Response to reviewers

Atmos. Chem. Phys. Discuss., 15, 7267-7308, 2015: "The impact of speciated VOCs on regional ozone increment derived from measurements at the UK EMEP supersites between 1999 and 2012" by Malley et al.

We thank the reviewers for their time spent reviewing our manuscript. 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:

Reviewer 1 comment: The authors present an in depth look at the regional ozone increment and what is possible when linking various analysis methods and data sources that are not necessarily typically combined. This provides for an interesting and relevant methodology that they present and some interesting insights. While I find the paper quite relevant, there are a number of issues with the presentation/clarity of some aspects of the analysis and process followed given the complexity of some of these linkages. I would recommend that the paper is published, if the comments can be sufficiently addressed.

Response: We are pleased the reviewer considered the paper interesting and recommends publication following satisfactory revisions. We thank them for their detailed analysis of the paper, and clear, specific comments.

General comments

Reviewer 1 comment: There are a variety of concepts and terms used throughout the paper that could do with a better definition or initial explanation, either initially or referenced throughout, to help the reader follow the thread. Some of these are chemical climate, 'positive' and 'negative' O3 increment and what the (+) and (-) indicate in terms of production vs reduction of ozone, as well as the link to photochemical depletion of the VOCs.

Response: The 'chemical climate' concept is detailed at the start of Section 2 (P7271 L21). Text has been amended to emphasise what the components of a chemical climate are (as defined in Malley et al. (2014b)), and how they relate to the analysis and structure of this work.

Original text P7271 L21: "The methodology is separated into the three elements of a chemical climate, the impact (here, regional O_3 increment), state (VOC diurnal photochemical depletion) and drivers (meteorology and emissions) as defined in Malley et al. (2014b)"

Amended text: "This work was undertaken by applying the chemical climatology framework outlined in Malley et al. (2014b). A chemical climate is derived through the linkage of a specific 'impact' of atmospheric composition (here, regional O_3 increment), through the 'state' of relevant atmospheric composition

variation (VOC diurnal photochemical depletion) to its causal 'drivers' (meteorology and emissions). The aim of this framework is to provide a consistent method for both consideration of impact severity and the conditions producing it, hence highlighting pathways for mitigation. The Methods and Results sections are subdivided into impact (Section 2.1 and 3.1 for Methods and Results respectively), state (Section 2.2 and 3.2) and drivers (Section 2.3 and 3.3) to emphasise the analyses used to derive the components of the chemical climate."

A more detailed explanation of the meaning of a positive and negative regional O_3 increment has been added to P7273 L25:

Additional text: "A positive regional O_3 increment indicates additional O_3 formation regionally in excess of hemispheric background concentrations, and vice versa."

A description of how the regional O₃ increment and VOC photochemical depletion are linked in this work has been expanded upon, P7276 L14:

Additional text: "The sum of positive daytime photochemical depletion of individual VOCs produces the total VOC diurnal photochemical depletion for each month. The monthly pattern of total VOC diurnal photochemical depletion was compared with the monthly pattern of the regional O_3 increment. During those months with a positive regional O_3 increment, the relative contribution of each VOC to total VOC photochemical depletion was used as an estimate of the relative contribution of each VOC to the VOC chemical loss which contributed to the production of the positive regional O_3 increment."

Reviewer 1 comment: P10: The description on this page (L5-31) is quite involved and complex as to which data is included where, used how, where assumptions are made, etc. It could be quite helpful and provide significant clarify if there were e.g., a flow chart or similar to elucidate the steps/process that is followed.

Response: Two new figures have been added which represent the processes used to derive the contribution from individual VOCs to the monthly trajectory emissions estimates (new Figure 2, description starting P7277 L22), and the contribution from NFR codes to the monthly trajectory emissions estimates (new Figure 3, description starting P7278 L14). The figures are also included at the end of this document.

Reviewer 1 comment: In many of the sections of this paper, there are a lot of statistics quoted and involved connections made, which are often mixed with a variety of examples for the different months where x might result in one case and y in another. To add clarity to the paper it would be good if these sections/paragraphs, especially in e.g., section 3.3.2 on emission, would include an initial statement of aim at the beginning, so that it is more obvious to the reader why/how the points are important and where the discussion is leading.

Response: Additional linking sentences to better highlight the relevance of the statistics presented have been added at various places throughout Section 3.

Firstly, the paragraph discussing the contribution of individual VOCs to the total VOC photochemical depletion is given a wider context through the following additional text:

P7281 L24 Additional text: "The association between the monthly variation in the regional O_3 increment and total VOC diurnal photochemical depletion at Harwell indicates that the variation in VOC chemical loss contributing to the regional O_3 increment is represented by the VOC diurnal photochemical depletion. The relative contribution of each measured VOC to total VOC diurnal photochemical depletion during months of enhanced regional O_3 increment therefore indicates where emissions reductions should be targeted to most effectively reduce VOC chemical loss and hence to reduce the magnitude of the regional O_3 increment."

In Section 3.3.2 (Emissions), the second and third paragraphs now include use of April-July 2011 to illustrate how variation in VOC TEE can result in variation in VOC photochemical depletion and regional O_3 increment. This is made clearer in the second sentence of this section.

P7284 L17 Original text: "The period of April-July 2011 provides a useful case study to demonstrate the nature of the emissions driver."

Additional text: "This period shows how variation in both the magnitude of the VOC TEE, as well as the proportion of emissions emitted closer to the receptor site (temporally) can influence the extent of VOC diurnal photochemical depletion and the magnitude of the regional O_3 increment."

The aim of the fourth paragraph of Section 3.3.2 (P7285 L10) is to demonstrate that, while reductions in the contribution of some VOCs to VOC TEE between 2001 and 2011 (i.e. toluene and iso-pentane) was reflected in the measurements, variation in the contribution of VOCs to TEE on a monthly scale were not reflected in changes in the contribution of VOCs to total VOC photochemical depletion. The discussion of changes in VOC contribution to TEE, and inconsistencies between VOC contribution to TEE and photochemical depletion are now considered separately in different paragraphs (the first paragraph ends at the end of the sentence on P7285 L17).

The following additional text has been added to make clear what Figure 10 (and its discussion in the text) is trying to convey:

P7285 L13 Original text: "Individual VOC trajectory emissions estimates were expressed as the percentage of the total POCP-weighted emissions" **Additional text:** "and the comparison between 2001 and 2011 illustrates the contrast and similarities in contribution from individual VOCs to the VOC TEE during the months of maximum regional O₃ increment."

The start of the new paragraph has been rephrased to better introduce the relevance of the statistics presented:

P7285 L17 Original text: "However, monthly variation in the contribution of measured VOCs to the VOC TEE was not consistent with variation in the

contribution of individual VOCs to total measured VOC diurnal photochemical depletion."

Additional text: "Monthly variation in the contribution of measured VOCs to the VOC TEE was not consistent with variation in the contribution of individual VOCs to total measured VOC diurnal photochemical depletion. This is in contrast to the observed changes between 2001 and 2011 in VOC contribution to TEE and VOC diurnal photochemical depletion, and is effectively illustrated using the April-July 2011 time period as an example."

Finally, the final two paragraphs of Section 3.3.2 investigate the effect of highly aggregated source sectors on VOC emissions. This discussion directly results from the previous paragraphs, and text has been added to more clearly show this linkage.

P7286 L16 Additional text: "Highly-aggregated SNAP source sectors, and a constant contribution of component activities to SNAP emissions were identified as a potential contributing factor to inconsistencies between VOC contributions to TEE and VOC diurnal photochemical depletion. Disaggregation of the VOC TEEs into 91 NFR codes, based on country-specific contributions of these NFR codes to annual VOC emissions in the 11 parent SNAP sectors, accounted for country-specific changes in NFR sector contributions to monthly VOC TEE at Harwell. The aim was to show that within each SNAP sector an increase in VOC SNAP emissions can result from an increase in a specific source activity (e.g. specific NFR code), rather than a general overall increase. Variability in the contribution of constituent activities to SNAP emissions could result in variation in the contribution of individual VOCs to those emissions. This would therefore demonstrate that the reporting of gridded VOC emissions in more disaggregated source sectors was required, so that more flexible VOC speciation profiles could be derived than those calculated for the 9 SNAP sectors in this study, and those calculated previously, e.g. Derwent et al. (2007a)."

P7287 L6 Original text: "The difference between the contribution of 91 NFR codes to the average VOC TEE between April and July 2011 is shown in Figure 12"

Additional text: "to demonstrate the variability in contribution of component activities to parent SNAP sector emissions."

Specific comments

Reviewer 1 comment: P2L21-22: There are a number of factors that affect the utility of gridded emissions for use in measurement and modeling studies, with the aggregated nature of source sectors being just one. This should be acknowledged as it may otherwise seem to be an over simplified assessment of emission inventories.

Response: The relevant sentence has been amended to reflect the multiple factors that affect the utility of gridded emissions.

P7268 L21 Original text: "This demonstrated that the effectiveness of VOC gridded emissions for use in measurement and modelling studies is limited by the highly aggregated nature of the 11 SNAP source sectors in which they are

reported, as monthly variation in speciated VOC trajectory emissions did not reflect monthly changes in individual 25 VOC diurnal photochemical depletion." **P7268 L21 Amended text:** "This demonstrated that one factor limiting the effectiveness of VOC gridded emissions for use in measurement and modelling studies is the highly aggregated nature of the 11 SNAP source sectors in which they are reported, as monthly variation in speciated VOC trajectory emissions did not reflect monthly changes in individual 25 VOC diurnal photochemical depletion."

Reviewer 1 comment: P3L24: It would be good to include a brief definition of 'chemical climates' here or at the point that it is first addressed beyond the introduction (beginning of methodology section), as most readers will likely not be familiar with the concept and will very likely not look up the referenced material.

Response: A brief definition of 'chemical climatology' has been added at the start of the Methods section, and is outlined in a previous comment.

Reviewer 1 comment: P4L12: This sentence doesn't make sense. Please clarify how one allows for the other.

Response: Text has been amended to more clearly state how chemical loss is quantified at urban sites. Full explanation of these methodologies are detailed in the references provided.

P7268 L21 Original text: "In urban environments, the chemical loss of VOCs has been calculated by estimating OH exposure of the VOC suite, allowing calculation of the initial emission ratio of two VOCs (Shao et al., 2009; Yuan et al., 2012)"

P7268 L21 Amended text: "In urban environments, the chemical loss of VOCs has been calculated through the estimation of initial emissions ratios of two VOCs, and calculation of photochemical age through parameters such as 'OH exposure' or 'VOC consumption' (Shao et al., 2009; Yuan et al., 2012)"

Reviewer 1 comment: P4L15: Here it is mentioned that you use monthly-averaged diurnal variations but offer no explanation why this averaging period was chosen, and unless I missed it, this choice is also not explained in the methods. A brief justification, here or elsewhere could be beneficial.

Response: Annual and diurnal O_3 variation are two key elements of O_3 variability, both in terms of accumulation of health and vegetation-relevant O_3 metrics (discussed in detail in relation to both Harwell and Auchencorth in Malley et al. (2015)), and in how O_3 variability is compared between sites and across regions (see for example Tarasova et al. (2007)). In order for this work to be placed in the larger context of other O_3 studies, and to provide transferability to other measurement sites, it was considered appropriate to assess the contribution of VOCs to regional O_3 using monthly-diurnal averaging. Additional text has been added justifying this choice. **P7271 L3 Additional text:** "Monthly-diurnal averaging was chosen as the annual and daily cycles are key features of O_3 variability associated with the driving processes on its concentrations and on its impact. For example, the monthly and diurnal variation in O_3 is central to determining the extent and spatiotemporal trends in health and vegetation-relevant O_3 metrics (Malley et al., 2015). Ozone variability at hundreds of monitoring sites globally has also been characterised based on monthly-diurnal variation (Tarasova et al., 2007). Monthly-diurnal averaging was therefore also appropriate for setting this work in the wider context, especially given the relative scarcity of hourly VOC measurements."

Reviewer 1 comment: P5L13: The sentence makes reference to '...the two shown previously...' but it is not clear what these are. Could the author please clarify?

Response: 'The two shown previously' refer to the spatial domain defined for Harwell and Auchencorth in Malley et al. (2014a) based on monthly-diurnal O_3 variation. This has been made clearer in the text.

P7272 L3 Additional text: "Here, regional background O_3 concentration is defined as that which is imported into a local spatial domain following modification of hemispheric background O_3 concentrations by European emissions. Examples of local spatial domains are south-east England and northern UK for which, based on monthly-diurnal O_3 variation, Harwell and Auchencorth respectively were shown previously to be representative of (Malley et al., 2014b)."

Reviewer 1 comment: P6L28-P7L2: While the substitution of Mace Head data to calculate the regional O3 increment at Auchencorth may be appropriate, but needs to be justified. How do the back trajectories compare? Is such a substitute reasonable?

Response: The O_3 measurements at Mace Head were not substituted for those at Auchencorth to calculate the regional O_3 increment. For both Auchencorth and Harwell, O_3 concentrations at Mace Head during westerly conditions (extracted using cluster analysis) were used as an estimate of hemispheric background O_3 concentrations. The assumption in using westerly Mace Head O_3 data to estimate hemispheric background concentrations is that these measurements have no influence from European emissions. The success of the cluster analysis algorithm in extracting these non-European influenced periods is compared with different methods outlined in Derwent et al. (2013), which include the use of chemical tracers and atmospheric modelling to differentiate between European and non-European influence. A high correlation is calculated between the monthly 'hemispheric background' concentrations calculated using the different methods (shown in Figure 1), and therefore it was considered appropriate to use monthly-diurnal variation in hemispheric background concentrations.

To calculate the regional O_3 increment, an estimate of regional background O_3 concentrations was also required. The approach differed at Harwell and Auchencorth. At Harwell, regional background O_3 concentrations were calculated for each monthlydiurnal time period using the y-intercept of Oxidant vs NO_x linear fit, i.e. the NO_x independent contribution to oxidant, based on the methodology outlined in Clapp and Jenkin (2001). To construct these plots, it is necessary to have multiple sites within the spatial domain with concurrent measurements of NO, NO₂ and O₃ to capture a range of NO_x and Oxidant concentrations. There were insufficient collated measurements within the spatial domain of Auchencorth to estimate regional background O₃ concentrations using this method. When Auchencorth was assessed in the context of O₃ variation across rural Europe, it was grouped among the least anthropogenically-influenced measurement sites, and monthly-diurnal O₃ variation was similar to sites across a large spatial domain, including sites in Norway and Sweden (Malley et al., 2014a). This indicated a low 'local' influence on measured O₃ concentrations at Auchencorth, and hence it was considered appropriate to use the Auchencorth measurement data as an estimate for regional background O₃ concentrations.

Reviewer 1 comment: P7L10: Please give an indication of what 'extensive periods' means in terms of a quantitative range or amount.

Response: More information is provided regarding the range of data capture, particularly at Auchencorth on P7276 L15. An indication of the range of data captures at Harwell and Auchencorth has been added on P7274 L9:

P7274 L9 Additional text: "The VOC datasets had extensive periods during which concentrations were below LOD, particularly at Auchencorth (e.g. between 6% and 81% below LOD at Harwell in 2011, and between 11% and 82% at Auchencorth)."

Reviewer 1 comment: P7L10-P8L10: The paragraph is currently quite long and contains different, but related types of information. To make it a bit more clear, I would suggest that the authors insert paragraph breaks at P7L22 and P8L4. In addition, the final part (P8L4-8) summarizes what the inclusion of non-detects means, but does not reiterate why this is important/has been considered. Given the complexity and multiple aspects covered here, it would be good to add information, e.g., at the end of the sentence finishing on P8L8, to say something along the lines of '...indicating that the inclusion of the nondetects as values assumed to be below the LOD was justified.' Otherwise the reader has to go back to the middle p.7 to make that connection. It would just be good to try and connect the dots in a more explicit way in this section.

Response: This paragraph has been split into three as per the recommendation. The new final summary paragraph has been reworded as follows to reiterate the importance of the consideration of non-detects:

P7275 L8 Original text: "In summary, for those VOCs with few unique nondetects, the potential inclusion of non-LOD related non-detects results in a small change in calculated concentration, while VOCs with a larger proportion of nondetects have concentrations more frequently close to the LOD, increasing the likelihood that the unique non-detects result from concentrations below the LOD. Intra-annual and monthly-diurnal variation in VOC concentrations were summarised using the monthly median concentrations and the 24 hourly median concentrations for each month from the best-fit distributions respectively." **P7275 L8 Amended text:** "In summary, for those VOCs with few unique nondetects, the potential inclusion of non-LOD-related non-detects resulted in a small change in calculated concentration, while VOCs with a larger proportion of nondetects had concentrations more frequently close to the LOD, increasing the likelihood that the unique non-detects resulted from concentrations below the LOD. This indicates that the decision to assign all unique non-detects as values below the LOD was justified, as the potential bias introduced was small, and therefore that the maximum of valid VOC concentration data was preserved and used in the MLE distribution calculations. Intra-annual and monthly-diurnal variation in VOC concentrations were summarised using the monthly median concentrations and the 24 hourly median concentrations for each month from the best-fit distributions respectively."

Reviewer 1 comment: P8L23: should the sentence say that ethane is the second least reactive? What is meant by second smallest? Also, if it is second smallest, what is the first and why wasn't that used – although I assume that maybe this was methane, in which case that would not make sense, but without this information, it leaves the reader guessing. Also, is there any literature that has done this previously (I'm pretty sure there is) and it would be good to cite. Although I think most analyses have used CO more frequently, but the concept is the same. Might also be worth it to mention lifetime in the reasoning here.

Response: The measured VOC with smallest POCP is ethyne, although it is similar to that of ethane (ethyne = 7, ethane = 8). The terminology 'smallest' is retained since in the context here the adjective is referring to a numerical value (the POCP value), rather than to the general concept of reactivity. Additionally, in response to a comment by Reviewer #2, a sentence has been added to the paragraph (P7275 L16) directly before the text highlighted in this comment. This sentence summarises the process by which Derwent et al. (2007a) derive each VOC POCP (see response to Reviewer #2 for details). This description provides additional context and emphasises to the reader that 'smallest POCP' refers to the VOC which resulted in the least additional O_3 formation under the conditions used to derive the POCP reactivity scale.

Ethane was chosen to remove the effects of boundary layer mixing depth as it had consistently high data capture (>89% at Harwell and Auchencorth). Data capture for ethyne at Harwell (2010 and 2012) and Auchencorth (2012) was approximately 3% lower than ethane, but between 1999 and 2001, data capture for ethyne was at most 57%. This did not facilitate comparison of the two periods at Harwell, and hence ethane with the marginally larger POCP was chosen.

We are grateful for the reviewer's suggestion of atmospheric lifetime. This justification, along with previously literature using ethane have been added to the manuscript.

P7275 L29 Original text: "Ethane has the second smallest POCP of the measured VOCs, 87 % smaller than the average, and 20 % smaller than the next smallest POCP (benzene), so using this ratio removed the effect on diurnal VOC concentration of changes in boundary layer mixing depth."

P7275 L29 Amended text: "Ethane has the second smallest POCP of the measured VOCs, 87 % smaller than the average, and 20 % smaller than the next smallest POCP (benzene), so using this ratio removed the effect on diurnal VOC concentration of changes in boundary layer mixing depth. The VOC with smallest POCP, ethyne, had low data capture at Harwell between 1999 and 2001 (maximum 57% in 2001). Additionally, ethane has a smaller rate coefficient for reaction with OH compared with ethyne (Table 1), and the POCPs were similar (7 for ethyne vs 8 for ethane). Ratios of VOC/ethane have been used previously to estimate the photochemical loss of VOCs (Yates et al., 2010;Helmig et al., 2008;Honrath et al., 2008)."

Reviewer 1 comment: P8L26-27: is this a reasonable assumption to make, that the magnitude of VOC emissions do not differ substantially between day and night? Something as simple as temperature would affect the magnitude of daytime/nighttime emissions of VOCs especially for biogenic VOCs, but also for e.g., evaporative emissions. If this is a reasonable assumption, could you please justify it somehow? Or if I have misinterpreted what is being assumed and refers instead to the emissions being brought in by the trajectories or something else, please clarify this. This statement also seems to be contradicted by the later sentence on L30 that states that night emissions were $\pm 12\%$ compared to day emissions. Or is that sentence meant to communicate that they are the same with a difference of no more than $\pm 12\%$? Please clarify.

Response: The statement does refer to emissions being brought in by trajectories. The assumption is that the emissions affecting the VOC concentrations during day and night do not differ and therefore that a depletion of VOC concentrations during the afternoon is due to photochemistry. Given the transport time from emissions source to monitoring site, daytime emissions of VOCs will affect night-time concentrations and vice-versa. In calculating the VOC trajectory emissions estimate, when the trajectory is over a given location, the emissions from that grid square are varied based on time of day. For some SNAP sectors, e.g. SNAP7 Road Transport, there are larger emissions during the day, while for others, e.g. SNAP4 Production Processes, the time factors are constant. The comparison between trajectory emissions estimates in day and night shows that they differ by no more than $\pm 12\%$. The text has been amended to clarify:

P7276 L4 Original text: "It is also assumed that the magnitude of VOC emissions which determine VOC concentrations measured at the sites do not 5 differ substantially between day and night. This can be evaluated from the monthly median VOC emissions emitted along the path of 96 h trajectories (outlined in Sect. 2.3) arriving at night (3 a.m.) and afternoon (3 p.m.), which were generally similar. For example at Harwell in 2011, night trajectory VOC emissions were ± 12 % compared to afternoon."

P7276 L4 Amended text: "It is also assumed that the diurnal variation of VOC at the site is not driven by differences in the magnitude of VOC emissions along the trajectories contributing VOC to that site during the day and at night. This can be verified by the similar monthly median VOC emissions emitted along the path of 96-h trajectories (outlined in Sect. 2.3) arriving at night (3 a.m.) and afternoon (3 p.m.). For example, at Harwell in 2011, night trajectory VOC emissions were no more than ± 12 % different from afternoon."

Reviewer 1 comment: P8L30: Does this refer to normal or pocp-weighted emissions?

Response: These are normal emissions which were not speciated to calculate the POCPweighting.

Reviewer 1 comment: P9L14-15: The authors mention those factors considered here. Are there other factors that play a large role and are not considered?

Response: This sentence has been revised to emphasise that it is the anthropogenic VOC emissions which are considered here. As noted in the manuscript and in response to Reviewer #2, this methodology does not consider the contribution from biogenic VOCs, which is another driver that should be considered in subsequent analysis. Additionally, another factor in determining the regional O₃ increment is the NO_x environment in the spatial domain of the site. The decision to focus solely on the interpretation of VOC measurements from anthropogenic VOC emissions in this analysis was due to the clear benefits in terms of reduction in health and vegetation-relevant O₃ resulting from regional-scale reductions in anthropogenic VOC emissions. As noted in the introduction, Gauss et al. (2014) show that improvement in health and vegetation-relevant O₃ results across large areas of north-west Europe from a 15% reduction in NO_x emissions, whereas these impact metrics actually increase from a 15% reduction in NO_x emissions, due to reduced O₃ depletion. This has been emphasised through additional text in Section 2.3:

P7276 L27 Additional text: "Other drivers such as biogenic VOC emissions, and NO_x concentrations are drivers of the regional O_3 increment. Meteorology and anthropogenic VOC emissions are the focus due to the benefits previously outlined in improvement in health and vegetation-relevant O_3 impacts that result from anthropogenic VOC emission reductions."

Reviewer 1 comment: P11L14: Why were 2001 and 2011 chosen for Harwell and 2012 for Auchencorth? If all the years looked pretty much the same and the middle year was chosen for all, that would be fine, but it seems a bit random. Please justify the choices. (Or since the other years were clearly also analyzed since they are discussed later on in the section, consider mentioning a justification and/or providing the other plots in SI.)

Response: Although we state that each of the chosen years is 'representative' of the three year period, this is not the same as stating that that all the years in each period looked pretty much the same. As noted in the next sentence, P7279 L9, there was inter-annual variability within these three year periods, due to inter-annual variability in meteorology and transport of emissions. This affected both the magnitude and timing of the regional O_3 increment within each three-year period. On P7279 L21, a description of the differences between the regional O_3 increment in 2011, and in 2012 and 2010, providing the reader with the necessary information to understand the differences between the regional O_3 increments presented in the figure, and those for the other two years. Additional text has been added to provide a similar comparison between 2001 and 1999 and 2000:

P7279 L17 Additional text: "A similar pattern occurred in 2000, but with a lower annual maximum (26 μ g m⁻³ in July). In 1999, regional ozone production was greater, extending from April to September with the annual maximum in July (53 μ g m⁻³), and production in excess of 30 μ g m⁻³ in June and August."

The key point which is emphasised in the text is that the inter-annual variability within each period is much smaller than the differences between 1999-2001 and 2010-2012 at Harwell and between Harwell and Auchencorth.

The reason for selecting particular years within each period is due to the effectiveness with which they can communicate the key messages of the analysis in terms of the impact of the measured VOCs on the regional O₃ increment. Picking the middle year is not necessarily justifiable, given that each period does not have any particular significance other than the availability of concurrent VOC and O₃ measurements. Firstly, the only viable year for analysis of measured VOCs at Auchencorth was 2012 due to the low data capture in 2010 and 2011 (outlined on P7276 L15). At Harwell, 2011 was selected as the example year due to the occurrence of a seasonal maximum in regional O₃ increment in April, and an annual maximum in July. The period from April-July 2011 is an effective example to demonstrate the association between VOC photochemical depletion and regional O₃ increment, the effect of emissions on the extent of VOC photochemical depletion and the limitation of highly aggregated SNAP source sectors in the reporting of gridded VOC emissions.

As noted by the reviewer, there is discussion throughout Section 3 to demonstrate the consistency of the main conclusions throughout the years studied. For example, one of the main utilities of this method is to show the individual contribution of VOCs to total VOC diurnal photochemical depletion. Hence in Figures 5 and 6 show this for each year during the month of maximum regional O_3 increment. The illustration of the key points using the example years, followed by discussion of the relevance of these points to the other years and emphasis in carefully chosen figures allows for an effective presentation of a large amount of data and analysis.

Reviewer 1 comment: P12L26-32: What are the standard deviations of the monthly contributions? This would help put the 22% vs 33% difference in perspective. Is this largely within the noise or is this a significant difference.

Response: Text has been amended to include the standard deviation.

P7281 L2 Amended text: "Ethane, propane and n-butane had the largest measured concentrations. Ethane contributed on average $22 \pm 4\%$ of total monthly measured VOC concentrations in 2001, compared with $33 \pm 6\%$ in 2011 (annual average monthly measured ethane concentration had a small increase from $2.0 \pm 0.8 \,\mu gm^{-3}$ in 2001 to $2.3 \pm 1 \,\mu gm^{-3}$ in 2011), while the relative contribution from propane did not vary (15% in each year, average monthly concentrations in 2001 and 2011 were 1.5 ± 0.9 and $1.2 \pm 0.8 \,\mu gm^{-3}$ respectively) and that from n-butane decreased from $11 \pm 2\%$ to $8 \pm 1\%$ ($1.1 \pm 0.6 \,\mu gm^{-3}$ in 2001 and $0.6 \pm 0.4 \,\mu gm^{-3}$ in 2011)."

Reviewer 1 comment: P12L23-24: The sentence states that six of the VOCs were not measured and gives a % range for their contribution to the monthly total. Could the authors provide a further statement as to whether that is significant enough that that would affect any of the conclusions made earlier in the paragraph? Also, the 2001 6 missing VOCs only pertains to Harwell correct?

Response: The six non-measured VOCs in 1999-2001 pertain only to Harwell. The conclusions from earlier in the paragraph are not affected by the non-measurement of these VOCs. The pertinent conclusions are that at Harwell between 1999-2001 and 2010-2012 in winter, total measured VOC concentrations were similar but with relatively large variability (6-18 μ g m⁻³). This variability is substantially greater than the proportion of total measured VOC accounted for by the 6 non-measured VOCs in 1999-2001. Secondly, during summer months, concentrations at Harwell in 2010-2012 were lower than in 1999-2001. The omission of six minor components from the 1999-2001 total VOC concentrations would result in a small increase in summer concentrations between 1999-2001, hence underscoring the reduction that has occurred between 1999-2001 and 2010-2012. A sentence has been added to the end of this paragraph to clarify this:

P7280 L26 Additional text: "The non-measurement of these VOCs does not alter the conclusions relating to the differences in total VOC concentrations observed between 1999-2001 and 2010-2012."

Reviewer 1 comment: Figure 4: Given that in Figure 5 there are also negative contributions from individual VOCs, should there also be negative contributions depicted in Figure 4? Or, if there is a reason they are not shown, can you explain?

Response: The positive contributions indicate those VOCs which have lower afternoon POCP-weighted VOC/ ethane ratios than the corresponding night-time values. This afternoon depletion of VOCs is interpreted as the photochemical loss of each VOC. As now clarified in Section 2 in response to previous comments from this reviewer, the total of the positive contributions quantifies the VOC chemical loss which contributes to the production of the regional O_3 increment. Hence it is only the VOCs with positive contributions (i.e. VOCs with afternoon depletion) that can be usefully compared with monthly variation in the regional O_3 increment (Figure 2) to assess the association between the magnitude of the regional O_3 increment and VOC diurnal photochemical depletion. Hence only the positive values are included in Figure 4. Those VOCs with negative values are of interest, and are therefore presented in Figures 5 and 6 and their relevance is discussed in the last two paragraphs of Section 3.2.

Reviewer 1 comment: Figures 5&6/P13L16-21: Given the presence of positive and negative values, could the authors provide a sentence either in the text or the figure captions to indicate what the positive vs negative contributions indicate, just for ease of reading and clarity. Similarly, L29-31, earlier m+p-xylene is stated to contribute to photochemical depletion (with positive values) and then negative values are discussed. It would be good to explain that these indicate photochemical production.

Response: An explanatory sentence has been added to the text and figure captions:

P7281 L26 Additional text: "A positive value indicates lower POCP-weighted VOC/ethane during the afternoon compared to night (i.e. photochemical depletion). A higher POCP-weighted VOC/ethane ratio during the afternoon results in the negative value."

Figure caption: "Figure 5. Individual VOC diurnal photochemical reactivity as defined by the difference between night (average of 1–5 a.m.) and afternoon (1–5 p.m.) POCP-weighted VOC/ethane ratios for (a) June 2010, (b) July 2011 and (c) July 2012, at Harwell. A lower ratio in the afternoon results in a positive value (i.e. photochemical depletion), while a higher afternoon ratio results in a negative value. These months correspond to the periods of annual maximum regional O3 increment at Harwell (see Fig. 2)."

These additional explanations of the source of negative POCP-weight VOC/ethane ratios give the reader more context as to why they are discussed. In addition, the subsequent sentence, which describes the m+p-xylene and ethene positive contributions (i.e. largest photochemical depletion), has been rephrased to emphasise the relevance of negative values:

P7282 L12 Original text: "However, there were much larger negative VOC/ethane diurnal variations for some anthropogenic VOCs compared to 2010–2012 (Fig. 5)."

P7282 L12 Amended text: "However, there were much larger negative VOC/ethane diurnal variations for some anthropogenic VOCs compared to 2010–2012 (Fig. 5), i.e. afternoon POCP-weighted VOC/ethane ratios were substantially higher than at night. This indicates that processes other than photochemical depletion, e.g. local emission patterns, contributed to diurnal variation in POCP-weighted VOC/ethane ratios for these VOCs in 1999-2001."

Reviewer 1 comment: P13L28-P14L2: Why when earlier summer/July was being discussed, is now the focus on April/(May)?

Response: The last paragraph of Section 3.3.1 has been reworded to emphasise that the period April-May 2011 is being used as an example to demonstrate that variation in meteorology does not explain all variation in the regional O_3 increment:

P7282 L12 Original text: "At Harwell in April 2011, there was a larger regional O_3 increment compared with April 2001. This coincided with 4 °C higher mean temperature and 95 more hours of sunshine in South East and Central South England. However, other factors, such as the strength of VOC emission sources over which an air mass passes, also influence VOC diurnal photochemical depletion, and in May 2011 the temperature and sunshine were similar to April 2011, but VOC diurnal photochemical depletion and the regional O_3 increment decreased."

P7282 L12 Amended text: "However, not all variation in VOC diurnal photochemical depletion and regional O_3 increment were associated with changes in meteorology. For example, at Harwell in April 2011, there was a larger regional

 O_3 increment compared with April 2001. This coincided with 4 °C higher mean temperature and 95 more hours of sunshine in South East and Central South England. In May 2011 the temperature and sunshine were similar to April 2011, but VOC diurnal photochemical depletion and the regional O_3 increment decreased. Hence other factors, such as the strength of VOC emission sources over which an air mass passes, also influence VOC diurnal photochemical depletion, and are discussed in Section 3.3.2."

Reviewer 1 comment: P14L1-2: Mention that this change/difference will be explored more later. My initial reaction as a reader was one of wanting more explanation since I thought that was where discussion of that point ended.

Response: The text has been amended in line with the recommendation (see above).

Reviewer 1 comment: P15L5-20: It would be worth including some discussion, or at least a mention, on the accuracy of the emission inventories. How do literature sources reporting the source apportionment results of measurement data agree or disagree with the emissions reported in the inventories. Either here, or possibly more appropriately, in the section on uncertainties.

Response: An acknowledgement and discussion of the sources of uncertainty in VOC emission inventory is provided in the methodology (P7278 L21). To keep this discussion in one place, the text has been amended in line with the recommendations in this comment to include more examples of literature which compare inventories to real-world VOC concentrations. Text has been added at the start of Section 3.3.2 to state that there are uncertainties associated with gridded emissions inventories, but studies have found broad agreement with those emissions reported and real-world variation in VOC concentrations:

P7278 L21 Original text: "The emission inventories used in this study have several sources of uncertainty (EEA, 2013). The $0.5^{\circ} \times 0.5^{\circ}$ grid squares mean that numerous distinct sources, each with uncertainties in emission factors and activity rates, are aggregated together to produce the estimate of emissions from a particular SNAP or NFR source sector. The 25 size of the grid square also does not necessarily reflect the size of the area from which emissions influence the atmospheric composition of the trajectory air mass as it passes over. The VOC TEE is therefore used as a relative comparison spatially and temporally, rather than a definitive quantification of the VOC emissions emitted into an air mass. In addition, there are uncertainties in the speciation of total VOC emissions to individual components (Borbon et al., 2013). However, the emissions inventories used here are the best estimate of the spatial distribution of anthropogenic VOC emissions across Europe."

P7278 L21 Amended text: "The emission inventories used in this study have several sources of uncertainty (EEA, 2013;Koohkan et al., 2013). The $0.5^{\circ} \times 0.5^{\circ}$ grid squares mean that numerous distinct sources, each with uncertainties in emission factors and activity rates, are aggregated together to produce the estimate of emissions from a particular SNAP or NFR source sector. The size of the grid square also does not necessarily reflect the size of the area from which

emissions influence the atmospheric composition of the trajectory air mass as it passes over. The VOC TEE is therefore used as a relative comparison spatially and temporally, rather than a definitive quantification of the VOC emissions emitted into an air mass. In addition, there are uncertainties in the speciation of total VOC emissions to individual components (Borbon et al., 2013). However, the emissions inventories used here are the best estimate of the spatial distribution of anthropogenic VOC emissions across Europe. While studies have shown discrepancies between the EMEP emission inventory and other estimates of European emissions (Koohkan et al., 2013), EMEP gridded emissions have also been shown previously to capture variation in VOC measurement data (Sauvage et al., 2009;Derwent et al., 2014)"

Reviewer 1 comment: P15L29-P16L9: add an aim/guiding sentence at the beginning of the paragraph. Might also provide clarity if one case e.g, that of April and July is followed through before comparing the conditions for May and June.

Response: In response to the general comment stating that greater guidance was required, a guiding sentence was added to the previous paragraph (P7284 L16) explaining that the April-July case study was chosen to investigate both the effects of variation in magnitude of VOC TEEs, and the proportion of emissions accumulated at different hours before arrival. The first sentence of this paragraph has been extended to make clear that it is the latter feature which is investigated in this paragraph.

P7284 L25 Original text: "The proportion of the total VOC TEE derived from the final 4 h prior to a trajectory's arrival, plus the hour of arrival, was labelled as the "final 4 h" VOC TEE"

P7284 L25 Amended text: "The proportion of the total VOC TEE derived from the final 4 h prior to a trajectory's arrival, plus the hour of arrival, was labelled as the "final 4 h" VOC TEE to investigate the effect of variation in the proportion of emissions emitted closer to the monitoring site"

Reviewer 1 comment: Figure 9: Could error bars be added to the plot? How does this compare to other years? Is this fairly consistent or is every year very different?

Response: The key point is that not the shape of this graph, but the relationship between the variation in the final 4 hour metric and VOC diurnal photochemical depletion and the regional O₃ increment. Hence there is variation inter-annually in the final 4-hour value for each month, but this is reflected in the VOC diurnal photochemical depletion and regional O₃ increment. For example, in 2011 in June and July approximately 40% and 20% of VOC TEE was accumulated in the final 4 hours (Figure 9), whereas in 2010 the situation is reversed. The consequence of this (and of variation in the magnitude of VOC TEE in these months), is that the regional O₃ increment in 2010 peaks in June (24 µg m⁻³), and drops off in July (19 µg m⁻³). For 2011, the regional O₃ increment in June was substantially lower than June 2010 (5 µg m⁻³), and instead peaks in July (31 µg m⁻³). The contrast between different years further demonstrates the nature of the association between regional O₃ increment and the final 4-hour metric, but does not give any new insight compared to the April-July 2011 example. **Reviewer 1 comment:** Figure 9/P16L4-9: Would it be possible to include information on all the aspects that are important to the regional O3 increment discussed here in one Figure? It might allow for assessing the relationships and connections better, rather than a discussion or listing of percentages in the text.

Response: Figure 9 (Figure 10 in the revised manuscript) has been modified to include the relevant information for the discussion in the paragraph starting on P7284 L25, and is included at the end of this document. Relevant additions have been made to this paragraph to guide the reader to the relevant panel on the figure.

Reviewer 1 comment: P16L15: '... the large negative VOC diurnal photochemical depletion...' is a bit confusing. The negative refers only to how this is portrayed in the figures, correct? And the photochemical depletion is what is represented by the fact that it is negative and not positive, correct? In this case I would put the 'negative' in () or somehow indicate that this relates to the representation in the figures. This was similarly an issue with earlier discussion of such information/figures.

Response: We agree that the use of this phrase is confusing. Text has been amended as follows:

P7285 L15 Original text: "These decreases mirror the absence of the large negative VOC diurnal photochemical depletion of the two VOCs in 2010–2012, which were observed in 1999–2001 (Figs. 5 and 6)"

P7285 L15 Amended text: "These decreases mirror the absence of much greater POCP-weighted VOC/ethane ratios in the afternoon compared to night for toluene and isopentane in 2010–2012, which were observed in 1999–2001 and attributed to variation in local emissions (discussed in Section 3.2 and visualised as 'negative' VOC diurnal photochemical depletion in Figs. 5 and 6)"

The discussion of negative values in Figures 5 & 6 has been addressed and rephrased based on previous comments.

Reviewer 1 comment: P16L10-P17L1: add guiding sentence at the beginning with aim.

Response: A guiding sentence has been added in response to the general comment above.

Reviewer 1 comment: P17L1: the previous text discusses VOC speciation, while the following text, starting on the referenced line then discusses emissions and their relationship to countries. I would insert a paragraph break here.

Response: This paragraph has been split into two paragraphs in response to a comment above, and additional text was added to improve the clarity of what is discussed.

Reviewer 1 comment: Section 3.3.3: None of this section seems to explicitly address uncertainty (except a brief mention regarding total Gg estimates), as the title would

imply, but rather focuses on the mitigation and monitoring part. There are a variety of uncertainties given the back trajectories, the averaging periods, the assumptions associated with POCP values, not to mention the emission inventories. At least some of these should be explicitly addressed.

Response: We contend that Section 3.3.3 does deal with uncertainty relating to this analysis. Only 27 VOCs are measured at each site, while hundreds are emitted into the atmosphere through anthropogenic and biogenic processes. Hence the uncertainty introduced from analysis on a small subset of these VOCs requires discussion and it is afforded the largest paragraph in Section 3.3.3. Additionally, it is a source of uncertainty in the analysis which directly relates to the future of monitoring, and was therefore most appropriately considered here. Some of the other sources of uncertainty mentioned in the comment are considered in other parts of the manuscript, as follows.

For POCPs, Section 2.2 details studies which show POCPs to be well correlated with other ozone formation potential quantification methods. The paragraph starting on P7275 L16 has been amended to explicitly state the experimental uncertainty in the calculated POCPs.

P7275 L26 Additional text: "Previous comparison with other VOC reactivity scales indicated uncertainty in POCP values up to \pm 5 POCP units which equates to an average of \pm 15% for the measured VOCs in this study (Derwent et al., 2007b)."

The combination of emissions inventories and air mass back trajectories also introduces uncertainty, and this is discussed in the methods during the detailed description of the use of emission inventories and back trajectories (P7278 L21).

Explicit acknowledgement of these additional sources of uncertainty has been added to Section 3.3.3:

P7289 L12 Additional text: "Other limitations, in addition to using measurements of a subset of the emitted VOC suite, include use of monthlydiurnal averages. Monthly-diurnal averages were required to use MLE to derive summary statistics, and to calculate hemispheric and regional background O_3 concentrations. Additionally, it is more appropriate to consider an ensemble of air mass back trajectories to reduce the random uncertainty associated with their calculation. Hence the integration of air mass back trajectories and gridded emissions inventories also benefitted from use of monthly averages. However, the contribution of VOCs to the average increase in regional O_3 increment in a given month was evaluated, rather than any short term episodic regional O_3 increment increases."

Reviewer 1 comment: P18L29-32: The total biogenic VOC emissions estimate in Gg is given, and some information on differing estimates. While the total is mentioned for anthropogenic VOCs, there is no additional information given. Given that the focus is also on mitigation and what can be done, it would be good to provide a range or at least mention some of the alternative estimates for anthropogenic VOC emissions, since this is also an area of uncertainty.

Response: The uncertainty in anthropogenic EMEP emissions is outlined in Section 2.3 (P7278 L21) but text has been added to detail alternative estimates and acknowledge that the anthropogenic value is also uncertain:

P7288 L22 Additional text: "The estimate of 752 Gg of UK anthropogenic emissions is also subject to uncertainty associated with defining accurate activity rates and emissions factors for a large number of source activities (EEA, 2013). The UK National Atmospheric Emissions Inventory (NAEI) calculated the uncertainty in UK anthropogenic VOC emissions to be \pm 10% (Misra et al., 2015)."

Reviewer 1 comment: P19L19-21: The point about disaggregated source sectors is valid, however, I think it also over simplified in that it assumes the emission inventory information to be correct or at least that more highly disaggregated source sector information would be able to be reported in enough detail and at a level of certainty that would allow for such precise identification of mitigation strategies. There is significant uncertainty associated with emission inventories, especially at the more detailed level, and measurements and emission inventories do not always agree. As suggested in a previous point, some literature comparing these two and the importance of sources to VOC emissions should be at least acknowledged, even if it is not discussed in detail.

Response: We do not assume that the information used to derive the gridded emissions inventories are correct or are not a source of uncertainty. It is our contention that IF the information used to derive the gridded emissions inventory were accurate, the highly aggregated nature of SNAP-level gridded emissions would limit the precise identification of the most important source sectors, and the suite of individual VOCs emitted. The contrasting contributions of NFR codes to the parent SNAP sector detailed in Section 3.3.2 demonstrate this.

We are pleased that the reviewer considers valid our argument that the high aggregation of source sectors limits the applicability of gridded emissions inventories. We have added text to make clear that the improvement derived from resolving this particular limitation of gridded emissions is dependent on the successful resolution of a number of other uncertainties associated with gridded emissions.

P7289 L13 Original text: "The future reporting of gridded VOC emissions in source sectors more highly disaggregated than currently (e.g. NFR codes) would facilitate a more precise identification of those VOC sources most important to mitigation strategies."

P7289 L13 Amended text: "An additional uncertainty is associated with the gridded emissions inventory itself. The derivation of the inventory requires accurate determination of emission factors and activity rates for a large number of source activities (EEA, 2013). Previous studies show the uncertainty associated with this process. For example, Koohkan et al. (2013) calculated VOC emissions across Europe using inverse modelling by data assimilation of measurements for 15 VOCs and comparison with the EMEP inventory showed an underestimation of emissions of some VOCs and an overestimation of others. Hence there is a requirement for improvement of emissions inventory derivation. However, this

analysis shows that the future reporting of gridded VOC emissions in source sectors more highly disaggregated than currently (e.g. NFR codes) would also facilitate a more precise identification of those VOC sources most important to mitigation strategies, and increase the accuracy in calculating emissions of individual VOCs."

Reviewer 1 comment: P19L29-32: constraints in what sense? Of what? Amplified how? Please be more explicit.

Response: Text has been amended to make clearer:

P7289 L24 Original text: "The work presented here highlights the constraints of representing spatial variation of VOC emissions across Europe with 11 highly aggregated SNAP sectors, and these constraints would be amplified with no disaggregation of gridded VOC emissions."

P7289 L24 Amended text: "The work presented here highlights the constraints of representing spatial variation of VOC emissions across Europe with 11 highly aggregated SNAP sectors in terms of accurately determining the suite of VOCs impacting atmospheric composition at a site. This results from a fixed contribution of component activities to the aggregated SNAP sector emissions spatially and temporally (see Section 3.3.2), although emissions from different SNAP sectors can vary independently of one another. These constraints would be amplified with no disaggregation of gridded VOC emissions and a constant contribution from component activities spatially and temporally to total VOC emissions, i.e. emissions from each aggregated SNAP sector do not vary independently from one another."

Reviewer 1 comment: Conclusions: An explicit comparison to other methodologies that are similar in some aspect would help communicate what is gained by applying the method presented in this paper. What makes this better than simply considering POCP? Why should people want to use this method?

Response: While the POCP concept is without doubt extremely useful, evidenced by its widespread application, including in this study, there are limitations to its application to measurement data, particularly at the classification of site in this study. As noted in the introduction, it is the chemical loss of VOCs which determine the impact on O_3 , and therefore simply considering the POCP of VOC measurement data is not appropriate.

The reviewer notes in their opening remarks that the paper presents 'what is possible when linking various analysis methods and data sources that are not necessarily typically combined'. We also consider the main strength of this methodology the ability to integrate different analysis methods to link a specific impact of VOCs, the regional O_3 increment, to its emissions and meteorological drivers. Text has been amended at the start of the conclusions to emphasise this.

P7290 L5 Original text: "A methodology has been demonstrated using measurement data at the two UK EMEP supersites (Harwell and Auchencorth)

which links the impact of regional O_3 increment to VOC photochemical depletion."

P7290 L5 Amended text: "A methodology has been demonstrated which links the impact of regional O_3 increment to VOC photochemical depletion and spatially gridded anthropogenic VOC emissions. The utility of this methodology, which integrates atmospheric composition measurements (O_3 and VOCs), meteorological data and gridded emissions inventory was shown through the derivation of policy-relevant conclusions using measurement data at the two UK EMEP supersites (Harwell and Auchencorth)."

Comparison is made with other methods used to interpret VOC measurements in other parts of the paper, along with justification as to why they are inappropriate to achieve the aims of this analysis. For example, in the introduction, previous studies used to interpret rural O_3 measurements are collated, and it is stated why a new methodology is required for this analysis, i.e. to investigate the chemical loss of VOCs. Previous studies which quantify the chemical loss of VOCs from measurements are also listed, but because of the assumptions made in these studies, they are only appropriate where local sources dominate, i.e. urban sites.

The conclusions section is reserved to state the novelty of this method, which has been strengthened by the additional text above, followed by stating specifically what has been gained from the application of this methodology to the Harwell and Auchencorth datasets. We feel that highlighting the specific knowledge gained from the application of this methodology effectively communicates the potential benefits from its wider application using other dataset/measurement sites.

Reviewer 1 comment: P20L17-19: Literature exists that also agrees with this point that you are making in these lines about needing further measurement of additional biogenic VOCs, including some of the literature previously referenced, it would be good to include some of these references here.

Response: The work included in von Schneidemesser et al. (2011) is most appropriate for citation here. A distinct analysis of measurements from sites in relatively close proximity to Harwell (including Harwell itself) leads to the conclusion that additional information would be gained from measurement of other biogenic VOCs. Appropriate reference has been added.

Minor comments/edits

Reviewer 1 comment: P3L7-8: it is advised to not only cite reports, but also peer reviewed literature, although the REVIHAAP is in this case quite appropriate.

Response: We agree that both REVIHAAP and RoTAP are highly relevant reports, and both are the synthesis of a large number of peer-review articles (REVIHAAP and RoTAP have approximately 1000 and 500 citations respectively). Following the citations, 'and references therein' has been added to make clear the peer-review basis on which these reports are based.

Reviewer 1 comment: P7L6-9: For clarity, I would suggest revising the text as follows: 'For 2010-2012, data were available for 27 species at both Harwell and Auchencorth. Concentrations of 6 VOCs at Auchencorth during this period were not above the reported limit of detection (LOD) so their cocntribution to thre regional O3 increment was not evaluated. For 1999-2001, data were available for 21 VOCs at Harwell only.'

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

Reviewer 1 comment: P8L5: '...LOD related non-detects resulted in a small change...'

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

Reviewer 1 comment: P8L12: Photochemical has a typo (currently: photochemcial)

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

Reviewer 1 comment: P9L9: *Remove one of the periods – there are two.*

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

Reviewer 1 comment: P12L15: '… and maximum monthly total median VOC…' correct?

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

Reviewer 1 comment: P13L9: it would be good to include the occasional reminder of 'at Harwell' for the 2001 data, since those years never include any Auchencorth data.

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

Reviewer 1 comment: P13L20: '71% of the remaining VOCs' is not clear. Is it that of the total VOCs, 71% were remaining beyond those discussed, or 71% of some other amount of VOCs that is not 100% of all the VOCs measured? If this is also e.g., # of the 27 measured VOCs it might be easier to just state the number of VOCs you are discussing. Similarly, L22 and L23.

Response: The 71% refers to the total number of VOCs excluding ethene and m+pxylene, which had been shown to have a disproportionately large contribution to total VOC diurnal photochemical depletion. Text has been amended to make this clear.

P7282 L1 Original text: "In July 2011, 71 % of the remaining VOCs contributed on average 3.4 ± 2.5 % to total positive VOC diurnal variation."

P7282 L1 Amended text: "In July 2011, 71 % of the remaining VOCs (i.e. all VOCs excluding ethene and m+p-xylene) contributed on average 3.4 ± 2.5 % to total positive VOC diurnal variation."

Reviewer 1 comment: P13L20: '...on average $3.4\% \pm 2.5\%$ to total ...'

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

Reviewer 1 comment: P14L16: '... in 2012 are shown in Figure 7.'

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

Reviewer 1 comment: P19L7-9: Please specify what the percentage is and ideally then also how much of the total would be accounted for at that point, as it seems that it should be close to 80 or 90%, but it is unclear since I was unsure if the % values refer to %s of the total emissions, or just %s of the VOCs that were not measured.

Response: The percentage values for ethanol, methanol and acetone on P7288 L24 are the percentage of total UK anthropogenic VOC emissions emitted as each of these VOCs, hence the addition of these percentages to the percentage of UK anthropogenic VOC emissions emitted as the measured VOCs (37.5%) quantifies the anthropogenic VOC emissions which would be accounted for if these three VOCs were measured. This has been reflected in changes to the text.

P7288 L24 Original text: "Of the 62.5 % of UK anthropogenic VOC emissions not emitted as one of the VOCs measured at the supersites, only the additional measurement of ethanol (13 % of 2011 anthropogenic UK emissions), 25 methanol (4 %) and acetone (3 %) would substantially increase the proportion of the UK VOC suite for which VOC diurnal photochemical depletion would be quantified. These three VOCs constitute 35 % of the unmeasured fraction of UK anthropogenic emissions. Contributions from the 40 unmeasured VOCs with the next highest emissions are required to make up the same percentage, and the remaining unmeasured emissions fraction comprises 464 VOCs."

P7288 L24 Amended text: "Of the 62.5 % of UK anthropogenic VOC emissions not emitted as one of the VOCs measured at the supersites, only the additional measurement of ethanol (13 % of 2011 anthropogenic UK emissions), 25 methanol (4 %) and acetone (3 %) would substantially increase the proportion of the UK VOC suite for which VOC diurnal photochemical depletion would be quantified. The measurement of these three VOCs would increase the proportion of UK anthropogenic emissions emitted as a measured VOC from 37.5% to 57.5%. Currently, ethanol, methanol and acetone constitute 35% of the unmeasured fraction of UK anthropogenic emissions are required to make up the same percentage, and the remaining unmeasured emissions fraction comprises 464 VOCs."

Reviewer 1 comment: P19L11: '...reductions in individual VOCs from whatever their source(s).'

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

Reviewer #2:

Reviewer 2 comment: The paper presented a method to determine the contribution of individual (anthropogenic) VOC to regional ozone increment from field measurements. It identified ethane and m+p-xylene emission reduction would be most effective in reducing the regional O3 increment, among the 27 measured VOCs. It also made recommendations for building future emission inventories to identify VOC source sectors for ozone mitigation. The conclusion and the method would be interesting for the air quality management and policy community. However, the paper should address the following concerns before being considered for publication.

Response: We thank the reviewer for their time spent reviewing the manuscript, and are pleased that they consider it of interest to air quality management and policy communities. The majority of their comments have been addressed by changes made in response to comments from Reviewer #1, as listed above.

Reviewer 2 comment: 1. My major concern is that the manuscript failed to consider the impact of biogenic VOCs especially isoprene, given isoprene concentration was reported at the supersites. It is well known that biogenic VOCs (mostly isoprene) impact the O3 formation by shifting between NOx-limited and radical-limited chemical regimes (e.g., in U.S., Jacob, et al. 1995, Hu et al., 2015; in UK, Vieno et al., 2010; in China, Xie et al., 2008). The manuscript as currently written would mislead readers that biogenic VOCs seem not to be important for ozone formation, but actually the authors are only (or mostly) considering anthropogenic VOCs emission reductions. I'd suggest that authors change some of the language/text and add additional discussion in the paper to emphasize that BVOCs are not discussed. Also, authors may consider adding "anthropogenic" in the title to reflect the main content of the paper.

Response: It was not the intention of the authors to mislead readers on the importance of biogenic VOCs in the formation of the regional O₃ increment. On P7288 L21 we state explicitly that 'Biogenic VOC contributions to regional O₃ increments were not studied using this methodology' and in the conclusions we emphasise the requirement for measurements of a wider variety of speciated biogenic VOCs. However, the limitation of the methodology presented here with regard to biogenic VOCs should not detract from the relevance of the conclusions derived with regard to the contribution from anthropogenic VOCs. The case for reduction of anthropogenic VOCs in terms of O₃ health and vegetation impact mitigation is clearly articulated in the introduction. Gauss et al. (2014) show that a 15% reduction in anthropogenic VOC emissions across the EU would reduce both health and vegetation-relevant O₃ impact metrics, in contrast to the analogous reduction of NO_x emissions, which would increase these metrics across large parts of north-west Europe. Hence there are substantial benefits which could be realised from the reduction of anthropogenic VOC emissions within the spatial domain of Harwell and Auchencorth, and the aim of this methodology is to understand how these might be most effectively realised.

In response to comments from Reviewer #1, a change has been made on P7276 L26 to emphasise that only the anthropogenic emissions driver of this chemical climate have been quantified in this study. Further changes to the abstract, introduction and conclusions to reiterate the specificity of this analysis to anthropogenic VOCs are as follows:

P7268 L10 Original text: "variation in the regional O₃ increment mirrored afternoon depletion of VOCs due to photochemistry"

P7268 L10 Amended text: "variation in the regional O₃ increment mirrored afternoon depletion of anthropogenic VOCs due to photochemistry"

P7268 L19 Original text: "The VOC diurnal photochemical depletion was linked to the sources of the VOC emissions through the integration of gridded VOC emissions estimates over 96 h airmass back trajectories."

P7268 L19 Amended text: "The VOC diurnal photochemical depletion was linked to anthropogenic sources of the VOC emissions through the integration of gridded anthropogenic VOC emissions estimates over 96 h airmass back trajectories."

P7269 L22 Original text: "resulting from 15% reductions in EU27 NO_x and VOC emissions and showed that VOC emissions reductions were more effective than NO_x emissions reductions in reducing the O3 impact metrics across much of north-west Europe."

P7269 L22 Amended text: "resulting from 15% reductions in anthropogenic NO_x and VOC emissions across the EU and showed that VOC emissions reductions were more effective than NO_x emissions reductions in reducing the O_3 impact metrics across much of north-west Europe."

P7271 L3 Original text: "The magnitude of VOC chemical loss at each site was linked to emissions by estimating the integrated VOC emissions along 96 h airmass back trajectories."

P7271 L3 Amended text: "The magnitude of VOC chemical loss at each site was linked to anthropogenic emissions by estimating the integrated VOC emissions along 96 h air-mass back trajectories."

P7290 L3 Original text: "Estimates of the integrated VOC emissions along back trajectories arriving at Harwell 20 have decreased substantially between 1999–2001 and 2010–2012, due to decreases in emissions from SNAP source sector 7 (road transport)."

P7290 L3 Amended text: "Estimates of the integrated anthropogenic VOC emissions along back trajectories arriving at Harwell 20 have decreased substantially between 1999–2001 and 2010–2012, due to decreases in emissions from SNAP source sector 7 (road transport)."

Reviewer 2 comment: 2. I am curious why some VOCs including isoprene showed negative diurnal photochemical reactivity. How to interpret these negative values? I understand that VOC concentrations (POCP-weighted) were scaled to ethane concentration (POCP scaled) to remove the effect of boundary layer mixing, but I don't see the reason to use the differences of day and night, in addition to weighting by ethane. Can authors reach the same conclusion if only looking at the ratio of POCP-weighted VOC concentrations/ POCP-weighted ethane? Without further discussion and justification of the method, readers would be very confused by the current version of the manuscript.

Response: The difference between night and day is required to quantify the chemical loss of the VOCs. It is this VOC reactivity which contributes to the formation of the regional O3 increment, not the quantity of VOC remaining in the air mass (which the POCPweighted VOC/ethane ratio represents). A negative diurnal photochemical reactivity indicates that POCP-weighted VOC/ethane ratio was higher in the afternoon than during the night. Clarity on the nature of negative values was also requested by Reviewer #1, and substantial changes have been made to Section 3.2 to achieve this (see response to Reviewer #1 above). The negative value occurs when the diurnal variation in POCPweighted VOC/ethane ratios is not dominated by chemical loss. This can occur for example due to diurnal variation in local emission patterns, for example biogenic isoprene emissions occur during the day. In the period 1999-2001, toluene and iso-pentane have negative values, and this is discussed on P7282 L11 in the context of previous studies which show a large decrease in emissions of these VOCs in the spatial domain of Harwell between the two study periods (1999-2001 and 2010-2012). Note that this paragraph has also been edited to improve the clarity of this explanation in response to comments by Reviewer #1.

Reviewer 2 comment: 3. How do the authors actually calculate the model-derived Photochemical Ozone Creation Potential (POCP)? The POCP seems to be a very important concept in terms of describing which VOC is more important for O3 production, however there was only very limited discussion/description on this.

Response: The authors have not directly calculated the POCPs. The methodology for deriving POCPs is comprehensively outlined in the cited work by Derwent et al. (2007a). A brief description of the process used to derive the POCPs has been added.

P7275 L19 Additional text: "In Derwent et al. (2007a), a VOC POCP was defined as the ratio (multiplied by 100) of the increase in O_3 due to increased emissions of the VOC simulated in a Lagrangian model along a trajectory traversing from central Europe to the UK, relative to the modelled increase in O_3 from the same mass increase in emissions of ethene (the reference POCP VOC assigned a value of 100)."

Reviewer 2 comment: 4. A more general comment: there are lots of acronyms as written in the manuscript, which really downgrade the readability of the paper. Also, authors seemed to describe the method to a great detail, but missed to interpret the results and provide thoughtful discussion. The paper would benefit from more discussion and interpretation of their results.

Response: The analysis required the integrated of multiple different data sources, and the rigorous consideration of issues such a censored datasets etc. Hence a detailed description of the method was necessary. Regarding interpretation of the results, it is our intention in this manuscript to focus on what can be learned from the linkage of a specific impact, the regional O_3 increment to its anthropogenic emissions drivers through interpretation of VOC measurements. To emphasise this linkage, Section 3 has been separated into three sections which consider firstly the impact, then the state of VOC measurement variation, and thirdly the meteorological and emissions drivers. We acknowledge that additional analysis could yield interesting results. For example, the O_3 record at Harwell extends

from 1983 to 2013, and therefore there is scope for a more detailed assessment of temporal changes in the regional O_3 increment at this site. However, in order to maintain the manuscript at a suitable length (the discussion paper contains 11 pages of results and discussion vs 8 pages of methodology description), and to emphasise the additional information gained from the integration of these data sources, we consider the level of results interpretation and discussion appropriate. The SOMO35 and POD_Y acronyms are standard in the fields of impacts of ozone on health and vegetation, respectively.

In the revised manuscript the relevance of the statistics presented is more clearly explained due to the recommendation of Reviewer #1 to have frequent 'guiding sentences' and additional clarity in the explanation of key concepts. This aids in the interpretation of results and improves the readability of this work.

Reviewer 2 comment: 5. I suggest that authors include a table showing the 27 VOCs with their chemical formula, main sources, and recommended OH reaction rates. This would be helpful for guiding the readers especially for those who are not familiar with a menagerie of hydrocarbons.

Response: A table has been added to the manuscript as outlined in the comment (included at the end of this document).

Specific comments:

Reviewer 2 comment: P7269, lines 20-25: here and later, what are the SOMO35, PODY and EU27? Should readers care about them? The acronyms really limited the smoothness and readability of the paper.

Response: SOMO35 is a health-relevant O_3 impact metric in line with the World Health Organisation (WHO) recommendations for the quantification of health-relevant O_3 . POD_Y is a flux-based method for quantifying the 'Phytotoxic O_3 Dose', i.e. the uptake of damaging O_3 by a specific plant species. We consider the current phrasing sufficient for the reader to infer, even without familiarity, that they are metrics for the quantification of health and vegetation-relevant O_3 . Full descriptions of these metrics are given in Gauss et al. (2014).

Reviewer 2 comment: P7283 line 25 and P7284 line 7: here and other places, these two sentences are repeating themselves.

Response: Text has been amended to avoid repetition.

P7284 L7 Original text: "The change in contribution from the 11 SNAP sectors to average VOC TEE between 2001 and 2011 at Harwell is shown in Fig. 8. The biggest change was for SNAP 7 (road transport), which averaged 31 % of the total 10 VOC TEE in 2001, compared to 9 % in 2011."

P7284 L7 Amended text: "The biggest change in contribution from the 11 SNAP sectors to average VOC TEE between 2001 and 2011 at Harwell was for SNAP 7 (road transport), which averaged 31 % of the total 10 VOC TEE in 2001, compared with 9 % in 2011 (Figure 8)."

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Additional tables and figures added to the manuscript:

Table 1: Summary data for the measured VOCs at Auchencorth and Harwell (note that m-xylene and p-xylene are reported as a single measurement). The rate coefficients at 298 K for reactions of each VOC with OH are taken from Atkinson and Arey (2003), and the POCPs are from Derwent et al. (2007a). The 'main source' column gives the SNAP sector with the largest contribution of that VOC to UK annual anthropogenic emissions in 2011 with the exception of isoprene which is mainly of biogenic origin (defined in Section 2.3). The listed SNAP sectors are SNAP 2: Non-industrial combustion plants, SNAP 4: Production processes, SNAP 5: Extraction and distribution of fossil fuels, SNAP 6: Solvent use, SNAP 7: Road transport and SNAP 8: Non-road transport.

VOC	Class	Chemical Formula	Main source	OH reaction rate constant (10 ¹² x k (298 K) (cm ³ molecule ⁻¹ s ⁻¹))	POCP
ethane	alkane	C ₂ H ₆	SNAP 5 (65%)	0.248	8
propane	alkane	C ₃ H ₈	SNAP 5 (36%)	1.09	14
n-butane	alkane	C4H10	SNAP 6 (44%)	2.36	31
isobutane	alkane	$C_{4}H_{10}$	SNAP 5 (61%)	2.12	28
n-pentane	alkane	C5H12	SNAP 5 (42%)	3.80	40
isopentane	alkane	C5H12	SNAP 5 (41%)	3.60	34
n-hexane	alkane	$C_{6}H_{14}$	SNAP 6 (42%)	5.20	40
2-methylpentane	alkane	C ₆ H ₁₄	SNAP 6 (43%)	5.20	41
n-heptane	alkane	C7H16	SNAP 5 (43%)	6.76	35
n-octane	alkane	C ₈ H ₁₈	SNAP 5 (64%)	8.11	34
isooctane	alkane	C ₈ H ₁₈	SNAP 4 (100%)	3.34	25
ethene	alkene	C_2H_4	SNAP 8 (27%)	8.52	100
propene	alkene	C ₃ H ₆	SNAP 4 (36%)	26.3	117
1-butene	alkene	C_4H_8	SNAP 7 (26%)	31.4	104
cis-2-butene	alkene	C ₄ H ₈	SNAP 5 (87%)	56.4	113
trans-2-butene	alkene	C ₄ H ₈	SNAP 5 (90%)	64.0	116
1,3-butadiene	alkene	C ₄ H ₆	SNAP 8 (57%)	66.6	89
isoprene	alkene	C ₅ H ₈	biogenic	100	114
ethyne	alkyne	C_2H_2	SNAP 7 (46%)	0.78	7
benzene	aromatic	C_6H_6	SNAP 2 (35%)	1.22	10
toluene	aromatic	C ₇ H ₈	SNAP 6 (63%)	5.63	44
ethylbenzene	aromatic	C_8H_{10}	SNAP 6 (54%)	7.0	46
o-xylene	aromatic	C_8H_{10}	SNAP 6 (50%)	13.6	78
m-xylene	aromatic	C_8H_{10}	SNAP 6 (71%)	23.1	86
p-xylene	aromatic	C_8H_{10}	SNAP 6 (50%)	14.3	72
1,2,3-trimethylbenzene	aromatic	C ₉ H ₁₂	SNAP 6 (79%)	32.7	105
1,2,4-trimethylbenzene	aromatic	C ₉ H ₁₂	SNAP 6 (74%)	32.5	110
1,3,5-trimethylbenzene	aromatic	C ₉ H ₁₂	SNAP 6 (71%)	56.7	107

Figure 2: Flowchart demonstrating the process used to calculate the contribution of 630 individual VOCs to the monthly total VOC trajectory emissions estimate (TEE, defined in Section 2.3). The green rectangles represent products or datasets, and the blue rounded rectangles represent processes applied to transform a dataset. Further explanation is provided in Section 2.3.



Figure 3: Flowchart representing the process used to derive the contribution from NFR codes to monthly trajectory emissions estimates (TEE, defined in Section 2.3). The green rectangles represent products or datasets, and the blue rounded rectangles represent processes applied to transform a dataset. Note that the separation of the TEE into contributions from two countries is illustrative, and in most cases a greater number of countries contributed to the TEE in a given month. Further explanation is provided in Section 2.3.



Figure 11 (Figure 9 in original manuscript): Summary of variables relevant to the assessment of the effect of variation in the proportion of emissions accumulated close (temporally) to the monitoring site: a) The final 4 hours TEE metric, i.e. the proportion of the TEE emitted into the air mass during the 4 hours prior to arrival at the site (defined in Section 3.3.2, b) Monthly average sum of measured VOCs, c) Monthly average sum of VOC diurnal photochemical depletion, d) Monthly maximum difference between hemispheric background concentrations and regional background concentrations (a positive value indicates additional regional O₃ production).



Marked-up version of revised manuscript:

- The impact of speciated VOCs on regional ozone increment 1 derived from measurements at the UK EMEP supersites 2 between 1999 and 2012 3 4 5 Christopher S. Malley,^{1,2} Christine F. Braban¹, Peter Dumitrean³, J. Neil Cape¹ 6 and Mathew R. Heal² 7 8 [1] {NERC Centre for Ecology & Hydrology, Edinburgh, United Kingdom} 9 [2] {School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom} [3] {Ricardo-AEA, Didcot, United Kingdom}
- 10
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1 Abstract

The impact of 27 volatile organic compounds (VOC) on the regional O₃ increment was 2 investigated using measurements made at the UK EMEP supersites Harwell (1999-2001 and 3 4 2010-2012) and Auchencorth (2012). Ozone at these sites is representative of rural O₃ in southeast England and northern UK, respectively. Monthly-diurnal regional O₃ increment was 5 defined as the difference between the regional and hemispheric background O3 concentrations, 6 respectively derived from oxidant versus NO_x correlation plots, and cluster analysis of back 7 trajectories arriving at Mace Head, Ireland. At Harwell, which had substantially greater 8 regional ozone increments than at Auchencorth, variation in the regional O₃ increment mirrored 9 afternoon depletion of anthropogenic VOCs due to photochemistry (after accounting for 10 diurnal changes in boundary layer mixing depth, and weighting VOC concentrations according 11 to their photochemical ozone creation potential). A positive regional O₃ increment occurred 12 consistently during the summer, during which time afternoon photochemical depletion was 13 calculated for the majority of measured VOCs, and to the greatest extent for ethene and m+p-14 15 xylene. This indicates that, of the measured VOCs, ethene and m+p-xylene emissions reduction would be most effective in reducing the regional O₃ increment, but that reductions in a larger 16 17 number of VOCs would be required for further improvement.

18 The VOC diurnal photochemical depletion was linked to the anthropogenic sources of the VOC emissions through the integration of gridded anthropogenic VOC emissions estimates over 96-19 hour air-mass back trajectories. This demonstrated that one factor limiting the effectiveness of 20 VOC gridded emissions for use in measurement and modelling studies is limited by the highly 21 aggregated nature of the 11 SNAP source sectors in which they are reported, as monthly 22 variation in speciated VOC trajectory emissions did not reflect monthly changes in individual 23 VOC diurnal photochemical depletion. Additionally, the major VOC emission source sectors 24 25 during elevated regional O₃ increment at Harwell were more narrowly defined through disaggregation of the SNAP emissions to 91 NFR codes (i.e. sectors 3D2 (domestic solvent 26 27 use), 3D3 (other product use) and 2D2 (food and drink)). However, spatial variation in the 28 contribution of NFR sectors to parent SNAP emissions could only be accounted for at the 29 country level. Hence, the future reporting of gridded VOC emissions in source sectors more highly disaggregated than currently (e.g. to NFR codes) would facilitate a more precise 30 31 identification of those VOC sources most important for mitigation of the impact of VOCs on 32 O₃ formation.

In summary, this work presents a clear methodology for achieving a coherent VOC regional O₃-impact chemical climate using measurement data and explores the effect of limited
 emission and measurement species on the understanding of the regional VOC contribution to
 O₃ concentrations.

5

6 1 Introduction

7 Production of ground-level ozone (O_3) is dependent on concentrations of NO_x (NO and NO₂), 8 methane, carbon monoxide, and volatile organic compounds (VOCs) (Jenkin and Clemitshaw, 9 2000). The formation of O₃ causes substantial deleterious human health and environmental impacts worldwide (RoTAP, 2012; REVIHAAP, 2013). Development of policies for the 10 11 mitigation of these impacts requires understanding of the influences on O₃ concentrations from local, regional and hemispheric scale processes. The range in VOC atmospheric lifetimes from 12 13 a few hours to several days (Atkinson, 2000) means that the major fraction of the VOC impact 14 on O₃ production occurs on the regional scale of air-mass movements. At the regional scale, 15 Gauss et al. (2014) modelled the reductions in O_3 impact across Europe on human health (using 16 the SOMO35 metric) and vegetation (using the deciduous forest POD_Y metric) resulting from 15% reductions in EU27 anthropogenic NOx and VOC emissions across the EU and showed 17 that VOC emissions reductions were more effective than NO_x emissions reductions in reducing 18 the O₃ impact metrics across much of north-west Europe. Hence knowledge of the contribution 19 20 of individual VOCs to O₃ production on the European (regional) scale will enable targeting of the most effective VOC reductions for reducing regionally-derived O₃ exposure relevant to O₃ 21 22 impacts.

23 Within Europe, the European Monitoring and Evaluation Programme (EMEP) makes in-situ atmospheric composition measurements at sites considered to have minimal influence from 24 25 local emissions sources (Torseth et al., 2012). The UK operates two EMEP Level II monitoring 26 sites (or 'supersites'), Auchencorth and Harwell, at which hourly concentrations of O_3 , NO_x 27 and 27 VOCs are measured. In this work, chemical climates (defined in Malley et al. (2014a)) are derived to quantify the impact of the measured VOCs on the regional increment of O₃ 28 29 concentrations (the difference between regional background and hemispheric background O₃ concentrations) measured at Harwell and Auchencorth. Full definitions of each of these O₃ 30 quantities are given in Section 2.1. Monthly-diurnal O₃ variation at the EMEP supersites has 31 32 previously been shown to be representative of wider geographical areas, namely rural background air of south-east England and northern UK for the Harwell and Auchencorth UK
 supersites, respectively (Malley et al., 2014b).

The interpretation of VOC measurements at rural sites has previously been undertaken using 3 4 Positive Matrix Factorisation (PMF) (Lanz et al., 2009), trajectory analysis (Sauvage et al., 2009), VOC variability as a measure of source proximity (Jobson et al., 1999), winter/summer 5 VOC ratios to indicate changing emissions sources (Jobson et al., 1999), and the ratio of VOCs 6 with similar reactivity to highlight changes in emission sources (Yates et al., 2010). These 7 8 studies identified VOC emissions sources based on measured VOC concentrations. However, the 'state' of atmospheric composition variation producing a regional O₃ increment above 9 10 hemispheric background concentrations is more rigorously evaluated by considering the chemical loss of the measured VOCs, since it is the VOC chemical loss in the air mass that 11 drives the production of a regional O₃ increment, not the VOC concentration remaining in the 12 13 air mass. In urban environments, the chemical loss of VOCs has been calculated by estimating 14 OH exposure through the estimation of the VOC suite, allowing calculation of the initial 15 emission ratioratios of two VOCs, and calculation of photochemical age through parameters such as 'OH exposure' or 'VOC consumption' (Shao et al., 2009; Yuan et al., 2012). This 16 17 method is not appropriate for rural studies since it assumes that local sources dominate emissions. 18

19 In this work, monthly averaged diurnal variations of individual VOC concentrations relative to ethane were used to assess the photochemical loss of each VOC and its contribution to the 20 regional O3 increment at Harwell and Auchencorth. The magnitude of VOC chemical loss at 21 each site was linked to In this work, monthly-averaged diurnal variations of individual VOC 22 concentrations relative to ethane were used to assess the photochemical loss of each VOC and 23 24 its contribution to the regional O₃ increment at Harwell and Auchencorth. Monthly-diurnal 25 averaging was chosen as the annual and daily cycles are key features of O₃ variability 26 associated with the driving processes on its concentrations and on its impact. For example, the 27 monthly and diurnal variation in O₃ is central to determining the extent and spatiotemporal 28 trends in health and vegetation-relevant O₃ metrics (Malley et al., 2015). Ozone variability at 29 hundreds of monitoring sites globally has also been characterised based on monthly-diurnal variation (Tarasova et al., 2007). Monthly-diurnal averaging was therefore also appropriate for 30 31 setting this work in the wider context, especially given the relative scarcity of hourly VOC 32 measurements. The magnitude of VOC chemical loss at each site was linked to anthropogenic 33 emissions by estimating the integrated VOC emissions along 96-hour air-mass back

1 trajectories. These emissions, from the 11 Selected Nomenclature for Air Pollution (SNAP, EEA (2013)) source sectors, were speciated to compare observed VOC variation with an 2 3 estimate of individual VOC integrated back-trajectory emissions. Integration of emissions, VOC chemistry and O₃ production has been reported previously for one location in the UK 4 5 using a photochemical trajectory model with a near-explicit chemical mechanism for a large suite of VOCs (Derwent et al., 2007b, a2007a, b). The advantage of the methodology presented 6 7 here, based on measurement data, is that uncertainties associated with the speciation of VOC 8 emission source categories can be identified. A country-specific disaggregation of emissions 9 into 91 more narrowly defined Nomenclature for Reporting (NFR, EEA (2013)) source sectors was used to determine more precisely the activities contributing to VOC back-trajectory 10 emissions estimates. This current work presents a clear methodology for achieving a coherent 11 VOC regional-O₃-impact chemical climate and explores the effect of limited emission and 12 measurement species on the understanding of the regional contribution to O₃ concentrations. 13

14

15 2 Methodology

16 The methodology is separated into the three elements of a chemical climate, the impact (here, the regional O₃ increment), state (VOC diurnal photochemical depletion) and drivers 17 (meteorology and emissions) as defined in Malley et al. This work was undertaken by applying 18 the chemical climatology framework outlined in Malley et al. (2014a). A chemical climate is 19 derived through the linkage of a specific 'impact' of atmospheric composition (here, regional 20 O₃ increment), through the 'state' of relevant atmospheric composition variation (VOC diurnal 21 photochemical depletion) to its causal 'drivers' (meteorology and emissions). The aim of this 22 framework is to provide a consistent method for both consideration of impact severity and the 23 conditions producing it, hence highlighting pathways for mitigation. The Methods and Results 24 sections are subdivided into impact (Section 2.1 and 3.1 for Methods and Results respectively), 25 26 state (Section 2.2 and 3.2) and drivers (Section 2.3 and 3.3) to emphasise the analyses used to derive the components of the chemical climate. Analyses were undertaken for the periods 1999-27 28 2001 and 2010-2012 at Harwell and 2010-2012 at Auchencorth. Measured data were obtained 29 from UK-AIR (http://uk-air.defra.gov.uk/) and EMEP (http://ebas.nilu.no/). For each year, the 30 monthly-averaged diurnal cycles of each atmospheric component were calculated, i.e. 24×12 31 = 288 values per year.

32

1 2.1 Regional O₃ increment impact

2 The regional O₃ increment is defined as the regional background O₃ concentrations minus the hemispheric background O₃ concentration. Here, regional background O₃ concentration is 3 4 defined as that which is imported into a local spatial domain, such as the two shown previously 5 to be represented by the O₃ measurements at Auchencorth and Harwell (Malley et al., 2014b), following the modification of hemispheric background O₃ concentrations by European 6 7 emissions. following modification of hemispheric background O₃ concentrations by European emissions. Examples of local spatial domains are south-east England and northern UK for 8 9 which, based on monthly-diurnal O3 variation, Harwell and Auchencorth respectively were 10 shown previously to be representative (Malley et al., 2014b). The hemispheric background O₃ concentration is in turn defined as that which is imported into the European domain, with 11 12 minimal influence from European emissions.

Hemispheric background O₃ concentrations were derived by applying Ward's method 13 14 hierarchical cluster analysis to pre-calculated 96-h air-mass back trajectories arriving at 3-h intervals at Mace Head, Ireland (R Core Development Team, 2008;Carslaw and Ropkins, 15 16 2012; Draxler and Rolph, 2013), to identify periods with no European influence. The discrimination achieved by cluster analysis may be influenced by user choices but the method 17 18 used here was shown to be the most accurate of commonly used clustering techniques 19 (Mangiameli et al., 1996). In Ward's method, each object (back trajectory) initially constitutes its own cluster. The algorithm then calculates which two clusters, when merged, gives the 20 smallest increase in total within-cluster variance. The process is repeated until all trajectories 21 are located in one cluster (Kaufman and Rousseeuw, 1990). The dendrogram summarising the 22 cluster merging process is then 'cut' at an appropriate level to produce the cluster set. The aim 23 is to maximise explained inter-trajectory variability using a small number of clusters to 24 highlight major distinctions between trajectory paths. The distance between a trajectory and its 25 cluster mean was quantified using the two-dimensional 'angle' of each trajectory (or cluster 26 27 mean trajectory) from the origin (i.e. the supersite) at common time points along the trajectory:

28

29

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

30

31 where

1
$$A_i = (X_1(i) - X_0)^2 + (Y_1(i) - Y_0)^2$$

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

3
$$C_i = (X_2(i) - X_1(i))^2 + (Y_2(i) - Y_1(i))^2$$

 $d_{1,2}$ is the distance between trajectory 1 and trajectory 2, X_0, Y_0 are the latitude and longitude 4 5 coordinates of the origin of the trajectory, and $X_1(i), Y_1(i)$, and $X_2(i), Y_2(i)$ are the coordinates at 6 time *i* of trajectories 1 and 2 respectively. The 2920 back trajectories arriving at Mace Head 7 each year were separated into four clusters. The monthly-diurnal cycles of O₃ concentrations for the westerly trajectory cluster were used as the estimate of hemispheric background O₃. 8 9 These values showed excellent agreement with the monthly average hemispheric background estimates derived by Derwent et al. (2007c) using Mace Head O₃ data and a combination of 10 11 pollutant tracers and atmospheric modelling to select 'clean' air masses (r = 0.93, p < 0.001, 12 Figure 1).

Regional background O₃ concentrations were estimated using the method of Clapp and Jenkin 13 (2001). In the region of south-east England characterised by the Harwell supersite nine 14 locations, ranging from rural background to kerbside, had hourly measurements of O₃, NO and 15 NO₂. The y-intercept of the linear fit to a total oxidant $(O_3 + NO_2)$ vs NO_x $(NO + NO_2)$ plot 16 yields the NO_x-independent oxidant contribution, interpreted as the regional background O₃ 17 18 concentration, i.e. the contribution to O_3 within south-east England from processes occurring 19 outside south-east England. Extraction of the *y*-intercept from an oxidant vs NO_x plot for each of the 288 'month-hour' averages yielded the monthly-diurnal cycle of regional background 20 21 O₃ variation in south-east England. The difference between the hemispheric background and regional background O₃ concentrations provided the magnitude and direction of the regional 22 23 modification to hemispheric background O₃ concentration. A positive regional O₃ increment indicates additional O₃ formation regionally in excess of hemispheric background 24 25 concentrations, and vice versa.

The spatial domain for which Auchencorth is representative does not have sufficient co-located NO_x and O₃ monitoring sites to derive regional background O₃ concentrations by the above method. The regional O₃ increment at Auchencorth was therefore estimated by subtracting the Mace Head hemispheric background estimates directly from the Auchencorth monthlyaveraged diurnal concentrations.

31

1 2.2 State

2 VOC concentrations were determined by automated gas chromatography (Dernie and Dumitrean, 2013). For 2010-2012, data were available for 27 species; for 1999-2001 (at both 3 4 Harwell), data were available for only 21 of these VOCs. and Auchencorth. Concentrations of 5 6 VOCs at Auchencorth <u>during this period</u> were not above the reported limit of detection (LOD) so their contribution to the regional O3 increment was not evaluated. For 1999-2001, data were 6 available for 21 VOCs at Harwell only. 7 The VOC datasets had extensive periods induring which concentrations were below LOD, 8 9 particularly at Auchencorth- (e.g. between 6% and 81% below LOD at Harwell in 2011, and 10 between 11% and 82% at Auchencorth). Therefore maximum likelihood estimation (MLE) was used to fit three positively-skewed distributions (lognormal, gamma and Weibull) to the dataset 11 12 for each VOC (Helsel, 2006;Gardner, 2012). The Akaike Information Criterion (AIC) was then

used to select the distribution which best fitted the data; this provides a relative estimate of the information lost when a given distribution is used to represent a dataset (Akaike, 1974). This process was performed on data for each month of the year, and separately for the 288 monthlydiurnal time periods. The fitted distributions estimated the probability that a 'non-detect' (below the LOD) was a concentration in the range 0 μ g m⁻³ to the LOD.

When non-detects occurred for all VOCs in a particular hour, these were excluded from the 18 MLE analysis on the assumption that this was due to instrument failure. To avoid the 19 20 unnecessary omission of valid concentration measurements, all other data were used, and 21 consequently all remaining non-detects were assumed to be values below LOD. A number of 22 non-detects due to the selective failure of the instrument to measure a particular VOC may be 23 falsely considered to be below the LOD. However, the following evidence indicates that any 24 bias introduced is likely to be small. Annual medians were calculated twice using MLE for Harwell in 2011, first, with the non-detects unique to each VOC, secondly with their omission 25 26 (i.e. assuming all these non-detects were due to reasons other than LOD). The increase when omitted was below 10% for 11 of the 27 VOCs, including the VOCs with concentrations 27 consistently well above the LOD. For example, the 5th percentile concentrations (of all valid 28 concentrations) of propane, ethane and toluene were 1200%, 800% and 175% above the LOD, 29 30 and consequently the number of unique non-detects was relatively low (4%, 2% and 1% of values respectively). The increase when the unique non-detects were omitted was 10%, 8% and 31 3% for propane, ethane and toluene respectively. Other VOCs had a 5th percentile concentration 32 much closer to the LOD, increasing the likelihood of periods during which concentrations were 33

below LOD. For nine of the 10 VOCs with the largest annual median increase, the 5th percentile
 concentration was the LOD.

3 In summary, for those VOCs with few unique non-detects, the potential inclusion of non-LOD 4 -related non-detects results resulted in a small change in calculated concentration, while VOCs with a larger proportion of non-detects havehad concentrations more frequently close to the 5 LOD, increasing the likelihood that the unique non-detects result from concentrations below 6 the LOD. resulted from concentrations below the LOD. This indicates that the decision to assign 7 8 all unique non-detects as values below the LOD was justified, as the potential bias introduced was small, and therefore that the maximum of valid VOC concentration data was preserved 9 10 and used in the MLE distribution calculations. Intra-annual and monthly-diurnal variation in 11 VOC concentrations were summarised using the monthly median concentrations and the 24 hourly median concentrations for each month from the best-fit distributions respectively. 12 For each VOC, each of the 288 median monthly-diurnal concentrations was multiplied by the 13 14 corresponding model-derived **Photochemical Photochemical** Ozone Creation Potential (POCP) (Derwent et al., 2007b)(Derwent et al., 2007a), to weight the observed diurnal variation of 15 16 VOCs according to their different propensities for O₃ formation. In Derwent et al. (2007a), a 17 VOC POCP was defined as the ratio (multiplied by 100) of the increase in O₃ due to increased 18 emissions of the VOC simulated in a Lagrangian model along a trajectory traversing from 19 central Europe to the UK, relative to the modelled increase in O₃ from the same mass increase in emissions of ethene (the reference POCP VOC assigned a value of 100). Multiple studies 20 have calculated reactivity scales of O₃ production potential (OPP) for a range of VOCs using 21 22 incremental reactivity methods (Luecken and Mebust, 2008;Derwent et al., 23 2007b2007a;Hakami et al., 2004;Martien et al., 2003), multi-parent assignment (Bowman, 2005) and 'tagging' of VOC degradation sequences (Butler et al., 2011). These varying 24 25 methods were shown to be generally well correlated (Butler et al., 2011;Luecken and Mebust, 26 2008; Derwent et al., 2010). The Derwent et al. (2007b)(2007a) POCPs are appropriate to use in this study as they were calculated under simulated north-western European conditions. 27 28 Previous comparison with other VOC reactivity scales indicated uncertainty in POCP values 29 up to \pm 5 POCP units which equates to an average of \pm 15% for the measured VOCs in this 30 study (Derwent et al., 2007b).

The diurnal variation of individual VOCs due to photochemical depletion was summarised by calculating the ratio of each POCP-weighted VOC concentration to the POCP-weighted ethane concentration. Ethane has the second smallest POCP of the measured VOCs, 87_% smaller than

the average, and 20 % smaller than the next smallest POCP (benzene), so using this ratio 1 2 removed the effect on diurnal VOC concentration of changes in boundary layer mixing depth. The VOC with smallest POCP, ethyne, had low data capture at Harwell between 1999 and 3 4 2001 (maximum 57% in 2001). Additionally, ethane has a smaller rate coefficient for reaction with OH compared with ethyne (Table 1), and the POCPs were similar (7 for ethyne vs 8 for 5 6 ethane). Ratios of VOC/ethane have been used previously to estimate the photochemical loss 7 of VOCs (Yates et al., 2010;Helmig et al., 2008;Honrath et al., 2008). It is also assumed that 8 the diurnal variation of VOC at the site is not driven by differences in the magnitude of VOC 9 emissions which determine VOC concentrations measured at the sites do not differ substantially between along the trajectories contributing VOC to that site during the day and at 10 night. This can be evaluated from verified by the similar monthly median VOC emissions 11 emitted along the path of 96-h trajectories (outlined in sectionSect. 2.3) arriving at night (3am)3 12 13 <u>a.m.</u>) and afternoon (3pm), which were generally similar. <u>3 p.m.</u>). For example, at Harwell in 2011, night trajectory VOC emissions were no more than ± 12 % compared to-different from 14 afternoon. Hence a daytime decrease in POCP-weighted VOC/ethane ratio indicates greater 15 photochemical depletion of the VOC relative to ethane. The magnitude of diurnal 16 photochemical variability for each VOC was derived from the difference between the average 17 18 POCP-weighted VOC/ethane ratio at night (1 am - 5 am) and in the afternoon (1 pm - 5 pm). 19 A positive value indicates daytime photochemical depletion of the VOC relative to ethane. The sum of positive daytime photochemical depletion of individual VOCs produces the total VOC 20 21 diurnal photochemical depletion for each month. The monthly pattern of total VOC diurnal photochemical depletion was compared with the monthly pattern of the regional O₃ increment. 22 23 During those months with a positive regional O₃ increment, the relative contribution of each VOC to total VOC photochemical depletion was used as an estimate of the relative contribution 24 25 of each VOC to the VOC chemical loss which contributed to the production of the positive 26 regional O₃ increment.

At Auchencorth, the analysis of VOC diurnal photochemical depletion was not possible in 2010 and 2011 due to low data capture, which compromises the ability of MLE to accurately estimate median VOC concentrations. This is particularly important for ethane, as a large error in the fitted distribution for ethane propagates to all VOC/ethane ratios. In 2011, the average proportion of non-detects for the measured VOCs was 56% when the 6 VOCs with no measurements above LOD were excluded (34% for ethane). In 2012 this decreased to 34% (10% for ethane), and VOC diurnal photochemical depletion was calculated. For comparison, at Harwell, there were on average 26% non-detects for each VOC species in 2011 (7% for
ethane).

3

4 **2.3 Drivers**

5 The two main drivers producing the 'state' of this chemical climate, i.e. VOC diurnal photochemical depletion, which are considered here are meteorology and VOC 6 7 emissions.anthropogenic VOC emissions. Other drivers such as biogenic VOC emissions, and 8 NO_x concentrations are drivers of the regional O₃ increment. Meteorology and anthropogenic 9 VOC emissions are the focus due to the benefits previously outlined in improvement in health and vegetation-relevant O₃ impacts that result from anthropogenic VOC emission reductions. 10 11 The meteorology was characterised by monthly mean, maximum and minimum temperature, and number of hours of sunshine for Harwell and Auchencorth obtained from the UK Met 12 13 Office climate summaries for 'South East and Central South England' and 'East Scotland', respectively (http://www.metoffice.gov.uk/climate/uk/datasets/#) (Perry and Hollis, 2005). 14 To investigate geographical emissions sources, the locations of each of the 96 hourly time 15 points of the 2920 HYSPLIT 96-h back trajectories arriving at 3 h intervals per year were 16 mapped to the $0.5^{\circ} \times 0.5^{\circ}$ gridded VOC emissions reported by EMEP and used in the EMEP 17 model (Mareckova et al., 2013;Simpson et al., 2012). This grid encompasses the region 18 30.25°N - 75.25°N and 29.75°W - 60.25°E, and the emissions in each grid square are 19 disaggregated 11 **SNAP** 20 into source sectors (http://ceip.at/ms/ceip_home1/ceip_home/webdab_emepdatabase/emissions_emepmodels/). 21 When the location of the trajectory during a particular hour fell within the gridded domain, the 22 annual emissions and country of the grid square over which the trajectory was located were 23 assigned to that time point. Emissions were assigned to the country which had the greatest 24 emissions when the grid square straddled an international border. Annual emissions were 25 modified by prescriptive month, day-of-week and hour-of-day time factors (Simpson et al., 26 2012) to obtain an estimate of the hourly emissions from each SNAP sector during the hour in 27 which the trajectory passed over the grid cell. The monthly average hourly SNAP emission 28 estimates at each of the 96 1 h time points were summed to give the average European VOC 29 emissions estimate of all the trajectories arriving in that month (henceforth the VOC trajectory 30 31 emissions estimate (TEE)), and the proportions derived from individual countries.

1 The total VOC TEE from the 11 SNAP sectors were speciated using the 114 VOC speciated 2 profiles from Passant (2002) to quantify the proportion of emissions emitted as one of the 27 measured VOCs. The profiles were first applied to UK annual emissions to obtain speciated 3 profiles for each SNAP sector which could be applied to the VOC TEEs. Each year, at the most 4 5 disaggregated level, the UK National Atmospheric Emissions Inventory (NAEI) reports total VOC emissions for 337 source activities (http://naei.defra.gov.uk/data/) (Passant et al., 2013). 6 7 In Passant (2002), each of these activities is assigned one of the 114 speciation profiles which 8 in total consider the contribution from 630 VOCs, including aggregated groups of VOCs, for 9 example, 'C7 alkanes'. The total annual UK emissions for each activity were apportioned between the VOCs in the assigned profile. This resulted in a matrix of 337 columns of source 10 activities, and 630 rows of VOCs. Activities were then grouped into the 55 NFR codes used by 11 NAEI, and then into SNAP sectors 1-9 based on the NFR-SNAP conversion recommended by 12 EMEP 13 the Centre Emission Inventories Projections (CEIP, for and http://www.ceip.at/fileadmin/inhalte/emep/pdf/nfr09_to_snap.pdf). There were no reported 14 VOC emissions from activities falling under SNAP 10 (agriculture) and SNAP 11 (other). The 15 relative contribution of each VOC to total annual UK SNAP emissions was calculated to 16 17 provide speciated emissions profiles which were used to speciate the monthly SNAP sector 18 VOC TEEs. This produced an estimate of the contribution to total monthly VOC TEE from 19 630 VOCs- (Figure 2). This contribution was then multiplied by the VOC's POCP to weight it 20 according to O₃ formation potential.

The EU emissions inventory disaggregates annual emissions from SNAP sectors 1-9 into 91 NFR codes for each EU member state (EEA, 2014). The monthly change in the SNAP sector VOC TEE was attributed to changes in the contribution from the more narrowly defined NFR codes, based on the country-specific contributions of each NFR sector to annual SNAP sector emissions. The VOC TEE from each of the 91 NFR codes for each country were summed across all countries to obtain the contribution of each NFR code to the total VOC TEE for each month-(Figure 3).

The emission inventories used in this study have several sources of uncertainty (EEA, 2013). The $0.5^{\circ} \times 0.5^{\circ}$ (EEA, 2013;Koohkan et al., 2013). The $0.5^{\circ} \times 0.5^{\circ}$ grid squares mean that numerous distinct sources, each with uncertainties in emission factors and activity rates, are aggregated together to produce the estimate of emissions from a particular SNAP or NFR source sector. The size of the grid square also does not necessarily reflect the size of the area from which emissions influence the atmospheric composition of the trajectory air mass as it 1 passes over. The VOC TEE is therefore used as a relative comparison spatially and temporally, rather than a definitive quantification of the VOC emissions emitted into an air mass. In 2 3 addition, there are uncertainties in the speciation of total VOC emissions to individual components (Borbon et al., 2013). (Borbon et al., 2013). However, the emissions inventories 4 5 used here are the best estimate of the spatial distribution of anthropogenic VOC emissions 6 across Europe. While studies have shown discrepancies between the EMEP emission inventory 7 and other estimates of European emissions (Koohkan et al., 2013), EMEP gridded emissions have also been shown previously to capture variation in VOC measurement data (Sauvage et 8 9 al., 2009; Derwent et al., 2014)

10

11 3. Results and Discussion

3.1 Impact: regional O₃ production/destruction assessment

The difference between hemispheric background O₃ concentrations and regional background 13 O₃ concentrations relevant for Harwell for 2001 (representative of 1999-2001), 2011 14 (representative of 2010-2012) and for Auchencorth in 2012 is shown in Figure 24. Although 15 there was inter-annual variability within each time period, the data for these years illustrate the 16 main differences between three different phases of the regional O₃ increment chemical climate 17 both temporally at Harwell (1999-2001 vs 2010-2012) and spatially (Harwell vs Auchencorth). 18 19 At Harwell in 2001, a positive regional O₃ increment occurred in each month between May and September (Figure 2a4a). The annual maximum regional O₃ increment (i.e. the difference 20 21 between hemispheric background and regional background O₃ concentrations) occurred in the afternoon in July 2001 (42 μ g m⁻³), while monthly regional O₃ increments peaked in excess of 22 20 µg m⁻³ in June and August, and in excess of 10 µg m⁻³ in May and September. A similar 23 pattern occurred in 2000, but with a lower annual maximum (26 µg m⁻³ in July). In 1999, 24 regional ozone production was greater, extending from April to September with the annual 25 maximum in July (53 μ g m⁻³), and production in excess of 30 μ g m⁻³ in June and August. In 26 2011 at Harwell positive regional O₃ increments occurred between April and September 27 (Figure 2b4b), but their magnitudes were reduced compared with the 1999-2001 phase. Only 28 two months, April and July, had maximum regional O₃ increments >10 μ g m⁻³ (11 μ g m⁻³ and 29 $32 \ \mu g \ m^{-3}$, respectively). In 2012, the monthly regional O₃ increment exceeded 10 $\mu g \ m^{-3}$ in 30 May (12 µg m⁻³), July (28 µg m⁻³) and August (11 µg m⁻³), and occurred more modestly in 31 April, June and September. In 2010, the regional O₃ increment in June was 24 µg m⁻³, which 32

then decreased in July (19 μ g m⁻³). Reductions in regional O₃ have been reported in the UK previously, using high percentile O₃ concentrations as an indicator of regionally-derived episodes, rather than calculation of the average monthly-diurnal regional O₃ increment. For example, Munir et al. (2013) attributed negative trends in highest O₃ concentrations calculated at 22 UK monitoring sites (13 sites with significant trends) to regional reduction in O₃ precursor emissions between 1993 and 2011.

The regional O₃ increments at Auchencorth were substantially lower than at Harwell. Between 2010 and 2012, the maximum regional O₃ increment observed was 14 μ g m⁻³ in July 2011. In 2012 (Figure <u>2c4c</u>), the maximum regional O₃ increment was 4 μ g m⁻³. The spatial differences in the extent of regional contribution to O₃ variation at Harwell and Auchencorth are consistent with a previous study of rural UK O₃ spatial variability (Jenkin, 2008).

12

3.2 State: VOC concentration and chemical depletion

The monthly median concentrations of the 27 VOCs measured at Harwell and Auchencorth 14 15 have a pronounced seasonal cycle with highest total summed VOC concentrations in winter at each site, albeit with concentrations at Auchencorth substantially lower than at Harwell (Figure 16 35 shows an example year for each of the three periods). Monthly variation was lower at 17 Auchencorth: the difference between minimum and maximum monthly total median VOC 18 concentrations at Auchencorth in 2012 was 6.2 µg m⁻³, compared with 9.5 µg m⁻³ and 13.1 µg 19 m⁻³ at Harwell in 2011 and 2001 respectively. Monthly median total VOC concentrations at 20 Harwell in 1999-2001 and 2010-2012 were similar in winter months (Jan, Feb, Dec), and 21 generally ranged between 6 μ g m⁻³ and 18 μ g m⁻³. In summer (Jun, Jul, Aug) between 1999 22 and 2001, total VOC concentrations were between 5 and 13 µg m⁻³, but between 2010 and 23 2012, concentrations were lower, between 3 and 6 µg m⁻³, and only June 2010 had higher total 24 VOC concentrations than the summer month in 1999-2001 with the lowest total VOC 25 concentration. In 2001 six VOCs were not measured, and these constituted between 2.1% and 26 27 7.4% of monthly total measured VOC concentrations in 2011. The non-measurement of these VOCs does not alter the conclusions relating to the differences in total VOC concentrations 28 29 observed between 1999-2001 and 2010-2012.

The relative composition of total measured VOCs showed differences between 2001 and 2011 at Harwell. Ethane, propane and n-butane had the largest measured concentrations. Ethane contributed on average $22 \pm 4\%$ of total monthly measured VOC concentrations in 2001,

1 compared with $33 \pm 6\%$ in 2011 (annual average monthly measured ethane concentration had a small increase from $2.0 \pm 0.8 \ \mu g \ m^{-3}$ in 2001 to $2.3 \pm 1 \ \mu g \ m^{-3}$ in 2011), while the relative 2 3 contribution from propane did not vary (15% in each year, average monthly concentrations in 2001 and 2011 were 1.5 μ g m⁻³ \pm 0.9 and 1.2 \pm 0.8 μ g m⁻³ respectively) and that from n-butane 4 decreased from $11 \pm 2\%$ to 8% ($\pm 1.\%$ ($1.1 \pm 0.6 \ \mu g \ m^{-3}$ in 2001 and $0.6 \pm 0.4 \ \mu g \ m^{-3}$ in 5 2011). Although these differences are not large, they may result from differences in the 6 7 reduction of VOC emission sources between 1999-2001 and 2010-2012. The aim of this work, however, was not the determination of long-term trends in absolute VOC concentrations, and 8 9 the reader is referred to Dollard et al. (2007), von Schneidemesser et al. (2010) and Derwent et al. (2014) which have undertaken analyses of trends in VOC concentrations at multiple UK 10 sites, including Harwell and Auchencorth. 11

12 The extent of diurnal photochemical loss of VOCs over the year is shown in Figure 46. At Harwell, periods of increased VOC diurnal photochemical depletion mirror the monthly 13 magnitude of regional O₃ increments (Figure 24 c.f. Figure 46). In 2001 at Harwell, both the 14 15 regional O₃ increment and VOC diurnal photochemical depletion increased from June to July, before declining in August. In 2011, there was a local maximum in the regional O₃ increment 16 17 in April, followed by the annual maximum in July, mirrored by VOC diurnal photochemical depletion. During 2012 the regional O₃ increment was minimal at Auchencorth, and the 18 19 magnitude of VOC diurnal photochemical depletion was low, with a small peak in August.

20 The association between the monthly variation in the regional O₃ increment and total VOC diurnal photochemical depletion at Harwell indicates that the variation in VOC chemical loss 21 contributing to the regional O₃ increment is represented by the VOC diurnal photochemical 22 depletion. The relative contribution of each measured VOC to total VOC diurnal 23 photochemical depletion during months of enhanced regional O₃ increment therefore indicates 24 25 where emissions reductions should be targeted to most effectively reduce VOC chemical loss and hence to reduce the magnitude of the regional O₃ increment. The contributions of each 26 27 measured VOC to total VOC diurnal photochemical depletion during the month of maximum 28 regional O₃ increment in 2010, 2011 and 2012 at Harwell are shown in Figure 5.7. A positive 29 value indicates lower POCP-weighted VOC/ethane during the afternoon compared to night (i.e. photochemical depletion). A higher POCP-weighted VOC/ethane ratio during the afternoon 30 31 results in the negative value. Ethene had the largest contribution during these months (34%, 32 29% and 45% of total measured VOC diurnal reactivity in 2010, 2011 and 2012 respectively).

1 (13%). The majority of the remaining measured VOCs made smaller, positive contributions. In July 2011, 71 % of the remaining VOCs (i.e. all VOCs excluding ethene and m+p-xylene) 2 3 contributed on average $3.4\% \pm 2.5\%$ to total positive VOC diurnal variation. In July 2012, the maximum regional O₃ increment was 12% lower than July 2011, and only 58% of remaining 4 5 VOCs made positive contributions. In June 2010, the maximum regional O₃ increment was 25% lower, and 54% of the remaining VOCs contributed. VOCs with larger VOC/ethane ratios 6 7 in the afternoon included isoprene, which is predominantly of biogenic origin (von Schneidemesser et al., 2011). Laurent and Hauschild (2014) modelled the impact on O₃ 8 9 formation of speciated VOC emissions from 31 countries, and also reported m-xylene and ethene to have the largest impact of 270 VOCs on regional O₃ formation. 10

Figure 68 is the analogous plot to Figure 57 for 1999-2001 at Harwell. In 1999-2001, - m+p-11 12 xylene had the largest diurnal photochemical depletion, followed by ethene. However, there were much larger negative VOC/ethane diurnal variations for some anthropogenic VOCs 13 14 compared to 2010-2012 (Figure 5). 2012 (Fig. 5), i.e. afternoon POCP-weighted VOC/ethane 15 ratios were substantially higher than at night. This indicates that processes other than photochemical depletion, e.g. local emission patterns, contributed to diurnal variation in 16 17 POCP-weighted VOC/ethane ratios for these VOCs in 1999-2001. Iso-pentane had the largest negative difference, but had a consistent positive contribution in 2010-2012. Toluene also had 18 19 a negative value in 1999 and 2000. Therefore from 1999-2001 to 2010-2012 there was a change in the balance between emissions of iso-pentane and toluene and their photochemical removal 20 to the point where photochemical depletion dominated during the day, and VOC/ethane ratios 21 were lower in the afternoon than at night. Derwent et al. (2014) calculated exponential 22 23 decreases in the concentrations of these VOCs at urban locations in the south-east of England, where Harwell is located, attributed to the effective control of evaporative and exhaust 24 emissions from petrol-engined vehicles. Toluene has an atmospheric lifetime of ~1.9 days with 25 respect to reaction with OH (Atkinson, 2000) so local daytime toluene emissions would not 26 27 deplete substantially during transport to the monitoring site. The observed decreasing trends at sites close to emission sources in the south-east of England suggest a decrease in the influence 28 of local iso-pentane and toluene emissions in determining the diurnal profile of these VOCs at 29 30 Harwell, and hence afternoon depletion of regionally-emitted toluene and iso-pentane was observed in 2010-2012. 31

32

33 3.3 Drivers of chemical climate state: Meteorology and emissions

1 3.3.1 Meteorology

2 The monthly-averaged meteorological data for the UK regions relevant for Harwell in 2001 and 2011 and Auchencorth in 2012 isare shown in Figure 79. Variation in temperature and 3 4 sunshine is often associated with spatio-temporal differences in VOC diurnal photochemical 5 depletion and regional O₃ increment. For example, temperatures were generally lower in East 6 Scotland than South East and Central South England but the number of hours of sunshine were comparable, although solar intensity is less in Scotland, hence a reduced VOC photochemical 7 depletion and regional O₃ increment at Auchencorth. At Harwell in 2001, annual maximum 8 VOC diurnal photochemical depletion occurred in July, coinciding with annual maximum 9 10 monthly temperature, while in July 2011, a combination of relatively high temperature and 11 hours of sunshine (although neither were annual maxima), coincided with annual maximum 12 VOC diurnal photochemical depletion. These summers were typical of the 1999-2012 period; 13 monthly mean temperatures were between -7% and +4% compared to the 1999-2012 average and hours of sunshine were between -14% to +11% compared to the average. 14

AtHowever, not all variation in VOC diurnal photochemical depletion and regional O3 15 16 increment were associated with changes in meteorology. For example, at Harwell in April 2011, there was a larger regional O₃ increment compared with April 2001. This coincided with 17 18 4 ²°C higher mean temperature and 95 more hours of sunshine in South East and Central South 19 England. However, In May 2011 the temperature and sunshine were similar to April 2011, but 20 VOC diurnal photochemical depletion and the regional O₃ increment decreased. Hence other 21 factors, such as the strength of VOC emission sources over which an air mass passes, also 22 influence VOC diurnal photochemical depletion, and in May 2011 the temperature and sunshine were similar to April 2011, but VOC diurnal photochemical depletion and the regional 23 O_3 -increment decreased. are discussed in Section 3.3.2. 24

25

26 **3.3.2 Emissions**

Variation in the monthly averaged European anthropogenic VOC trajectory emissions estimate
(TEE) is shown in Figure <u>810</u>. The VOC TEE is the sum of hourly emissions from the grid
squares the trajectories passed over in the 96 hours prior to arrival at the supersites (units:
Mg/96 hours), rather than a definitive quantification of the emissions directly impacting upon
the measured atmospheric composition at the supersites. Compared with Harwell in 2001, the
annual average VOC TEE, by mass, was 64% smaller in 2011 at Harwell, and 76% smaller in

1 2012 at Auchencorth. For the purposes of clarity the following assessment focuses on Harwell, 2 where significant regional O₃ increment has been demonstrated (Section 3.1). The biggest change in contribution from the 11 SNAP sectors to average VOC TEE between 2001 and 2011 3 4 at Harwell is shown in Figure 8. was for SNAP 7 (road transport), which averaged 31 % of the 5 total 10 VOC TEE in 2001, compared with 9 % in 2011 (Figure 10). The biggest change was for SNAP 7 (road transport), which averaged 31% of the total VOC TEE in 2001, compared to 6 7 9% in 2011. Emissions from SNAP 6 (solvents) were the largest contribution to the VOC TEE during both periods, contributing 50% of total emissions on average in 2011, compared to 34% 8 9 in 2001. Emissions from SNAP 4 (production processes) were the second largest contributor on average in 2011 (11% of the total VOC TEE), followed by SNAP 7 (road transport), and 10 SNAP 5 (extraction and distribution of fossil fuels), both contributing 9%. 11

Monthly variation in VOC TEE mirrors that of VOC diurnal photochemical depletion and 12 hence the magnitude of the regional O₃ increment. The period of April-July 2011 provides a 13 14 useful case study to demonstrate the nature of the emissions driver. This period shows how 15 variation in both the magnitude of the VOC TEE, as well as the proportion of emissions emitted closer to the receptor site (temporally) can influence the extent of VOC diurnal photochemical 16 17 depletion and the magnitude of the regional O₃ increment. April and May 2011 have similar meteorological conditions (Figure 79), but VOC diurnal photochemical depletion was lower in 18 May due to a 62% decrease in the VOC TEE compared to April. The VOC TEE decreased in 19 June, then increased in July. This latter increase, coupled with increased temperatures and solar 20 21 intensity in summer, provided conditions conducive to producing the observed annual 22 maximum in VOC diurnal photochemical depletion for 2011.

23 The proportion of the total VOC TEE derived from the final 4 hoursh prior to a trajectory's arrival, plus the hour of arrival, was labelled as the "final 4 hoursh" VOC TEE- to investigate 24 25 the effect of variation in the proportion of emissions emitted closer to the monitoring site. In 26 2011 the final 4 hours was on average 28% of the total VOC TEE (Figure 911a). In May and June 2011 it was above average (36% and 44% respectively), and in April and July it was lower 27 28 (17% and 20% respectively). While the 4-hour cut-off for this calculation was somewhat 29 arbitrary, it was based on consideration of the average atmospheric lifetimes of the individual VOCs (Atkinson, 2000) which indicate that most VOCs emitted in the final 4 hours have 30 31 insufficient time to form O₃. Between June and July 2011 there was a 32% increase in median 32 VOC concentrations due to an increased VOC TEE- (Figure 11b). However, there was a 275% increase in VOC diurnal photochemical depletion as a larger proportion of emissions were 33

1 emitted earlier along the air-mass trajectory- (Figure 11c). Hence in May and June, lower total 2 VOC TEE compared to April and July, respectively, coupled with a larger proportion of VOCs 3 emitted in the final 4 hours, resulted in the reduced regional O₃ increment impact- (Figure 11d). 4 The speciated VOC monthly trajectory emissions estimates, based on a UK-specific speciation of the total VOC TEE for 9 SNAP sectors are shown in Figure <u>1012</u> for July 2001 and 2011. 5 6 Individual VOC trajectory emissions estimates were expressed as the percentage of the total 7 POCP-weighted emissions- and the comparison between 2001 and 2011 illustrates the contrast 8 and similarities in contribution from individual VOCs to the VOC TEE during the months of maximum regional O3 increment. The biggest decreases between 2001 and 2011 were for iso-9 10 pentane (4.1% total POCP emissions in 2001, 1.7% in 2011), and toluene (6.5% in 2001, 4.5% in 2011). These decreases mirror the absence of much greater POCP-weighted VOC/ethane 11 ratios in the large negative VOC diurnal photochemical depletion of the two VOCs afternoon 12 compared to night for toluene and isopentane in 2010-2012, which were observed in 1999-13 14 2001 (and attributed to variation in local emissions (discussed in Section 3.2 and visualised as 15 'negative' VOC diurnal photochemical depletion in Figures 57 and 6). However, monthly8) Monthly variation in the contribution of measured VOCs to the VOC TEE was not consistent 16 with variation in the contribution of individual VOCs to total measured VOC diurnal 17 18 photochemical depletion. This is in contrast to the observed changes between 2001 and 2011 19 in VOC contribution to TEE and VOC diurnal photochemical depletion, and is effectively illustrated using the April-July 2011 time period as an example. For example, in 2011, the VOC 20 diurnal photochemical depletion peak in July (Figure 46) was much greater than in April due 21 to more intense sunshine and higher temperatures. This increase was not equally reflected 22 across the measured VOCs, indicating differences in the speciation of the VOC TEEs prior to 23 arrival at the site. For example, toluene was 4.2% of total VOC diurnal photochemical depletion 24 in April, increasing to 9.6% in July and the 1,3,5-trimethylbenzene contribution increased from 25 0.1% in April to 8% in July. The monthly-averaged speciated VOC TEEs do not reflect these 26 changes, and show little monthly variation within a given year. The speciated VOC monthly 27 28 TEE calculation assumes that the SNAP sector component activities (i.e. the activities for 29 which speciated profiles are defined (Passant, 2002)) contribute similarly to the emissions exposure of the parent SNAP sector in each month of the year. For example, it is assumed that 30 31 an x% increase in SNAP emissions results from an x% increase in emissions from all 32 component activities. It is unlikely that the SNAP sector emissions in every region over which 33 an air mass travels are similarly apportioned between component emissions activities. The

inability of this method to account for these spatial differences will result in the 1 2 underestimation of the TEE of some VOCs, and the overestimation of others. Currently, data are only available on changes in the contribution of more narrowly defined NFR codes to SNAP 3 sector emissions at a country level and for annual VOC emissions. In 2011 the average 4 contribution to monthly VOC TEE at Harwell from the UK was 62%, with France the second 5 largest contributor at 14%. Comparing April and July 2011, the contributions from the UK to 6 7 the VOC TEE were 50% and 95% respectively, with the other 50% in April resulting from 8 contributions from Germany, France, Belgium and the Netherlands (Figure 1113). These 9 countries all have different relative contributions to total SNAP sector emissions from component NFR source sectors (EEA, 2014). 10

11 <u>Highly-aggregated SNAP source sectors, and a constant contribution of component activities</u>

12 to SNAP emissions were identified as a potential contributing factor to inconsistencies between

VOC contributions to TEE and VOC diurnal photochemical depletion. Disaggregation of the 13 14 VOC TEEs into 91 NFR codes, based on country-specific contributions of these NFR 15 sectors codes to annual VOC emissions in the 11 parent SNAP sectors, accounted for countryspecific changes in NFR sector contributions to monthly VOC TEE at Harwell. The aim was 16 17 to show that within each SNAP sector an increase in VOC SNAP emissions from a SNAP sector in a specific country can result from an increase in a specific source activity (e.g. specific 18 19 NFR code), rather than a general overall increase. For example, in 1999-2001, the large contribution from SNAP 7 (road transport, Figure 8 Variability in the contribution of constituent 20 21 activities to SNAP emissions could result in variation in the contribution of individual VOCs 22 to those emissions. This would therefore demonstrate that the reporting of gridded VOC 23 emissions in more disaggregated source sectors was required, so that more flexible VOC speciation profiles could be derived than those calculated for the 9 SNAP sectors in this study, 24

and those calculated previously, e.g. Derwent et al. (2007a). For example, in 1999-2001, the

large contribution from SNAP 7 (road transport, Figure 10) is more precisely attributed to NFR 26 27 sectors 1A3bi (passenger cars) and 1A3by (gasoline evaporation) which contributed 19% and 11% to the total VOC TEE in July 2001 (month of maximum regional O₃ increment) 28 respectively, and 87% of the SNAP 7 emissions estimate. The next largest contribution was 29 from 3D2 (domestic solvent use, 10%), a component of SNAP 6 (solvents). Between 2010 and 30 2012, SNAP 6 was the major contributor to the VOC TEE. During July 2011 SNAP 6 31 component NFR sectors, 3D2 (domestic solvent use) and 3D3 (other product use) contributed 32 33 18% and 12% of the total VOC TEE (65% of the SNAP 6 emissions estimate). The SNAP 4 (production processes) component 2D2 (food and drink) was the third largest contributor (10%
 in July 2011). The two road transport categories contributed 4% (1A3bi) and 1% (1A3bv) to
 the total VOC TEE in July 2011.

4 The difference between the contribution of 91 NFR codes to the average VOC TEE between 5 April and July 2011 is shown in Figure 12.14 to demonstrate the variability in contribution of component activities to parent SNAP sector emissions. Between these months, the cumulative 6 change in the contribution of the 9 SNAP sectors to the total VOC TEE was 13.4%, compared 7 8 to a change of 15.9% for the 91 NFR codes. However, the changes in NFR code contributions were not equally spread between the constituent activities of a SNAP sector; they were 9 concentrated in relatively few NFR sectors. For example, between April and July 85% of the 10 NFR change resulted from a decrease in 10 out of the 91 NFR sectors. The sectors 'residential: 11 stationary plant combustion' and 'industrial coating application' show the greatest decrease, 12 while sectors 'food and drink' and 'venting and flaring' show the largest increase (identified 13 14 by stars on Figure $\frac{1214}{1}$). The disaggregation of SNAP sector VOC TEEs also illustrates 15 changes of opposite sign in the contribution of component NFR sectors under the net changes in SNAP sector. For example, SNAP sector 4 (Production processes) increased in contribution 16 17 between April and July by 2.7% (12.0 to 14.7%). Following disaggregation, this change was seen to result from a 3.4% increase in NFR sector 2D2 (food and drink) and a 0.76% decrease 18 19 in 2B5 (other chemical industry). NFR sector level speciated profiles can therefore give much more specific information on the emissions source drivers of VOC diurnal photochemical 20 21 depletion, though it is noted that the accuracy of many emission source speciation profiles is subject to discussion (Borbon et al., 2013). However, the changes in contribution of NFR 22 23 sectors to the VOC TEE calculated here only account for country-level variation, not for variation in the contribution of NFR sectors to SNAP emissions on finer spatial scales, such as 24 differences in NFR sector contribution to SNAP emissions in different $0.5^{\circ} \times 0.5^{\circ}$ grid squares 25 26 for which the SNAP sector gridded emissions are reported. Hence the future reporting of gridded emissions to NFR code level would more accurately represent the true nature of VOC 27 emissions across Europe. 28

29

30 **3.3.34** Uncertainties and implications for future mitigation and monitoring

31 Two VOCs, ethene and m+p-xylene, consistently had larger contributions to total VOC diurnal

32 photochemical depletion compared to the remaining VOC suite. Therefore a targeted reduction

of these two VOCs (compared to other measured VOCs) would be most effective in reducing
the regional O₃ increment. Further reduction of total measured VOC diurnal photochemical
depletion would require a reduction across a larger number of the remaining measured VOCs.
This could be achieved by lowering emissions from large VOC-_emitting sources, rather than
a focus on individual VOC species. As previously identified (section 3.3), between 2010 and
2012, the largest VOC-_emitting sources (NFR codes) were 3D2 (domestic solvent use
including fungicides), 3D3 (other product use) and 2D2 (food and drink).

8 The 27 measured VOCs studied here are a subset of the total VOC species emitted by a multitude of anthropogenic activities and biogenic processes. In 2011, 37.5% of the reported 9 annual UK anthropogenic VOC emissions were emitted as one of the 27 measured VOCs, when 10 speciated using the Passant (2002) speciation profiles. The UK biogenic VOC emissions 11 estimate reported to EMEP for 2011 was 91.2 Gg (c.f. anthropogenic emissions of 752 Gg), 12 but this value is uncertain and studies have estimated considerably higher UK annual biogenic 13 VOC emissions, in excess of 200 Gg (Karl et al., 2009;Oderbolz et al., 2013). Biogenic VOC 14 15 contributions to regional O₃ increments were not studied using this methodology. The estimate of 752 Gg of UK anthropogenic emissions is also subject to uncertainty associated with 16 defining accurate activity rates and emissions factors for a large number of source activities 17 (EEA, 2013). The UK National Atmospheric Emissions Inventory (NAEI) calculated the 18 19 uncertainty in UK anthropogenic VOC emissions to be \pm 10% (Misra et al., 2015). Of the 62.5% of UK anthropogenic VOC emissions not emitted as one of the VOCs measured at the 20 21 supersites, only the additional measurement of ethanol (13% of 2011 anthropogenic UK 22 emissions), methanol (4%) and acetone (3%) would substantially increase the proportion of the 23 UK VOC suite for which VOC diurnal photochemical depletion would be quantified. These three VOCs The measurement of these three VOCs would increase the proportion of UK 24 anthropogenic emissions emitted as a measured VOC from 37.5% to 57.5%. Currently, ethanol, 25 methanol and acetone constitute 35% of the unmeasured fraction of UK anthropogenic 26 emissions. Contributions from the 40 unmeasured VOCs with the next highest emissions are 27 28 required to make up the same percentage, and the remaining unmeasured emissions fraction comprises 464 VOCs. The large number of VOC contributing to the 'unmeasured' VOC 29 30 emissions fraction supports the argument that the targeting of high VOC emitting sources would be more beneficial than reductions in individual VOCs from whatever sources.their 31 32 source(s). The large proportion of UK VOC emissions emitted as ethanol, methanol and acetone (mainly from SNAP6 (solvents), from which 39%, 97% and 91% of UK anthropogenic 33

emissions of ethanol, methanol and acetone derived in 2011, and SNAP4 (production processes), which contributed 57% of ethanol emissions) suggests that, like ethene and m+pxylene, they may have a disproportionately high contribution to VOC diurnal photochemical depletion, and hence to the magnitude of the regional O₃ increment. Measurement of these oxygenated VOCs at the supersites would allow their contribution to be quantified.

6 TheOther limitations, in addition to using measurements of a subset of the emitted VOC suite, 7 include use of monthly-diurnal averages. Monthly-diurnal averages were required to use MLE 8 to derive summary statistics, and to calculate hemispheric and regional background O₃ concentrations. Additionally, it is more appropriate to consider an ensemble of air-mass back 9 10 trajectories to reduce the random uncertainty associated with their calculation. Hence the integration of air-mass back trajectories and gridded emissions inventories also benefitted from 11 use of monthly averages. However, the contribution of VOCs to the average increase in 12 regional O₃ increment in a given month was evaluated, rather than any short term episodic 13 14 regional O₃ increment increases. An additional uncertainty is associated with the gridded emissions inventory itself. The 15 16 derivation of the inventory requires accurate determination of emission factors and activity rates for a large number of source activities (EEA, 2013). Previous studies show the uncertainty 17 18 associated with this process. For example, Koohkan et al. (2013) calculated VOC emissions 19 across Europe using inverse modelling by data assimilation of measurements for 15 VOCs and comparison with the EMEP inventory showed an underestimation of emissions of some VOCs 20 and an overestimation of others. Hence there is a requirement for improvement of emissions 21 inventory derivation. However, this analysis shows that the future reporting of gridded VOC 22 emissions in source sectors more highly disaggregated than currently (e.g. NFR codes) would 23 also facilitate a more precise identification of those VOC sources most important to mitigation 24 25 strategies. For example, Derwent et al. (2007a), and increase the accuracy in calculating emissions of individual VOCs. For example, Derwent et al. (2007b) applied the POCP concept 26 27 to calculate the contribution of 248 VOC source categories to regional O₃ production using a 28 photochemical trajectory model with a near-explicit chemical mechanism which followed a 29 'worst case' 5-day trajectory bringing aged air masses from Europe to a location on the England-Wales border. A UK-derived VOC emissions speciation was derived and applied to 30

- total gridded VOC emissions estimates across north-west Europe. While the POCP concept
- 32 provides an effective means of comparison between different source categories, source

category POCPs were calculated without accounting for the spatial variation in the contribution
 of the different source categories to total VOC emissions.

The work presented here highlights the constraints of representing spatial variation of VOC 3 4 emissions across Europe with 11 highly aggregated SNAP sectors, and these constraints would 5 be amplified with no disaggregation of gridded VOC emissions. in terms of accurately 6 determining the suite of VOCs impacting atmospheric composition at a site. This results from 7 a fixed contribution of component activities to the aggregated SNAP sector emissions spatially 8 and temporally (see Section 3.3.2), although emissions from different SNAP sectors can vary 9 independently of one another. These constraints would be amplified with no disaggregation of 10 gridded VOC emissions and a constant contribution from component activities spatially and temporally to total VOC emissions, i.e. emissions from each aggregated SNAP sector do not 11 vary independently from one another. The effectiveness of the POCP concept in the 12 determination of the strongest O₃-influencing VOC emission sources, and hence the most cost 13 14 effective mitigation strategies, would be substantially improved by the reporting of gridded 15 emissions at NFR sector level. Finally, the future measurement at supersites of VOCs which are distinct markers for source sectors (e.g. NFR codes) could be used to quantify the 16 17 contribution from different VOC source sectors.

18

19 4 Conclusions

A methodology has been demonstrated using measurement data at the two UK EMEP 20 21 supersites (Harwell and Auchencorth) which links the impact of regional O₃ increment to VOC photochemical depletion- and spatially-gridded anthropogenic VOC emissions. The utility of 22 23 this methodology, which integrates atmospheric composition measurements (O₃ and VOCs), meteorological data and gridded emissions inventory, was shown through the derivation of 24 25 policy-relevant conclusions using measurement data at the two UK EMEP supersites (Harwell 26 and Auchencorth). The regional O₃ increment at Harwell in 2010-2012 was substantially larger 27 than at Auchencorth, but substantially smaller than in 1999-2001. Of the 27 measured anthropogenic VOCs, ethene and m+p-xylene consistently contributed the most VOC 28 29 photochemical depletion during regional O₃ production at Harwell, and therefore reductions in emissions of these VOCs would be most effective in reducing regional O₃ production. To 30 reduce VOC diurnal photochemical depletion further, reductions across a larger number of the 31 VOCs would be required. Of these, ethanol, methanol and acetone appear to be the most 32

important, and measurement of these VOCs at the supersites would provide data for targeting
future emissions reductions. Additionally, more detailed speciated measurement of biogenic
VOCs at the supersite, <u>highlighted previously by von Schneidemesser et al. (2011)</u>, would also
advance understanding of the relative contribution of anthropogenic vs biogenic VOCs in
determining the regional O₃ increment.

6 Estimates of the integrated anthropogenic VOC emissions along back trajectories arriving at 7 Harwell have decreased substantially between 1999-2001 and 2010-2012, due to decreases in 8 emissions from SNAP source sector 7 (road transport). Currently, SNAP sector 6 (solvent and product use) provides most of the total VOC trajectory emissions estimate. The disaggregation 9 10 of highly aggregated SNAP trajectory emissions estimates to NFR codes, accounting for country variation in the NFR sector contribution to parent SNAP sector, allowed the source 11 sectors which determine the VOC contribution to the regional O₃ impact to be more precisely 12 defined, i.e. NFR sectors 3D2 (domestic solvent use), 3D3 (other product use) and 2D2 (food 13 14 and drink), which were the top three contributors to total VOC emissions exposure at Harwell 15 (2010-2012) during the month of maximum regional O₃ increment. It is concluded that considerable additional benefits to the interpretation of measurement data, to modelling of 16 17 future O₃ concentrations and hence to determining policy for abatement of detrimental O₃ impacts would be gained from the availability of gridded VOC emissions data reported in more 18 19 narrowly defined source sectors such as the NFR codes.

20

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- 1 <u>Table 1: Summary data for the measured VOCs at Auchencorth and Harwell (note that m-</u>
- 2 xylene and p-xylene are reported as a single measurement). The rate coefficients at 298 K for
- 3 reactions of each VOC with OH are taken from Atkinson and Arey (2003), and the POCPs are
- 4 from Derwent et al. (2007a). The 'main source' column gives the SNAP sector with the largest
- 5 contribution of that VOC to UK annual anthropogenic emissions in 2011 with the exception of
- 6 isoprene which is mainly of biogenic origin (defined in Section 2.3). The listed SNAP sectors
 7 are SNAP 2: Non-industrial combustion plants, SNAP 4: Production processes, SNAP 5:
- 8 Extraction and distribution of fossil fuels, SNAP 6: Solvent use, SNAP 7: Road transport and
- 9 <u>SNAP 8: Non-road transport.</u>
- 10

VOC	<u>Class</u>	<u>Chemical</u> Formula	<u>Main source</u>	OH reaction rate constant (10 ¹² x k (298 K) (cm ³ molecule ⁻¹ s ⁻¹))	<u>POCP</u>
<u>ethane</u>	<u>alkane</u>	<u>C₂H₆</u>	<u>SNAP 5 (65%)</u>	<u>0.248</u>	8
<u>propane</u>	<u>alkane</u>	<u>C₃H₈</u>	<u>SNAP 5 (36%)</u>	<u>1.09</u>	<u>14</u>
<u>n-butane</u>	<u>alkane</u>	<u>C4H10</u>	<u>SNAP 6 (44%)</u>	<u>2.36</u>	<u>31</u>
<u>isobutane</u>	<u>alkane</u>	<u>C₄H₁₀</u>	<u>SNAP 5 (61%)</u>	<u>2.12</u>	<u>28</u>
<u>n-pentane</u>	<u>alkane</u>	<u>C₅H₁₂</u>	<u>SNAP 5 (42%)</u>	<u>3.80</u>	<u>40</u>
<u>isopentane</u>	<u>alkane</u>	<u>C₅H₁₂</u>	<u>SNAP 5 (41%)</u>	<u>3.60</u>	<u>34</u>
<u>n-hexane</u>	<u>alkane</u>	<u>C₆H₁₄</u>	<u>SNAP 6 (42%)</u>	<u>5.20</u>	<u>40</u>
2-methylpentane	<u>alkane</u>	<u>C₆H₁₄</u>	<u>SNAP 6 (43%)</u>	<u>5.20</u>	<u>41</u>
<u>n-heptane</u>	<u>alkane</u>	<u>C₇H₁₆</u>	<u>SNAP 5 (43%)</u>	<u>6.76</u>	<u>35</u>
<u>n-octane</u>	<u>alkane</u>	<u>C₈H₁₈</u>	<u>SNAP 5 (64%)</u>	<u>8.11</u>	<u>34</u>
<u>isooctane</u>	<u>alkane</u>	<u>C₈H₁₈</u>	<u>SNAP 4 (100%)</u>	<u>3.34</u>	<u>25</u>
<u>ethene</u>	<u>alkene</u>	<u>C₂H₄</u>	<u>SNAP 8 (27%)</u>	<u>8.52</u>	<u>100</u>
propene	<u>alkene</u>	<u>C₃H₆</u>	<u>SNAP 4 (36%)</u>	<u>26.3</u>	<u>117</u>
<u>1-butene</u>	<u>alkene</u>	<u>C₄H₈</u>	<u>SNAP 7 (26%)</u>	<u>31.4</u>	<u>104</u>
<u>cis-2-butene</u>	<u>alkene</u>	<u>C₄H₈</u>	<u>SNAP 5 (87%)</u>	<u>56.4</u>	<u>113</u>
trans-2-butene	<u>alkene</u>	<u>C₄H₈</u>	<u>SNAP 5 (90%)</u>	<u>64.0</u>	<u>116</u>
<u>1,3-butadiene</u>	<u>alkene</u>	<u>C₄H₆</u>	<u>SNAP 8 (57%)</u>	<u>66.6</u>	<u>89</u>
<u>isoprene</u>	<u>alkene</u>	<u>C₅H₈</u>	<u>biogenic</u>	<u>100</u>	<u>114</u>
<u>ethyne</u>	<u>alkyne</u>	C_2H_2	<u>SNAP 7 (46%)</u>	<u>0.78</u>	<u>7</u>
<u>benzene</u>	<u>aromatic</u>	<u>C₆H₆</u>	<u>SNAP 2 (35%)</u>	<u>1.22</u>	<u>10</u>
<u>toluene</u>	<u>aromatic</u>	<u>C₇H₈</u>	<u>SNAP 6 (63%)</u>	<u>5.63</u>	<u>44</u>
<u>ethylbenzene</u>	<u>aromatic</u>	<u>C₈H₁₀</u>	<u>SNAP 6 (54%)</u>	<u>7.0</u>	<u>46</u>
<u>o-xylene</u>	<u>aromatic</u>	<u>C₈H₁₀</u>	<u>SNAP 6 (50%)</u>	<u>13.6</u>	<u>78</u>
<u>m-xylene</u>	<u>aromatic</u>	<u>C₈H₁₀</u>	<u>SNAP 6 (71%)</u>	<u>23.1</u>	<u>86</u>
<u>p-xylene</u>	<u>aromatic</u>	<u>C₈H₁₀</u>	<u>SNAP 6 (50%)</u>	<u>14.3</u>	<u>72</u>
1,2,3-trimethylbenzene	<u>aromatic</u>	<u>C₉H₁₂</u>	<u>SNAP 6 (79%)</u>	<u>32.7</u>	<u>105</u>
1,2,4-trimethylbenzene	<u>aromatic</u>	<u>C₉H₁₂</u>	<u>SNAP 6 (74%)</u>	<u>32.5</u>	<u>110</u>
1,3,5-trimethylbenzene	<u>aromatic</u>	<u>C_9H_{12}</u>	<u>SNAP 6 (71%)</u>	<u>56.7</u>	<u>107</u>

1 Figure 1: Correlation between monthly hemispheric background O₃ concentrations derived by

2 Derwent at al. (2007c) using pollutant tracers and atmospheric modelling to select 'clean' air

3 masses, and derived by the method described in Section 2.1 using cluster analysis. Black

4 regression line is calculated by the ordinary least squares (OLS) method, with confidence

5 intervals (95th percent) shown in grey.



- 1 Figure 2: Flowchart demonstrating the process used to calculate the contribution of
- 2 630 individual VOCs to the monthly total VOC trajectory emissions estimate (TEE, defined in
- 3 Section 2.3). The green rectangles represent products or datasets, and the blue rounded
- 4 rectangles represent processes applied to transform a dataset. Further explanation is provided
- 5 <u>in Section 2.3.</u>



- 1 Figure 3: Flowchart representing the process used to derive the contribution from NFR codes
- 2 to monthly trajectory emissions estimates (TEE, defined in Section 2.3). The green rectangles
- 3 represent products or datasets, and the blue rounded rectangles represent processes applied to
- 4 transform a dataset. Note that the separation of the TEE into contributions from two countries
- 5 <u>is illustrative</u>, and in most cases a greater number of countries contributed to the TEE in a given
- 6 <u>month. Further explanation is provided in Section 2.3.</u>



1 Figure 4: Monthly-hourly average differences between hemispheric background O_3 and 2 regional background O_3 concentrations ($\mu g m^{-3}$) for (a) 2001 and (b) 2011 in south-east 3 England, the area for which Harwell is representative, and (c) the difference between 4 hemispheric and measured O_3 concentrations for 2012 at Auchencorth.


- 1 Figure <u>35</u>: Stacked barchart of median VOC concentrations at (a) Harwell 2001, (b) Harwell
- 2 2011, and (c) Auchencorth 2012. The error bars show the sum of the 95th percentile
- 3 confidence interval in the median VOC concentrations. This represents the error introduced
- 4 by representing the dataset with the chosen fitted distribution (see text).



- 1 Figure 46: Monthly variation in VOC diurnal photochemical reactivity as defined by the
- 2 difference between night (average of 1 am–5 am) and afternoon (1 pm–5 pm) POCP-weighted
- 3 VOC/ethane ratios for (a) Harwell 2001, (b) Harwell 2011, and (c) Auchencorth 2011. Note
- 4 the very different vertical scales.



Figure 57: Individual VOC diurnal photochemical reactivity as defined by the difference between night (average of 1 am - 5 am) and afternoon (1 pm - 5 pm) POCP-weighted VOC/ethane ratios for (a) June 2010, (b) July 2011 and (c) July 2012, at Harwell. A lower ratio in the afternoon results in a positive value (i.e. photochemical depletion), while a higher afternoon ratio results in a negative value. These months correspond to the periods of annual maximum regional O₃ increment at Harwell (see Figure 2).



Figure 68: Individual VOC diurnal photochemical reactivity as defined by the difference between night (average of 1 am - 5 am) and afternoon (1 pm - 5pm) POCP-weighted VOC/ethane ratios in (a) July 1999, (b) July 2000 and (c) July 2001, at Harwell. <u>A lower ratio</u> in the afternoon results in a positive value (i.e. photochemical depletion), while a higher afternoon ratio results in a negative value. These months correspond to the periods of annual maximum regional O₃ increment. To emphasise the positive contributions to VOC photochemical cycling, the negative values have been truncated.



Figure 79: Average monthly mean temperatures (blue, maximum and minimum temperatures shown as whiskers) and hours of sunshine (red) from the UK Meteorological Office (<u>http://www.metoffice.gov.uk/climate/uk/datasets/#</u>) for (a) South East and Central South England 2001, (b) South East and Central South England 2011 and (c) East Scotland 2012.



- 1 Figure <u>810</u>: Monthly average VOC 96-hour back-trajectory emissions estimates prior to its
- 2 arrival at the receptor site, disaggregated into 11 SNAP source sectors for (a) Harwell 2001,
- 3 (b) 2011 Harwell, and (c) Auchencorth 2012.



- 1 Figure 9: Proportion of average VOC 96 hour back trajectory emissions estimate for Harwell,
- 2 2011, emitted in the final 4 hours before arrival over the emission grid containing Harwell.



- 1 Figure 11: Summary of variables relevant to the assessment of the effect of variation in the
- 2 proportion of emissions accumulated close (temporally) to the monitoring site: a) The final 4
- 3 hours TEE metric, i.e. the proportion of the TEE emitted into the air mass during the 4 hours
- 4 prior to arrival at the site (defined in Section 3.3.2), b) Monthly average sum of measured
- 5 VOCs, c) Monthly average sum of VOC diurnal photochemical depletion, d) Monthly
- 6 maximum difference between hemispheric background concentrations and regional
- 7 <u>background concentrations (a positive value indicates additional regional O₃ production).</u>



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- 1 Figure <u>1012</u>: Speciation of average VOC back-trajectory emissions estimates in (a) July
- 2 2001, and (b) July 2011 at Harwell. The speciation was based on source profiles catalogued
- 3 in Passant (2002) and the relative contribution of individual activities to annual total VOC
- 4 emissions.



- 1 Figure <u>4413</u>: Contributions to the average VOC 96-hour back-trajectory emission estimates
- 2 in April 2011 (green bars) and July 2011 (blue bars) from countries which contributed at least
- 3 0.5% during one of the months. The contribution of the UK in July 2011 was 95.8 %, and has
- 4 been truncated in the plot.



- 1 Figure <u>1214</u>: Difference between NFR source sector contributions to average VOC back
- 2 trajectory emission estimates (VOC TEE) in April and July 2011 at Harwell. Also shown are
- 3 the change in contribution of the SNAP source sectors. These were calculated from the VOC
- 4 TEE prior to disaggregation, and do not represent the sum of the contribution changes of the
- 5 constituent NFR source sectors. The source sectors identified by stars have the largest
- 6 changes between April and July (Section 3.3.2).

