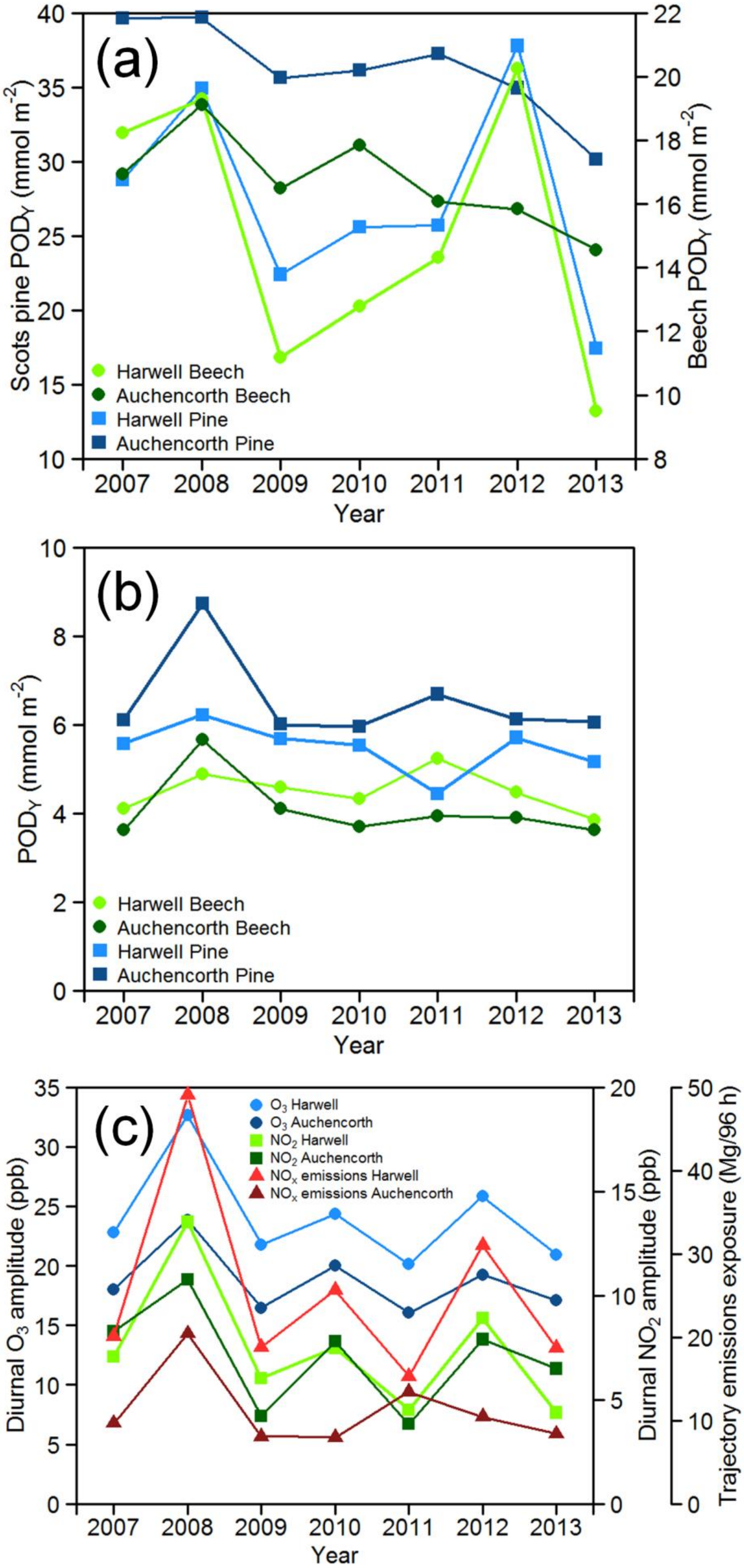

Figure 14: Crop-relevant AOT40 (calculated between May and July) at Harwell for the period 1990 to 2013. The Theil-Sen trend estimate of median trend (shown in red) is –3.6 % y^{-1} (p = 0.001).