RESPONSE TO REVIEWER No 2

For ‘Sources of Surface O_3 in the UK: Tagging O_3 within WRF-Chem’ by Johana Romero-Alvarez, Aurelia Lupaşcu, Douglas Lowe, Alba Badia, Scott Acher-Nicholls, Steve R. Dorling, Claire E. Reeves, and Tim Butler

This paper describes the application of a regional chemical transport model using an ozone tagging scheme to quantify source contributions to surface tropospheric ozone in the UK during May-Aug 2015. The application of such a scheme in this context is novel, and the paper provides useful insight into the local, wider European, and extra-European contributions to ozone, broken down by local region within the UK. The paper explores differences in source contributions during episodes of higher surface ozone concentrations, and explores contributions using air quality and vegetation-relevant metrics, which provide some policy-relevant context. The paper is well written, and the methods applied appear robust and well described. There are some aspects of the model information and evaluation, and well as improvements in the discussion of results that would improve the manuscript. I recommend that once these issues (described below) are addressed, that the paper be published in ACP where it will be a valuable addition to the literature on European ozone air quality.

We appreciate the reviewer’s positive assessment of the manuscript. Per the suggestion, we have carefully edited the document to improve presentation of results and discussion. Changes to the manuscript have been highlighted in yellow.

General comments

For high ozone episodes in summer, biogenic emissions may be an important driver of ozone formation (e.g. see point made in Introduction on Page 7). Even if it is not possible to evaluate the model-simulated isoprene with observations, it might be informative to include a supplementary plot of isoprene during high ozone and more average conditions. The authors could also refer to previous studies evaluating MEGAN isoprene emissions in WRF-Chem, if relevant.

We thank the reviewer for this recommendation. In the supplementary material, we have included a time series (Figure S.9) comparing measured and modeled isoprene during July 2015 in the East Anglia region. We also added the following paragraph:

‘The model’s representation of organic NMVOCs may be an additional source of bias. Figure S.9 in the supplementary material shows that the model largely underestimates observations of isoprene particularly during the first days of July which were characterized by high O_3 mixing rations. The impacts of isoprene chemistry in O_3 concentrations have been reported largely in the literature. For instance, in box modelling studies, Knote et al. (2014) show large variations in isoprene concentrations between different chemical mechanisms despite using identical biogenic emissions. Moreover, Zhao et al. (2016) demonstrate that more recent versions of the Model of Emissions of Gases and Aerosols from Nature (MEGAN) better reproduce the observed isoprene than the publicly available version of the MEGAN model integrated into WRF-Chem.’

Is it possible to calculate population-weighted MDA8 ozone contributions using population data and the model output? This would really strengthen the relevance of the results to air quality and human health. At the moment the discussion does not differentiate based on population distributions among the different regions, so it is difficult to interpret the relevance of the results to air quality.

We appreciate the reviewer’s suggestion. Although assessing the population exposure to MDA8 O_3 is beyond the scope of this paper, we have reinforced the discussion based on the regions that matter most from a population exposure perspective, see below.

‘The mean contribution from the Eu super-region (FRA, GER, NET, LUX, BEL, NOS, Rest_CEu and Rest_Eu) accounts for nearly 16 % of the simulated monthly mean O_3. The largest Eu super-region contributions are observed in the UK locations closer to the continental Europe and that together contain about 40% of UK population (East Anglia, London area, South-East England and Yorkshire)’

‘The LB is the principal contributor to the modelled mean O_3 mixing ratios in every receptor region. The contributions peak in May (mean absolute contribution 25 ppbv), reflecting the seasonal cycling in the northern hemispheric background O_3 (e.g., Monks, 2000; AQEG, 2009). Contributions from this source are more prominent in the regions located in the north, east, and north-west of the UK, e.g., Scotland (30 ppbv), Northern Ireland (28 ppbv), North-East (27 ppbv), the North-West, and Wales (26 ppbv). These regions contain about 20% of UK population and are primarily impacted by westerly flows and associated hemispheric O_3 background due to their geographical positions (AQEG, 2009). Also, they generally experience less than 10 days with O_3 concentrations above the EU limit of 120 µg m^{-3} (DEFRA 2020) because of low NOx emissions locally’

‘The UK contributions are generally more significant in the east, south-east, and the Midlands, showing a maximum value in June and July in every receptor area, figures S.9 and S.10 in the Supplemental Material. The source region provides up to 20% of the surface O_3 mixing ratios in East Anglia, 18% in the London area and East Midlands, and 16% in Yorkshire and the South East, making it the second-biggest source of O_3 in these locations after the LB. This area incorporates about 50% of UK population and often experiences more than 10 days with O_3 concentrations above the EU and UK threshold (concentration > 120 and 100 µg m^{-3}) (DEFRA 2020).’

‘The mean contribution from each source region for the hours when the MDA8 O_3 exceeded 50 ppbv at each receptor area from May to August is presented in Fig. 10. The figure shows large contributions from source regions that were not seen as dominant sources. France, for example, becomes a major source, particularly in receptors in densely populated areas such as the south and east of the UK.’

During ozone episodes (presented as when MDA8 O3 exceeds 50 or 60 ppbv), it would be informative to provide more in-depth discussion of meteorological conditions alongside the source region contributions. Are these periods dominated by anticyclonic conditions? What are the atmospheric transport pathways that dominate the France-sourced O3 influence on UK ozone? Are there any specific features that characterize the MDA8 > 60 ppbv episodes from the more moderate 50 ppbv exceedances?

We thank the reviewer for this observation. We have added information regarding the predicted meteorological conditions during the O_3 episodes (MDA8 above 50 and 60 ppbv) as suggested. Below are the paragraphs that have been modified in Results and Discussion.

‘The summer months see an increase in the input from France, Germany and the Benelux region, in particular during anticyclonic weather conditions and over the receptor regions located in the south and east of the UK (e.g., South East England, East Anglia, the London area and the East Midlands). This is consistent with results of studies on extreme O_3 in the EU and the UK reporting an increase in surface O_3 concentrations under anticyclonic conditions (e.g., Pope et al. (2016); Ordóñez et al. (2016); Romero-Alvarez et al. (2022)). Romero-Alvarez et al. (2022), in particular, has shown that a wide area of high pressure centred over the Netherlands coast affected most of England during the first days of July 2015. During the same period, regions such as the East Anglia reported increases in O_3 mixing ratios of up to 16.6 ppbv h^{-1} that overlapped with wind direction changes from south-southwest to south-southeast. Depending on the predominance of the wind direction (south- southeast and south-southwest), O_3 from anthropogenic sources within France can impact both the west and the east of the UK.'

'The contribution is greater in the southern UK due to the proximity to the source region. The contributions from the Benelux region and Germany are more significant in the east of the UK due to the proximity with the continent and association with easterly flows (east and southeast) (about 14% and 6% of the Eu super-region in the East Anglia during the summer months comes from these two source regions, respectively).'

'France was the most significant contributor to O_3 build-up when the mixing ratios exceeded the EU threshold in South East England (mean ~18 ppbv), East Anglia (mean ~21 ppbv), and the London area (mean ~26 ppbv) because convergence of westerly and south-easterly winds in the west of the UK diverted the contributions of domestic sources from these regions, as reported in Romero et al., (2022).'

'As in the contributions to the MDA8 O_3 value of 50 ppbv above, the lateral boundary component remained nearly constant in all receptor areas with a mean contribution of about 12 ppbv. This is because most of the UK's weather was dominated by anticyclonic conditions.'

'When exceedances to the hourly surface O_3 mixing ratios above 40 ppbv is considered, the LB component becomes the dominant source in both receptor regions (estimated mean concentration between 21-24 ppbv) as its threshold is close to the tropospheric baseline ozone level associated with maritime Nort Atlantic air masses.'

'Romero-Alvarez et al. (2022) has shown that MDA8 O_3 above 50 ppbv in the Southeast and East Anglia regions coincided in July 2015 with days when easterly winds prevailed (east-southeast flows). In contrast, MDA8 O_3 above 60 ppbv coincided with a shift in the wind direction from east-southeast to south-southeast and south and a sharp rise in the surface temperature.'

Specific Comments

Introduction - be more explicit about describing ozone production dependencies in NOx and VOC-limited conditions, and importance of NO+O3 in high NOx environment. This effect is variously referred to as 'titration' and 'scavenging'. It would help the reader to point out the reaction specifically.

The introduction now includes the O_3 titration reaction and an extended description of the NOx and VOC-limited ozone formation regimes. We also added HNO_3 formation to highlight ozone titration as a loss mechanism for ozone:

'The production of O_3 in the troposphere is highly non-linear. It depends on the abundance of nitrogen oxides (NOx = NO_2 + NO) and peroxy radicals (HO_2) generally produced after the oxidation of volatile organic compounds (VOCs) by hydroxyl radical (OH) (Monks, 2005). The reaction of NO with HO_2 and the subsequent photolysis of NO_2

generating O_3 is the primary known mechanism of O_3 production (Atkinson, 2000; Monks, 2005). NOx concentrations determine whether O_3 is produced or chemically removed (Monks, 2005). In the rural areas of most industrialized countries, where NOx is available at moderate levels, the rate of O_3 formation increases with increasing NOx concentrations (NOx-limited regime). In more polluted areas, by contrast, high NOx concentrations inhibit O_3 formation as this begins being depleted by NO (NOx titration effect). Subsequent formation of nitric acid (HNO_3) from the reaction of NO_2 with OH constitutes a major endpoint for O_3 in such environments (Monks, 2005). However, elevated inputs of non-methane VOCs (NMVOCs) can increase the production of O_3 as the reaction of VOCs with OH radicals become more significant (NOx-saturated regime).'

Line 79: Not clear what is meant by "the second warmest year in a row in Europe".

The sentence has been removed as it was not longer relevant.

Line 80: "EU information threshold of 1 hour (h) average mixing ratio of 180 µg m-3": the value of 180 µg m-3 is a concentration not a mixing ratio. Is the threshold defined as the 90 ppbv mixing ratio, or the 180 µg m-3 concentration? These are not necessarily equivalent (dependent on local meteorological conditions).

Thank you for the observation. The EU information threshold is defined as 90 ppbv (mixing ratio). We modified the sentence as follows:

'Several heat waves causing elevated O_3 values in Central and Western Europe that exceeded the EU information threshold of 1 hour (h) average mixing ratio of 90 ppbv.'

Line 97-99: Please clarify how the IC concentrations are applied. The phrase implies that they are used to initialise the model simulation at the outset, however the text implies that they are applied every 3 hours. Does this mean that the model fields are essentially overwritten with MOZART fields every 3 hours? Please clarify.

With thank the reviewer for the observation. Only BCs are ingested by the model every 3 hours. We have changed the sentence as follows:

'IC and BC for the chemistry fields were extracted from global simulations produced by the Chemistry Transport Model for O_3 and Related Chemical Tracers MOZART-4 GEOS-5 (Emmons et al., 2010). BCs were ingested into the model every 3 hours.'

Line 103: Presumably aerosol are also simulated in the model? Please provide information on the aerosol scheme used in the simulations.

Simulations were conducted only for gas-phase chemistry.

Line 169: Mean bias in µg m-3, ppb, or %? Please clarify.

Mean bias is in µg m^{-3}. We changed the line as follows: 'domain mean bias (MB)= -3.71 µg m^{-3}'

Figure S1 - Do you have an explanation for the lack of diurnal cycle in the model surface temperature at coastal sites? Does this imply issues regarding diurnal variation in mixing height / boundary layer? Is there any potential link to biases in the NOx and ozone shown? It would be helpful to expand more on some of these evaluations and comparisons in the main text.

The temperature at coastal stations is strongly influenced by sea surface temperature, therefore the coastal air temperatures are less variable than inland temperatures. We checked the land cover map and the selected grid cells and they correspond to a water body (ocean). We therefore removed the panels from the plots and corresponding statistical analysis as it is no longer relevant analysis.

Fig. 3, 4, 6 captions: the plots depict mixing ratio, not concentration. Please change wording to reflect this.

Caption in Figs. 3, 4 and 6 was changed to mixing ratio.

Typographical errors:

Line 35: "Concentration of …" -> "The concentration of..'

The line was corrected as suggested

Line 94: Erroneous "G. a."?

The line was corrected 'Grell et al., 2005'

Line 100: "shipping lines' -> "shipping lanes"?

The line was corrected as suggested