Supplement of

Sources of Surface O_3 in the UK: Tagging O_3 within WRF-Chem

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S1. Model evaluation

S1.1 Meteorology

The meteorological dataset used in the model evaluation includes hourly observations of near ground air temperature (T) and wind speed and direction at 10 meters above the ground (WS and WD, respectively) at 21 sites using the land surface observational data UK's Met Office Integrated Data Archive System (MIDAS) (Met Office, 2006). The statistical analysis was performed using the R-Openair package (Carslaw and Ropkins, 2012) and statistical scores that include the mean bias (MB), the normalized mean bias (NMB), and Person correlation coefficient (*r*). Table S1 lists the average statistical performance of modelled temperature and wind speed across UK.

Table S1. Average statistics for modelled temperature and wind speed performance, from May to August 2015, across the UK. The units of MB are the same as the observations.

Parameter	MB	NMB (%)	r	No sites
T (°C)	0.7	8	0.7	21
WS (m $s^{-1)}$	-3.7	-39	0.4	6

The model represents well the observed near-surface air temperature variability over the UK, with correlation values ranging between 0.9 and 0.5 across tue selected sites. The poorest correlation is obtained in sites near the coast, e.g., Rhoose (0.51), Brawdy (0.54) and Holsom (0.59), where the model struggles to capture the diurnal variation in the air temperature, as shown in Fig. S1. The model is biased positively in most of the assessed sites. The largest warm bias (MB = 3.7°C) is obtained at Boxworth Cambridgeshire, and the cold biases (MB = -2.3 °C) is obtained at Holsome Devon. The values of MB in the temperature over the UK are consistent with that reported by Mar et al. (2016) in the June-July-August 2006 evaluation of WRF-Chem over Europe, where cold bias mostly concentrates over Northern Ireland and the North and the southwest UK. The simulation gives a average NMB of 8% for the period between May and August.

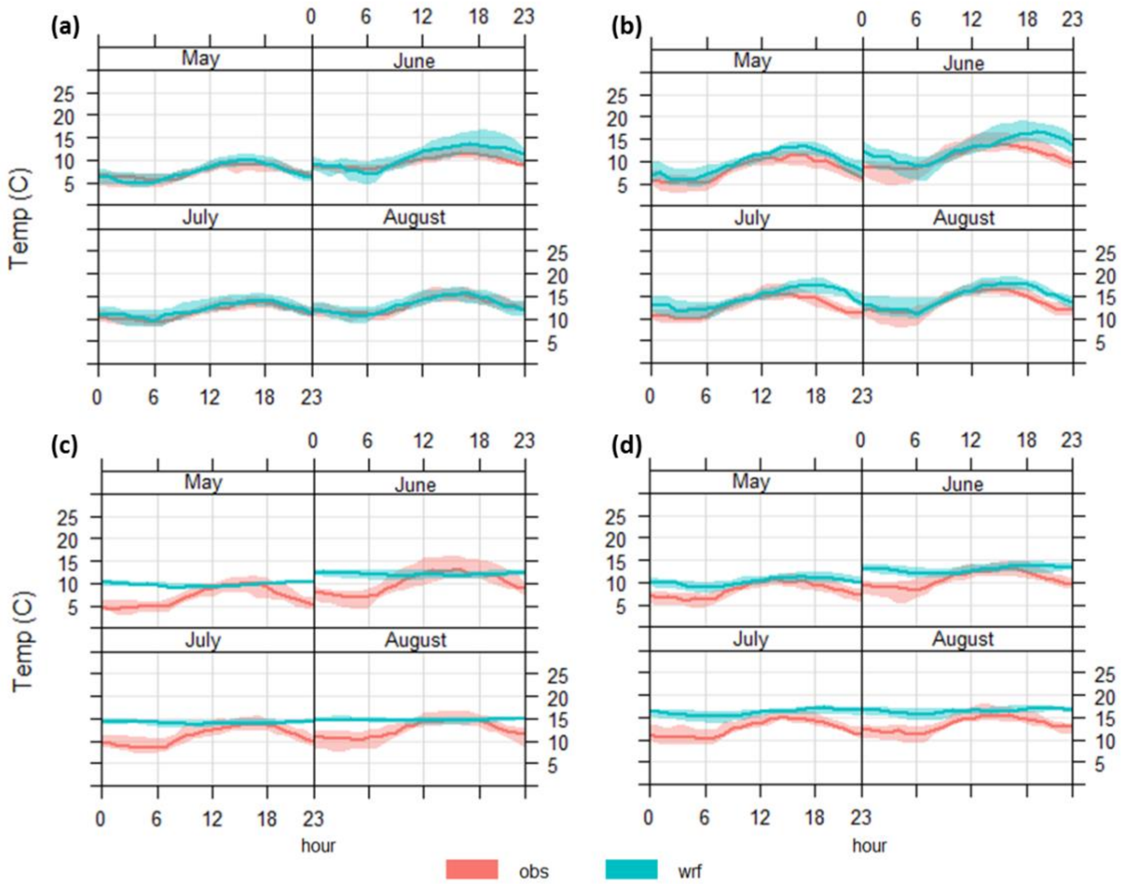

Figure S1. Comparison of the mean diurnal variation in temperature from May to August 2015 on land sites Bainbridge and Wellingborough (a and b, respectively) and near the coast sites Brawdy and Westleton (c and d, respectively).

Wind speed predictions exhibited inferior statistical performance. The average correlation coefficient is 0.4, with the lowest values showing no geographical preference. In particular, the model tends to predict moderate wind speed more frequently and fails to reproduce the highest observed wind speed values. Furthermore, the model is biased negatively in the majority of the sites with both the lowest biases (MB = -5.3 ms^{-1}) and the highest biases (MB = +0.9 ms^{-1}) obtained for the southwest. The MB values are closer to those reported by Zhang et al. (2013) in the model validation of WRF/Chem-MADRID and WRF/Polyphemus over Europe where wind speed is under-predicted at many sites in the UK (with MBs of −4 to −0.8 m s^{-1}). The simulation gives an average NMB of 39% for the period between May and August.

Comparison of modelled and observed wind speed direction. Fig. S2 shows that the sites are predominately positive bias (bias shown in polar coordinates) ranging between 3 and 23.7° North. The model does a better job simulating winds from south, southwest and southeast. The spread in the wind direction tends to be narrower across land sites in the midlands, such as Cirencester, Dagenham and Wilford Hill, when compared to those sites that are closer to the coast, e.g., Sibsey. The figure also shows that positive biases in wind speed tend to predominate during southerly, easterly and westerly winds at most of the stations, while negative biases in wind speed are mostly associated with northerly winds.

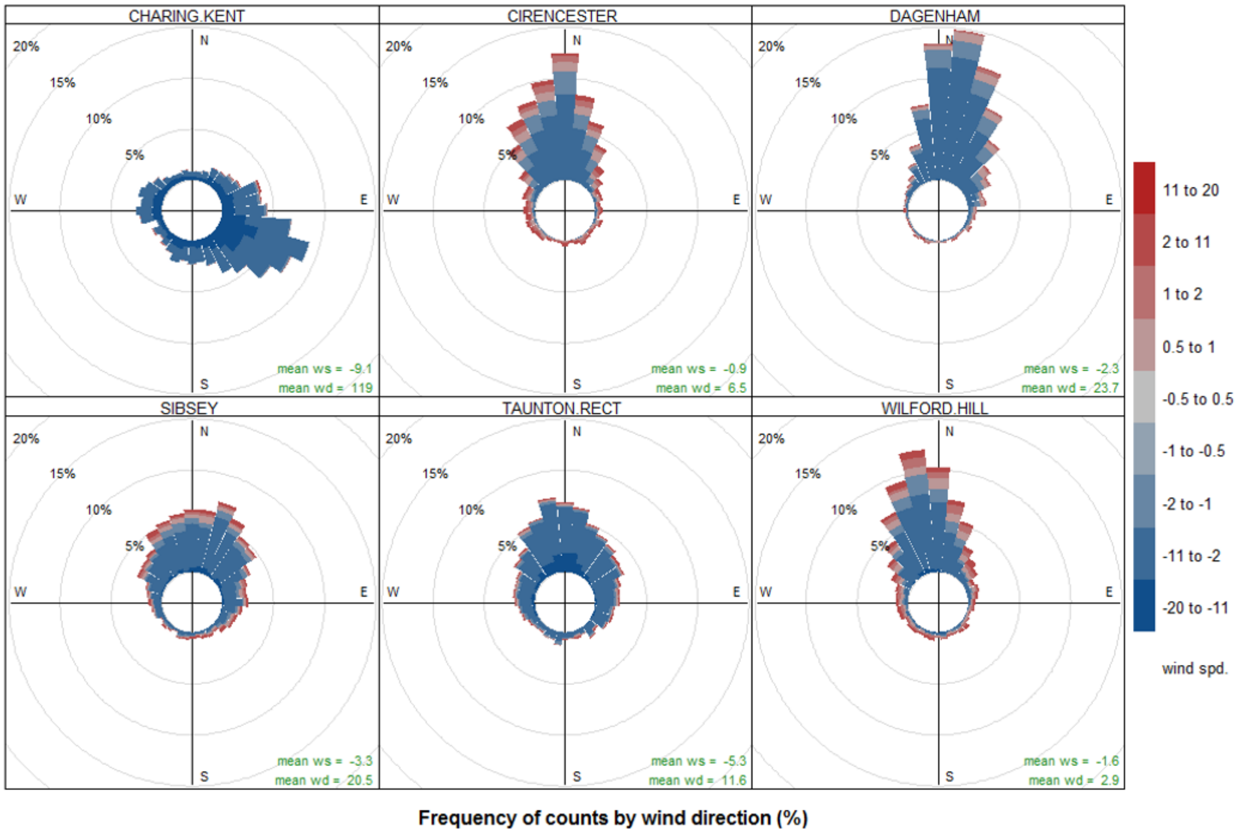

Figure S2. Bias between modelled and observed wind direction and speed, from May to August 2015, at six Met-office sites in the UK. Colours denote whether wind speed tend to be positively or negatively biased with respect to observations. Mean wind speed and direction bias are included as numerical values.

S1.2 Chemistry

Hourly surface O_3 measurements, on the other hand, were taken from the European Monitoring and Evaluation Programme (EMEP) (http://www.nilu.no/projects/ccc/) from April to August 2015 at available sites in the UK, Ireland, France, The Netherlands, Switzerland, Denmark, Austria, and Germany. Surface measurements of NO and NO_2 were also taken for the same stations when available. Table S2. Sumarises the statistical performance.

Table S2. Statistics of hourly NO, NO_2 and O_3 calculated between May and August 2015. MB is given in ppbv.

Parameter	MB	NMB (%)	r	No sites
NO (ppbv)	-0.36	-39	0.29	15
NO_2 (ppbv)	0.31	19	0.25	16
O_3 (ppbv)	-3.71	6	0.65	52

The predicted temporal correlation coefficient for NO and NO_2 is fairly low in the majority of the analyzed sites, with values ranging between 0.1 and 0.5, which is a feature exhibited also in other regional studies in Europe using WRF-Chem with MOZART as a chemical mechanism. The model simulation tends to underestimate NO concentrations in most of the analysed sites with MB of up to -3 ppbv. In particular, observed night-time concentrations for NO typically remain above zero, whereas modelled concentrations at night reach zero most of the time. By contrast, NO_2 concentrations are generally overestimated with MB of up to 8 ppbv, and no specific patterns are distinguished in the distribution of the bias. This is consistent with the negative NO biases and positive NO_2 biases obtained across Europe and reported in Mar et al. (2016), negative NO biases were attributed, among other reasons, to deficiencies of the model to represent NO_x chemical cycles and to errors in reported low NO observations due to artifacts introduced when recording NO concentrations approaching the minimum detection limit. Further comparison of the diurnal cycles for NO at selected stations in the UK, Fig. S3, shows that the model underestimates nocturnal NO concentrations and has difficulties predicting the timing of the NO peaks. NO_2 diurnal cycles, on the other hand, are well captured.

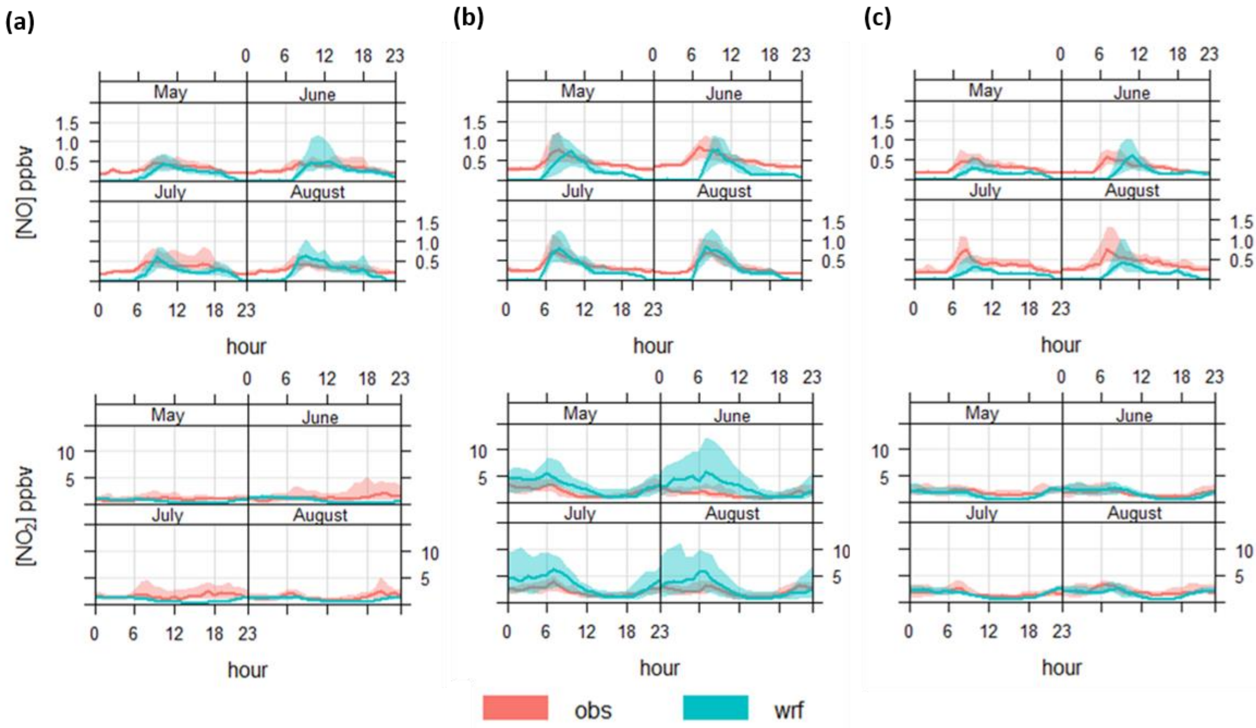

Figure S3. Mean diurnal variation in observed (red) and modelled (blue) NO and NO_2 mixing ratios at Bush State (a), Wicken Fen (b) and Charlton Mackrell (c). The shaded areas represent the variability between the different days, showing the 25th and 75th percentiles.

Table S2 also summarizes the statistics of modelled and observed hourly O_3 performance of the individual sites and the domain wide average. The temporal variation in hourly O_3 concentrations at most sites is well represented by the model with an average *r* value of 0.6 . Values of *r* above 0.5 are obtained in most sites particularly over the UK, see Fig. S4a, while low values (*r* values about 0.4) are concentrated on high altitude sites which might indicate difficulties in the representation of O_3 concentrations at different vertical levels. The results in terms of correlation values are consistent with hourly *r* values of summer O_3 (June, July and August) > 0.40 reported on the WRF-Chem model evaluation over a European domain on Mar et al. (2016) using MOZART as a chemical mechanism.

The model tends to underestimate concentrations in most of the sites, with model negative biases of up to -15 ppbv and positive MB of up to and + 5 ppbv, see Fig. S4b. Negative biases are mostly restricted to sites in the North, and West of the UK and the throughout the Alps. Mace Head, for instance, exhibits a negative MB of -4.6 ppbv. Due to its geographical location on the western fringe of the UK, this site is strongly influenced by the model boundary conditions. Hence, the underestimations are most likely caused by biases in the representation of background O_3 entering the western fringe of the domain, particulatly the O_3 predictions in the model used for boundary conditions (MOZART-4).

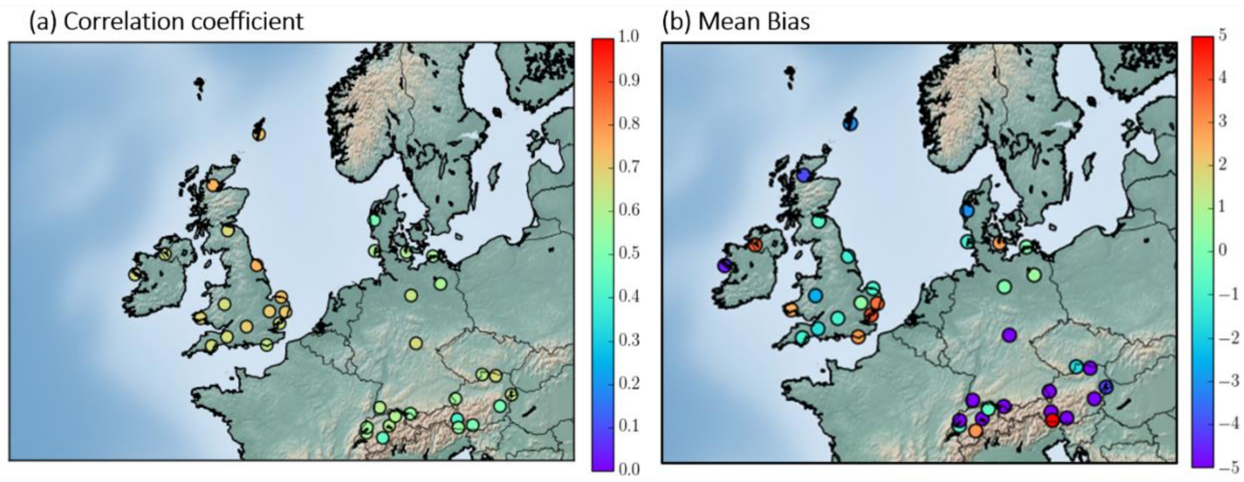

Figure S4. Temporal correlation coefficient r (a) calculated from hourly measurements at each site and mean bias MB ppbv (b).

Fig. 5S shows that underestimations of O_3 in Mace Head are greatest during July and August. In contrast, underestimations of O_3 in sites such as Charlton Mackrell, Strathvaich, Weybourne, Auchencorth Moss and High Muffles, arise from the model having difficulties in capturing the diurnal changes in O_3, and in particular day time concentrations during the summer months. Positive biases, on the other hand, are mostly observed in the east and southeast UK and north of Germany, with a few exceptions, see Fig. 4S. Overestimated O_3 concentrations at Lough Navar, Bush Estate, Narberth, Sibton and Wicken Fen, for instance, are due to the model struggling to reproduce the diurnal changes in O_3, giving high O_3 concentrations during night-time, Fig. 5S. This is consistent with insufficient titration of O_3 at night due to the underestimated NO discussed in the previous section. An additional source of model bias may be also caused by the limitation of comparing grid cell averages with point observations and by the choice of the grid cell representing each site. As an example Lough Navar which is located about 6 km from Lough Ern the second-biggest lake system in Northern Ireland so it is likely that the obtained diurnal concentration is influenced by the nearby lake.

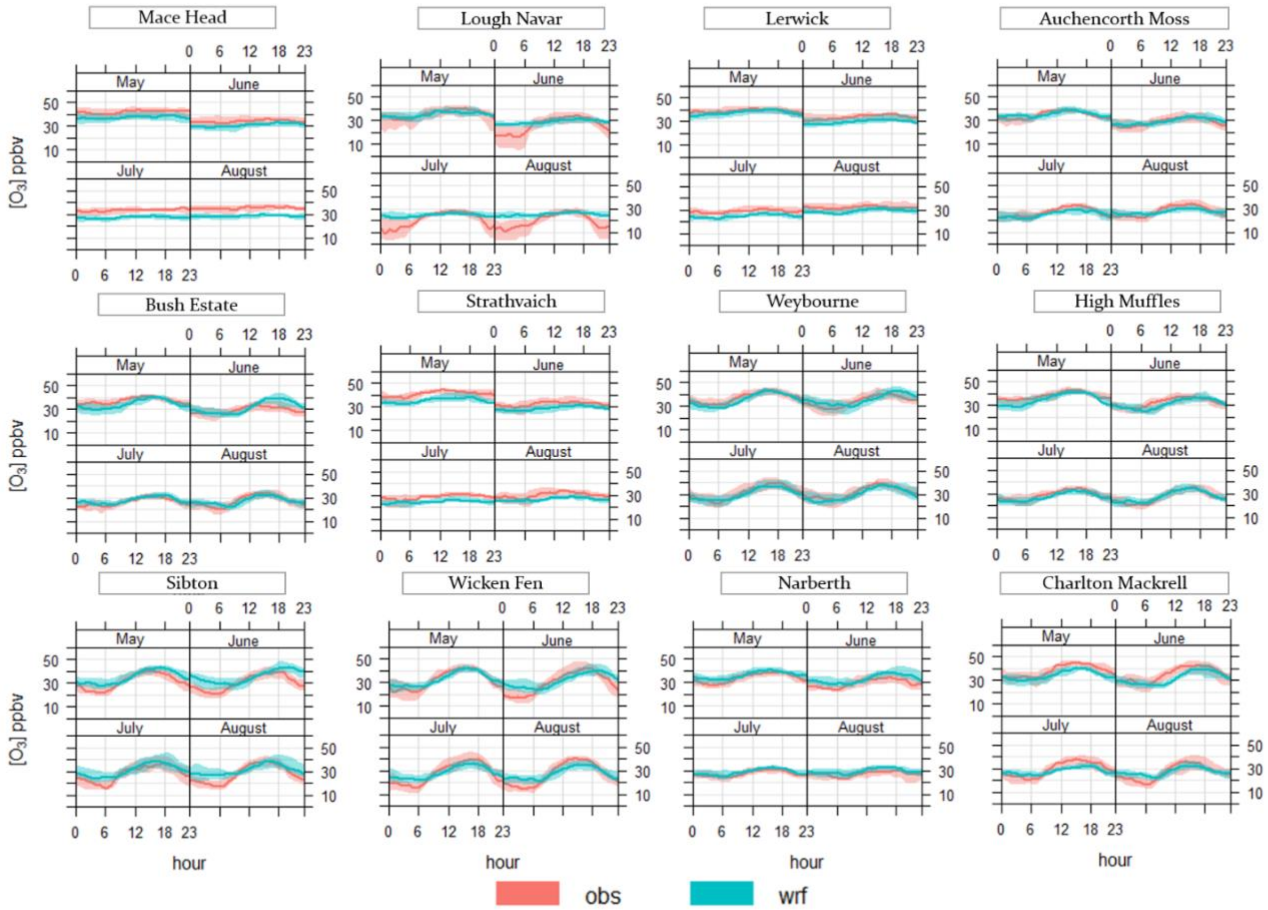

Figure S5. Diurnal variation in modelled and observed O_3 mixing ratios at selected sites in UK and the Republic of Ireland. The shaded areas represent the variability between the different days, showing the 25th and 75th percentiles.

Two additional metrics were considered for O_3, the MDA8 O_3, and the AOT40. The MDA8 O_3 was estimated by computing 8-h moving mean of O_3, for both modeled and observations at each site, and by selecting the hours when the MDA8 of 50 and 60 ppbv was exceeded, following the current European and national air quality standards. The AOT40 was calculated by extracting the hours when O_3 mixing ratios exceeded the hourly 40 ppbv thresholds between 08:00 and 20:00 CET.

Fig. S6 shows the number of days with the MDA8 O_3 above 50 ppbv at 15 EMEP monitoring sites from May to August over the UK and the Republic of Ireland. The UK's Air quality strategy states that the MDA8 O_3 should not exceed the threshold value of 50 ppbv more than ten times a year. The figure shows that most of the observed concentrations at the stations had less than ten days above 50 ppbv apart from those located in the East Anglia region, southwest and southeast England. The largest MDA8 O_3 is seen at Wicken Fen, Yarner Wood, Weybourne, Sibton and Lullington Heath with 17, 15, 14, 12 and 12 days with MDA8 O_3 values above 50 ppbv respectively. Fig. 5S further shows that the model does a fair job capturing the spatial distribution of the MDA8 O_3 above 50 ppbv with the largest number of days concentrated in the East Anglia region and Southeast England. Nonetheless, the model tends to underestimate the number of days with MDA8 O_3 above 50 ppbv, in particular over the East Anglia region, which is in line with earlier studies stressing the poor performance of many air quality models in simulating peak O_3 concentrations in the UK (e.g., Archer-Nicholls et al., 2014; Francis et al., 2011).

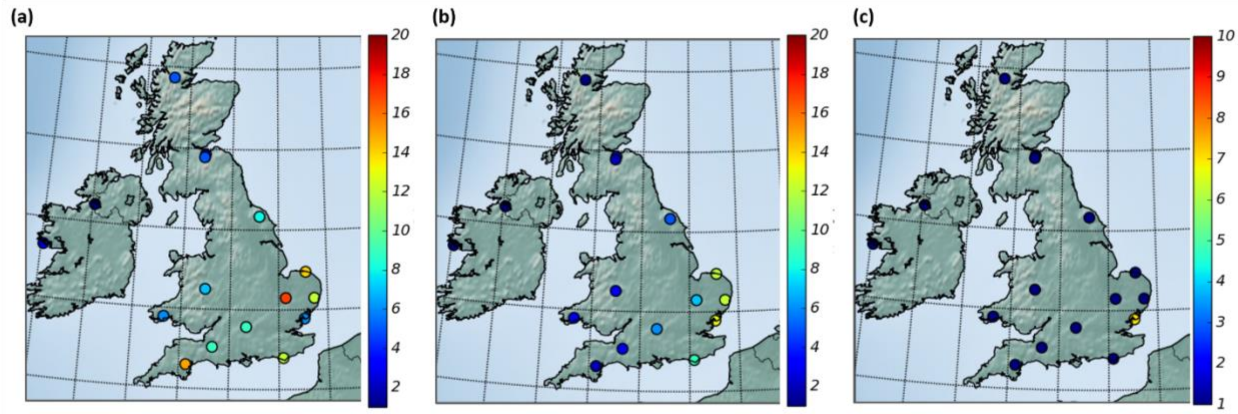

Figure S6. Spatial distribution of (a) observed and (b) modelled number of days with a daily MDA8 O_3 above 50 ppbv at EMEP monitoring sites calculated from May to September. The difference between observed and modelled MDA8 (observations – model) is also shown in (c). Please note the different scale used on (c).

The spatial distribution of the number of days with MDA8 O_3 above 60 ppbv is shown in Fig. S7. The European Union's Air Quality Directive long term objective states that the MDA8 O_3 should not exceed the threshold value of 60 ppbv within a calendar year. The observed values show that most of the sites have less than five days above 60 ppbv, except for some sites in the East of UK (East Anglia and the East Midlands). Similar to the MDA8 O_3 above 50 ppbv metrics, the model tends to underestimate the number of days with MDA8 O_3 above 60 ppbv in particular in the East Anglia Region. This is consistent with what has been reported for coarse simulations over a European domain for summertime using MOZART chemistry within WRF-Chem (Mar et al., 2016). Some overestimations of the metric, never higher than 5 days, are observed in the northeast UK.

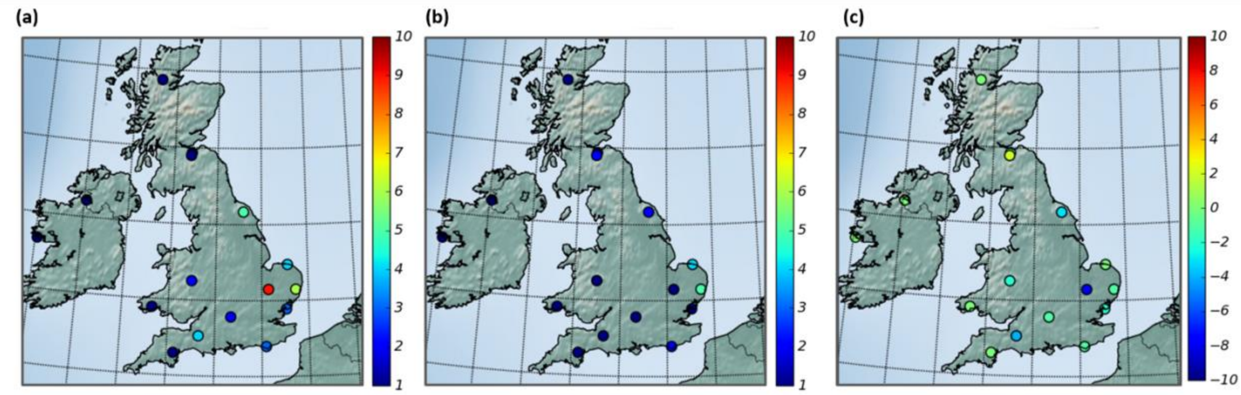

Figure S7. Spatial distribution of (a) observed and (b) modelled number of days with a daily MDA8 O_3 above 60 ppbv at EMEP monitoring sites calculated from May to September. The difference between observed and modelled MDA8 (observations – model) is also shown in (c).

The metric for vegetation exposure AOT40 is shown in Fig. 8S. The UK's Air Quality Directive states a target value of 9000 ppb h (~18000 µg m^{-3} hours) averaged over five years. The highest observed values are seen in the east of England (with up to 6000 µg m^{-3} hours observed at Weybourne and Wicken Fen) and the southwest. The model captures most of the spatial distribution of the AOT40, with the largest values obtained for East Anglia. However, it tends to underestimate observations in the southeast (up to - 3000 μg m^{-3} hours), and overestimate them mostly in the southeast and Suffolk coast (e.g. St. Osyth up to 3000 μg m^{-3} hours).

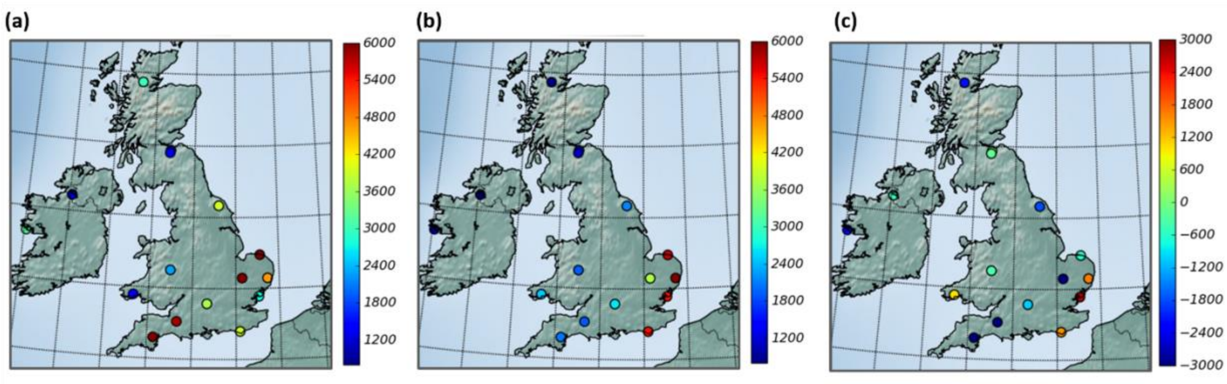

Figure S8. Spatial distribution of (a) observed and (b) modelled AOT40 (μg m^{-3} hour) calculated from May to September. The difference between observed and modelled AOT40 (observations – model) is also shown in (c). Please note the different scale used on (c).

References

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., & Hodnebrog, Ø. (2014). Gaseous chemistry and aerosol mechanism developments for version 3.5.1 of the online regional model , WRF-Chem. *Geoscientific Model Development*, *7*, 2557–2579. https://doi.org/10.5194/gmd-7-2557-2014

Carslaw, D. C., & Ropkins, K. (2012). Openair - An r package for air quality data analysis. *Environmental Modelling and Software*, *27–28*, 52–61. https://doi.org/10.1016/j.envsoft.2011.09.008

Francis, X. V., Chemel, C., Sokhi, R. S., Norton, E. G., Ricketts, H. M. A., & Fisher, B. E. A. (2011). Mechanisms responsible for the build-up of ozone over South East England during the August 2003 heatwave. *Atmospheric Environment*, *45*(38), 6880–6890. https://doi.org/10.1016/j.atmosenv.2011.04.035

Mar, K. A., Ojha, N., Pozzer, A., & Butler, T. M. (2016). Ozone air quality simulations with WRF-Chem (v3.5.1) over Europe: Model evaluation and chemical mechanism comparison. *Geoscientific Model Development*, *9*(10), 3699–3728. https://doi.org/10.5194/gmd-9-3699-2016

Met Office (2006): MIDAS: UK Hourly Weather Observation Data. NCAS British Atmospheric Data Centre, 2016. Retrieved fromhttp://catalogue.ceda.ac.uk/uuid/916ac4bbc46f7685ae9a5e10451bae7

Zhang, Y., Sartelet, K., Zhu, S., Wang, W., Wu, S. Y., Zhang, X., Wang, K., Tran, P., Seigneur, C., & Wang, X. F. (2013). Application of WRF / Chem-MADRID and WRF / Polyphemus in Europe – Part 2 : Evaluation of chemical concentrations and sensitivity simulations. *Atmos. Chem. Phys.*, 6845–6875. https://doi.org/10.5194/acp-13-6845-2013