

## **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’ O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> increment has been added to P7273 L25:

**Additional text:** “A positive regional O<sub>3</sub> increment indicates additional O<sub>3</sub> formation regionally in excess of hemispheric background concentrations, and vice versa.”

A description of how the regional O<sub>3</sub> 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<sub>3</sub> increment. During those months with a positive regional O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> increment and total VOC diurnal photochemical depletion at Harwell indicates that the variation in VOC chemical loss contributing to the regional O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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 O<sub>3</sub> 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<sub>3</sub> variation are two key elements of O<sub>3</sub> variability, both in terms of accumulation of health and vegetation-relevant O<sub>3</sub> metrics (discussed in detail in relation to both Harwell and Auchencorth in Malley et al. (2015)), and in how O<sub>3</sub> 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<sub>3</sub> studies, and to provide transferability to other measurement sites, it was considered appropriate to assess the contribution of VOCs to regional O<sub>3</sub> 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<sub>3</sub> variability associated with the driving processes on its concentrations and on its impact. For example, the monthly and diurnal variation in O<sub>3</sub> is central to determining the extent and spatiotemporal trends in health and vegetation-relevant O<sub>3</sub> 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<sub>3</sub> variation. This has been made clearer in the text.

**P7272 L3 Additional text:** “Here, regional background O<sub>3</sub> concentration is defined as that which is imported into a local spatial domain following modification of hemispheric background O<sub>3</sub> concentrations by European emissions. Examples of local spatial domains are south-east England and northern UK for which, based on monthly-diurnal O<sub>3</sub> 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 O<sub>3</sub> 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<sub>3</sub> measurements at Mace Head were not substituted for those at Auchencorth to calculate the regional O<sub>3</sub> increment. For both Auchencorth and Harwell, O<sub>3</sub> concentrations at Mace Head during westerly conditions (extracted using cluster analysis) were used as an estimate of hemispheric background O<sub>3</sub> concentrations. The assumption in using westerly Mace Head O<sub>3</sub> 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 westerly Mace Head O<sub>3</sub> concentrations as an estimate of monthly-diurnal variation in hemispheric background concentrations.

To calculate the regional O<sub>3</sub> increment, an estimate of regional background O<sub>3</sub> concentrations was also required. The approach differed at Harwell and Auchencorth. At Harwell, regional background O<sub>3</sub> concentrations were calculated for each monthly-diurnal time period using the y-intercept of Oxidant vs NO<sub>x</sub> linear fit, i.e. the NO<sub>x</sub>

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, NO<sub>2</sub> and O<sub>3</sub> to capture a range of NO<sub>x</sub> and Oxidant concentrations. There were insufficient collated measurements within the spatial domain of Auchencorth to estimate regional background O<sub>3</sub> concentrations using this method. When Auchencorth was assessed in the context of O<sub>3</sub> variation across rural Europe, it was grouped among the least anthropogenically-influenced measurement sites, and monthly-diurnal O<sub>3</sub> 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 O<sub>3</sub> concentrations at Auchencorth, and hence it was considered appropriate to use the Auchencorth measurement data as an estimate for regional background O<sub>3</sub> 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 non-detects, the potential inclusion of non-LOD related non-detects results in a small change in calculated concentration, while VOCs with a larger proportion of non-detects 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 non-detects, the potential inclusion of non-LOD-related non-detects resulted in a small change in calculated concentration, while VOCs with a larger proportion of non-detects 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<sub>3</sub> 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  $\pm 12\%$  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  $\pm 12\%$  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 POCP-weighting.

**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 O<sub>3</sub> increment is the NO<sub>x</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> results across large areas of north-west Europe from a 15% reduction in EU VOC emissions, whereas these impact metrics actually increase from a 15% reduction in NO<sub>x</sub> emissions, due to reduced O<sub>3</sub> 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<sub>x</sub> concentrations are drivers of the regional O<sub>3</sub> increment. Meteorology and anthropogenic VOC emissions are the focus due to the benefits previously outlined in improvement in health and vegetation-relevant O<sub>3</sub> 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<sub>3</sub> increment within each three-year period. On P7279 L21, a description of the differences between the regional O<sub>3</sub> increment in 2011, and in 2012 and 2010, providing the reader with the necessary information to understand the differences between the regional O<sub>3</sub> 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 ( $26 \mu\text{g m}^{-3}$  in July). In 1999, regional ozone production was greater, extending from April to September with the annual maximum in July ( $53 \mu\text{g m}^{-3}$ ), and production in excess of  $30 \mu\text{g m}^{-3}$  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  $\text{O}_3$  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  $\text{O}_3$  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  $\text{O}_3$  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  $\text{O}_3$  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  $\text{O}_3$  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  $2.0 \pm 0.8 \mu\text{gm}^{-3}$  in 2001 to  $2.3 \pm 1 \mu\text{gm}^{-3}$  in 2011), while the relative contribution from propane did not vary ( $15\%$  in each year, average monthly concentrations in 2001 and 2011 were  $1.5 \pm 0.9$  and  $1.2 \pm 0.8 \mu\text{gm}^{-3}$  respectively) and that from n-butane decreased from  $11 \pm 2\%$  to  $8 \pm 1\%$  ( $1.1 \pm 0.6 \mu\text{gm}^{-3}$  in 2001 and  $0.6 \pm 0.4 \mu\text{gm}^{-3}$  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  $\mu\text{g m}^{-3}$ ). 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<sub>3</sub> 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<sub>3</sub> increment (Figure 2) to assess the association between the magnitude of the regional O<sub>3</sub> 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 O<sub>3</sub> 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<sub>3</sub> increment:

**P7282 L12 Original text:** “At Harwell in April 2011, there was a larger regional O<sub>3</sub> 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<sub>3</sub> increment decreased.”

**P7282 L12 Amended text:** “However, not all variation in VOC diurnal photochemical depletion and regional O<sub>3</sub> increment were associated with changes in meteorology. For example, at Harwell in April 2011, there was a larger regional

O<sub>3</sub> 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<sub>3</sub> 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° × 0.5° 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° × 0.5° 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 O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> increment in 2010 peaks in June (24 µg m<sup>-3</sup>), and drops off in July (19 µg m<sup>-3</sup>). For 2011, the regional O<sub>3</sub> increment in June was substantially lower than June 2010 (5 µg m<sup>-3</sup>), and instead peaks in July (31 µg m<sup>-3</sup>). The contrast between different years further demonstrates the nature of the association between regional O<sub>3</sub> 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 O<sub>3</sub> 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 monthly-diurnal averages. Monthly-diurnal averages were required to use MLE to derive summary statistics, and to calculate hemispheric and regional background O<sub>3</sub> 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<sub>3</sub> increment in a given month was evaluated, rather than any short term episodic regional O<sub>3</sub> 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<sub>3</sub>, 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<sub>3</sub> 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<sub>3</sub> increment to VOC photochemical depletion.”

**P7290 L5 Amended text:** “A methodology has been demonstrated which links the impact of regional O<sub>3</sub> increment to VOC photochemical depletion and spatially gridded anthropogenic VOC emissions. The utility of this methodology, which integrates atmospheric composition measurements (O<sub>3</sub> 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<sub>3</sub> 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 contribution to the regional O<sub>3</sub> 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+p-xylene, 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  $3.4 \pm 2.5$  % 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  $3.4 \pm 2.5$  % 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. 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.”

**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 O<sub>3</sub> 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 O<sub>3</sub> formation by shifting between NO<sub>x</sub>-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 O<sub>3</sub> increment. On P7288 L21 we state explicitly that 'Biogenic VOC contributions to regional O<sub>3</sub> 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 O<sub>3</sub> 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 O<sub>3</sub> impact metrics, in contrast to the analogous reduction of NO<sub>x</sub> 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 Auchincorth, 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 O<sub>3</sub> increment mirrored afternoon depletion of VOCs due to photochemistry”

**P7268 L10 Amended text:** “variation in the regional O<sub>3</sub> 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 air-mass 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 air-mass back trajectories.”

**P7269 L22 Original text:** “resulting from 15% reductions in EU27 NO<sub>x</sub> and VOC emissions and showed that VOC emissions reductions were more effective than NO<sub>x</sub> emissions reductions in reducing the O<sub>3</sub> impact metrics across much of north-west Europe.”

**P7269 L22 Amended text:** “resulting from 15% reductions in anthropogenic NO<sub>x</sub> and VOC emissions across the EU and showed that VOC emissions reductions were more effective than NO<sub>x</sub> emissions reductions in reducing the O<sub>3</sub> 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 air-mass 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 O<sub>3</sub> increment, not the quantity of VOC remaining in the air mass (which the POCP-weighted 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 POCP-weighted 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 O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>Y</sub> 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<sub>3</sub> impact metric in line with the World Health Organisation (WHO) recommendations for the quantification of health-relevant O<sub>3</sub>. POD<sub>Y</sub> is a flux-based method for quantifying the ‘Phytotoxic O<sub>3</sub> Dose’, i.e. the uptake of damaging O<sub>3</sub> 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<sub>3</sub>. 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 ( $10^{12} \times k$ (298 K) ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ))	POCP
ethane	alkane	C <sub>2</sub> H <sub>6</sub>	SNAP 5 (65%)	0.248	8
propane	alkane	C <sub>3</sub> H <sub>8</sub>	SNAP 5 (36%)	1.09	14
n-butane	alkane	C <sub>4</sub> H <sub>10</sub>	SNAP 6 (44%)	2.36	31
isobutane	alkane	C <sub>4</sub> H <sub>10</sub>	SNAP 5 (61%)	2.12	28
n-pentane	alkane	C <sub>5</sub> H <sub>12</sub>	SNAP 5 (42%)	3.80	40
isopentane	alkane	C <sub>5</sub> H <sub>12</sub>	SNAP 5 (41%)	3.60	34
n-hexane	alkane	C <sub>6</sub> H <sub>14</sub>	SNAP 6 (42%)	5.20	40
2-methylpentane	alkane	C <sub>6</sub> H <sub>14</sub>	SNAP 6 (43%)	5.20	41
n-heptane	alkane	C <sub>7</sub> H <sub>16</sub>	SNAP 5 (43%)	6.76	35
n-octane	alkane	C <sub>8</sub> H <sub>18</sub>	SNAP 5 (64%)	8.11	34
isooctane	alkane	C <sub>8</sub> H <sub>18</sub>	SNAP 4 (100%)	3.34	25
ethene	alkene	C <sub>2</sub> H <sub>4</sub>	SNAP 8 (27%)	8.52	100
propene	alkene	C <sub>3</sub> H <sub>6</sub>	SNAP 4 (36%)	26.3	117
1-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP 7 (26%)	31.4	104
cis-2-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP 5 (87%)	56.4	113
trans-2-butene	alkene	C <sub>4</sub> H <sub>8</sub>	SNAP 5 (90%)	64.0	116
1,3-butadiene	alkene	C <sub>4</sub> H <sub>6</sub>	SNAP 8 (57%)	66.6	89
isoprene	alkene	C <sub>5</sub> H <sub>8</sub>	biogenic	100	114
ethyne	alkyne	C <sub>2</sub> H <sub>2</sub>	SNAP 7 (46%)	0.78	7
benzene	aromatic	C <sub>6</sub> H <sub>6</sub>	SNAP 2 (35%)	1.22	10
toluene	aromatic	C <sub>7</sub> H <sub>8</sub>	SNAP 6 (63%)	5.63	44
ethylbenzene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP 6 (54%)	7.0	46
o-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP 6 (50%)	13.6	78
m-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP 6 (71%)	23.1	86
p-xylene	aromatic	C <sub>8</sub> H <sub>10</sub>	SNAP 6 (50%)	14.3	72
1,2,3-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>12</sub>	SNAP 6 (79%)	32.7	105
1,2,4-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>12</sub>	SNAP 6 (74%)	32.5	110
1,3,5-trimethylbenzene	aromatic	C <sub>9</sub> H <sub>12</sub>	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.

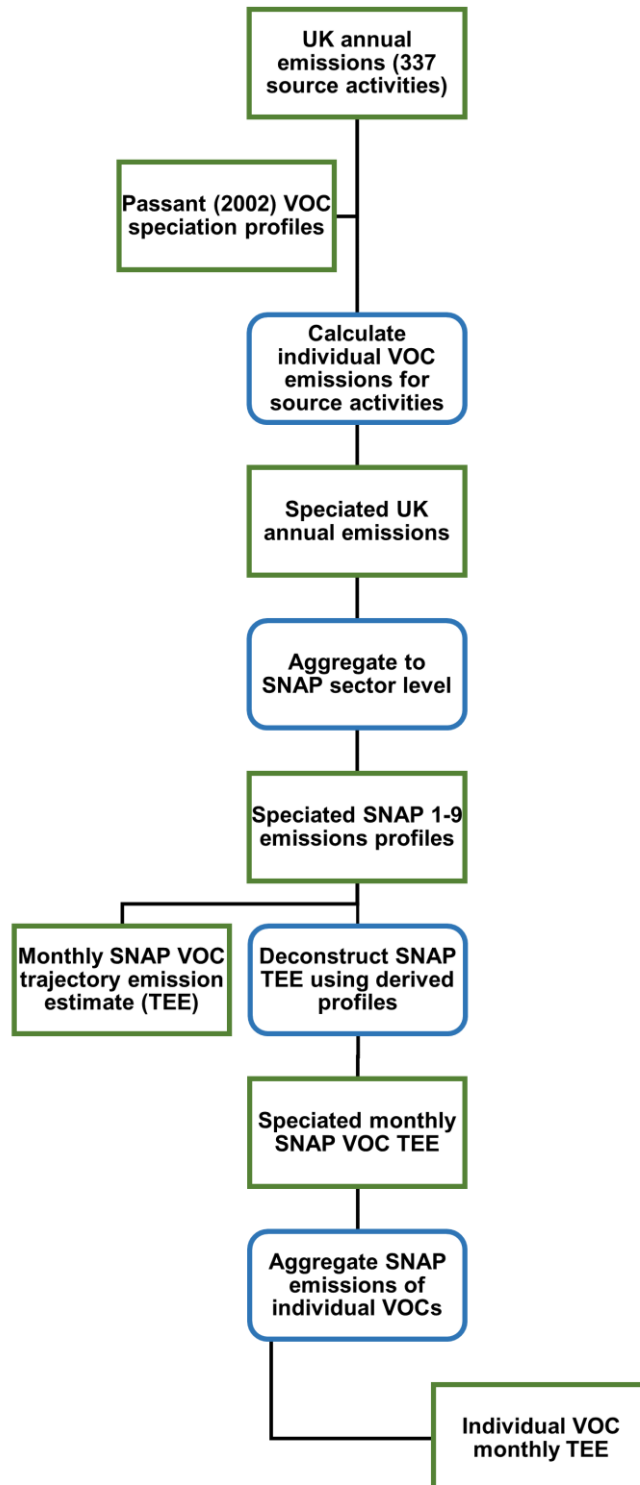




Figure 3: Flowchart representing the process used to derive the contribution from NFR codes to monthly trajectory emissions estimates (TEE, defined in Section 2.3). The green rectangles represent products or datasets, and the blue rounded rectangles represent processes applied to transform a dataset. 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.

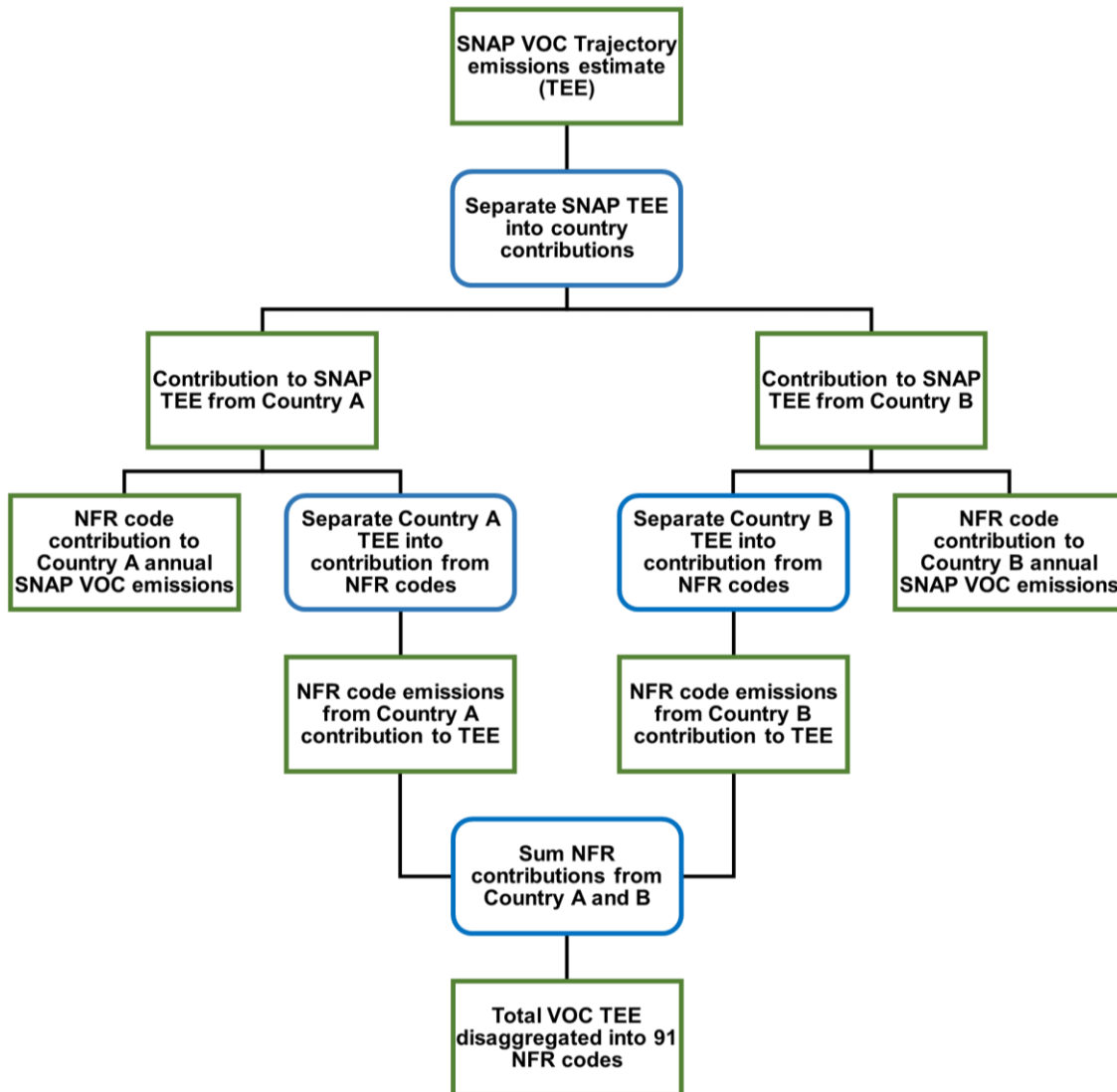


Figure 11 (Figure 9 in original manuscript): Summary of variables relevant to the assessment of the effect of variation in the proportion of emissions accumulated close (temporally) to the monitoring site: a) The final 4 hours TEE metric, i.e. the proportion of the TEE emitted into the air mass during 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 O<sub>3</sub> production).

