AIR QUALITY EXPERT GROUP

Ozone in the UK
- Recent Trends and Future Projections

Prepared for:
Department for Environment, Food and Rural Affairs;
Scottish Government; Welsh Government; and
Department of Agriculture, Environment and Rural Affairs in Northern Ireland

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of Agriculture, Environment and Rural Affairs in Northern Ireland, on recent trends in surface ozone over the United Kingdom and future trajectories. The information contained within this report represents a review of the understanding and evidence available at the time of writing.

Front cover image credit: Ozone damage on leaves: Felicity Hayes (UKCEH)

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PB14701

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AQEG's functions are to:

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- Suggest priority areas for future work, and advise on Defra's implementation of the air quality evidence plan (or equivalent);
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Ozone in the UK – recent trends and future projections

Why a report on ozone?

Ozone in the lower atmosphere is a significant air pollutant with a wide range of different impacts. The negative effects of ozone pollution in the lower atmosphere (below ~10 km) are in contrast to the highly beneficial properties of stratospheric ozone (above ~20 km), the latter forming a critical shield that protects life on Earth from excess UV radiation. Ozone in the lower atmosphere is well-established to affect health through both short-term and, probably, long-term exposure. It is a highly reactive gas which also damages plants and trees and leads to substantial losses in agricultural crop yields. This reactive property means that it also causes damage to buildings and materials such as rubbers and plastics when exposed to outdoor air. In the middle and upper troposphere (~ 4 -10 km) ozone pollution is also a significant anthropogenic greenhouse gas, with post-industrial effects on radiative forcing broadly similar in scale to those arising from increases in atmospheric methane. Chemical reactions involving ozone also indirectly affect the concentrations of other pollutants in the air which have their own adverse impacts. This diverse range of environmental impacts means that the control of ozone (and its chemical precursors) is linked not only to delivering better public health, but also to the successful management of ecosystems, biodiversity, food supply and climate change. Large changes in emissions of pollutants responsible for ozone production in the lower atmosphere have occurred in recent years, both in the UK, more widely in continental Europe and throughout the northern hemisphere. The ozone climate of the UK is therefore changing, hence the need for this new assessment.

Executive Summary

Ozone near the planetary surface is considered an air pollutant because of its adverse effects on human health, crop yields, and ecosystems more broadly. In addition, ozone in the free troposphere is a greenhouse gas with climate impacts. Ozone is a relatively long-lived air pollutant so can be transported for periods of days to several weeks over large distances. The concentrations that arrive over the UK in the prevailing westerly winds from the Atlantic are influenced by the cumulative effects of emissions that occur throughout the mid-latitudes of the Northern Hemisphere.

UK population and ecosystem exposure to ozone is frequently lower than the north Atlantic baseline due to dominant ozone sink processes of removal by reaction with local emissions of NO and deposition to the terrestrial surface. In spring and summer, net ozone production from UK emissions, in addition to advection from mainland Europe, leads to episodes of elevated concentrations.

Control of surface ozone is complex since it is not emitted directly from any source but is formed in the atmosphere in a non-linear manner from reactions involving nitrogen oxides (NO_x), methane, volatile organic compounds (VOCs) and sunlight. Air quality policies have been in place to reduce surface ozone since the 1980s, through control of emissions of NO_x and VOCs from sources such as vehicles, combustion, fuels and solvents. The 1990s saw reductions in peak concentrations and fewer severe ozone pollution events – a consequence of substantial reductions in emissions implemented internationally through agreements such as the Gothenburg protocol. Overall, since the UK is a net sink for ozone, changes in ozone concentration are controlled by the changes in the chemical and deposition sinks as well as changes in baseline concentration and local chemical production.

The distribution of ozone across the UK shows highest concentrations over upland and rural locations, with annual average concentrations of >60 µg m^{-3} widespread over rural areas in Scotland, Northern Ireland, Wales, south-west England and the Pennines. Urban and suburban concentrations are typically ~15 µg m^{-3} lower than rural values, although this is very sensitive to local emissions from road transport, and in heavily-trafficked roadside locations ozone concentrations can locally be close to zero. Ozone typically reaches its highest concentrations in the UK during April and May, although anticyclonic weather patterns in summer can also lead to significantly elevated concentrations.

Since 2000 there has been little observed change in UK rural ozone concentrations, or ozone in the air arriving from the wider Atlantic region to the UK. There have however been some upwards trends in suburban and urban ozone (average increases of the order 5 – 9 µg m^{-3} over the 20-year period 2000-2019). These upwards trends in suburban and urban ozone are a consequence of reductions in primary emissions of NO; the NO has the effect of locally suppressing ozone.

All areas of the UK have been compliant with the EU target value for the protection of human health for at least the last 12 years (≤25 days per year with daily maximum 8-hour mean ozone concentration >120 μg m^{-3}, averaged over 3 years). Substantial parts of the UK are however routinely not compliant with the EU long-term objective of zero exceedance of this metric, although the number and geographical extent of these exceedance days has generally been declining over the last 20 years. All areas of the UK have been compliant with the EU target value for the protection of vegetation for at least the last 12 years (AOT40 not exceeding 18000 μg m^{-3}.hour per year, averaged over 5 years). The EU long-term objective for the protection of vegetation is lower (AOT40 <6000 μg m^{-3}.hour each year). Attainment of this is sensitive to meteorology; in a recent high ozone year (2018) much of England and Wales did not meet this long-term objective, although it was met in most parts of the UK in the previous four years. Other measures to quantify human health and vegetation impacts exist and trends in these metrics can differ from those above. Health impact metrics that use lower or zero ozone concentration cut-offs have increased in magnitude over the last 20 years. For vegetation, stomatal uptake (phytotoxic ozone dose) metrics are now widely accepted as a better measure of vegetation damage than AOT40 and these show continued exceedances and little change in recent years.

The prediction of future surface ozone in the UK is complex and subject to multiple drivers. Wider hemispheric trends in ozone resulting from global trends in emissions, in particular of methane, will have a significant impact on UK concentrations, but the direction of change is unclear. Further UK reductions in NO_x emissions are anticipated and these will likely lead to further increases in urban ozone but be beneficial more widely and reduce ozone at a transboundary scale. Projections indicate little change to UK VOC emissions in the coming decade and this will become a limiting factor for reducing ozone in an optimal manner. Climate change will have multiple effects on ozone precursor emissions, chemical production and loss, dispersion and deposition. Whilst climate change is likely to lead to periods of higher temperatures that are known to increase biogenic VOC emissions and to reduce the surface dry deposition of ozone, the net effect on ozone of all climate-change influences is not known.

As other air pollutants in the UK continue to decline it seems likely that the importance of ozone will grow, especially as its contribution to climate provides further motivation for control measures.

Extended answers to policy-relevant questions

How is surface ozone currently distributed across the UK in space and time?

Maps of ‘air pollution’ frequently show patterns of highest concentrations located in cities, along roads and near major sources of combustion. The distribution of ozone is however noticeably different since it is a secondary pollutant formed relatively slowly through atmospheric reactions, and ozone concentrations can be locally suppressed in cities by reaction with locally-emitted nitric oxide (NO).

Annual-average ozone concentrations vary by approximately a factor of two across the UK. Average concentrations of >60 μg m^{-3} are widespread over Scotland, Northern Ireland, Wales, south-west England and the Pennines (except over urban areas) and exceed 70 μg m^{-3} over the highest ground in these regions. Upland areas tend to have the highest average ozone concentrations since the greater vertical mixing with altitude replenishes the ozone that is lost by dry deposition to the surface compared with locations at lower altitude. The effect is particularly prevalent at night when vertical mixing is generally suppressed. Over the rest of rural England, average ozone concentrations are in the range 50-60 μg m^{-3}. Annual average ozone concentrations are smaller over major urban/industrial areas and transport corridors compared with the concentrations in their neighbouring rural areas because of the rapid chemical removal of ozone by reaction with NO close to the sources of NO emissions. A typical urban decrement of around 10-15 μg m^{-3} results in average ozone concentrations of 40 μg m^{-3} or less in the centre of the largest conurbations, and strong intra-urban spatial gradients in ozone between suburban background and heavily trafficked roadside locations.

Ozone exhibits strong seasonal and diurnal cycles. Monthly average ozone concentrations in the UK are at their maximum in April and May, in contrast to most of continental Europe where monthly ozone has a maximum in June and July. The amplitude of the annual cycle is around 25-30 μg m^{-3} ,being slightly greater at urban sites, which likely reflects increased rates of chemical removal in winter from increased NO emissions in winter. There is some evidence that the annual amplitude in ozone has been decreasing slightly (amplitude change approx. −0.5 μg m^{-3} y^{-1}).

Ozone generally shows a strong diurnal cycle with maximum concentrations in the mid to late afternoon. The amplitude of the diurnal ozone profile at urban background sites (~15-20 μg m^{-3} between minimum and maximum) is usually greater than that seen at rural sites. At elevated (hence generally windier) rural sites and for coastal sites influenced by onshore winds, diurnal cycles can be very small. Urban areas frequently have higher ozone concentrations at weekends, of the order of 15% (or ~6 μg m^{-3}) greater on Sundays compared with weekdays, whilst rural sites generally show no significant difference in ozone concentration across the week. Higher weekend ozone in urban areas reflects the weekday-weekend differences in NO emissions, particularly those related to transport.

Superimposed on these broad patterns of ozone distribution are episodes of higher ozone concentrations that typically occur for a few days at a time in spring and summer. These occur when stagnant air masses lead to build-up of NO_X and VOC pollution, and higher solar intensity and temperatures increase rates of the photochemical oxidation of VOCs that generates ozone.

What are the trends in surface ozone over the last 20 years?

Ozone concentrations can vary substantially between years (differences in annual averages of several µg m^{-3}) because of inter-annual variability in meteorology. Meteorology affects ozone concentrations by altering the balance of air masses arriving in the UK of Atlantic origin compared to mainland Europe or Arctic. Meteorological variability also affects the frequency of low wind-speed anticyclonic events, the temperature dependent emissions of biogenic VOC emissions, and soil moisture-dependent ozone dry deposition rates. The effects of meteorological variability can be different across different areas of the UK in any given year, so, consequently, long time series (>10 years) of consistent measurements and model simulations are needed to evaluate the long-term trends in averages and extremes in ozone concentrations.

There is clear observational evidence that average urban ozone concentrations have been increasing in recent years, whilst average rural concentrations and concentrations associated with the higher percentiles have changed little since 2000. This contrasts with significant reductions in rural and higher percentile concentrations in the latter decades of the 20th century. The quantitative trends in urban background ozone are sensitive to the statistical approaches used. The median trend in deseasonalised monthly mean ozone across 12 UK urban background sites over the 20-year period 2000-2019 is +0.26 µg m^{-3} y^{-1}, which corresponds to a median increase of +5.2 µg m^{-3}. The mean trend in non-deseasonalised annual mean ozone across all AURN urban background sites (not taking account differing lengths of available data) is +0.47 µg m^{-3} y^{-1}. There is considerable site-to-site variation however; whilst trends at some urban sites indicate 20-year increases in average ozone in excess of 12 µg m^{-3}, other urban sites exhibit no significant upward trend. This reduction in the ozone decrement over urban areas and major transport corridors because of decreasing urban NO emissions (particularly from traffic) means that urban ozone concentrations are gradually converging with adjacent rural concentrations.

Changes in average ozone concentrations at UK rural background sites over the period 2000-2019 have been modest. The median trend in deseasonalised monthly means at 13 rural background sites is +0.11 µg m^{-3} y^{-1}, corresponding to an increase of 2.2 µg m^{-3} over the 20-year period, but many rural sites show no statistically significant trends.

Measurements made at the Mace Head observatory on the west coast of Ireland can be used to quantify the westerly import of ozone into the British Isles. After clear increases in ‘hemispheric baseline’ Atlantic ozone at Mace Head from the 1970s to the mid-2000s, concentrations over the last 15-20 years have been largely constant, with conclusions on recent trends being sensitive to the exact time period chosen and the nature of the statistical processing applied to the raw concentration data (e.g. deseasonalisation, temporal decomposition or filtering by air mass direction). The deseasonalised trend for 2000-15 is downwards but for 2000-19 the trend is statistically-significantly upwards (+0.11 µg m^{-3} y^{-1}). However, 2017 and 2018 were relatively ‘high’ ozone years due to meteorological patterns in those years. There is no statistically significant trend in annual average 50th percentile ozone for the period 2000-19.

In general, there have been no statistically significant trends in the upper percentiles of ozone concentration for the period 2000-2019 at both rural and urban sites. Upper percentiles of ozone are indicators of ‘episodic’ or the worst ozone pollution events. Since average concentrations at urban sites have increased, the magnitudes of the high concentration episodes above the local urban background must have decreased slightly. Overall, however, decreases in high ozone concentration episodes across the UK over this 20-year period have been modest.

Evidence from geographical differences in ozone concentration distributions, supported by trends in ozone attributed to particular air-mass types, including data at Mace Head, suggests that although the majority of ozone arrives in the UK in westerly air, the recent trends in average and episodic ozone are more significant in easterly than in westerly (background) air flows. This reflects both the greater impacts in the east of the UK from changes in precursor emissions in continental Europe and larger reductions in NO_x concentrations in eastern areas of the UK – the latter arise because the UK population (and associated activities that give rise to NO_x emissions) are greater in the east than the west.

What are the changes in UK population and ecosystem exposure to ozone over the last 20 years?

The impacts of ozone on human health and on ecosystems are quantified by a number of more complex metrics than simply the average atmospheric concentration. Inferences on spatial patterns and temporal trends in ozone impacts on health and ecosystems are sensitive to which of these metrics are used.

All areas of the UK have been compliant with the EU target value for the protection of human health for at least the last 12 years (defined as ≤25 days per year with daily maximum 8-hour mean ozone concentration >120 µg m^{-3}, averaged over the last 3 years). On the other hand, substantial areas of the UK routinely continue not to be compliant with the EU long-term objective which is zero exceedance of this metric. However, over the last 20 years there has generally been a reduction in the number of exceedance days and geographical area covered by those exceedances.

The World Health Organization (WHO) recommends that health impacts are quantified using the annual sum of the daily maximum 8-hour mean ozone exceedances of either 70 µg m^{-3} (35 ppb, referred to as SOMO35), which is also used by the European Environment Agency, or 20 µg m^{-3} (10 ppb, referred to as SOMO10). The daily maximum 8-hour mean ozone cut-off concentrations used in these metrics are lower than the 120 µg m^{-3} (60 ppb) concentration used in the European Union. In the last 20 years, SOMO35 (and SOMO10) values have increased in the most urbanised areas, and slightly decreased in rural areas. The trend in (short-term) human health impacts of ozone is therefore sensitive to the cut-off concentration that is used. The UK Committee on the Medical Effects of Air Pollutants (COMEAP) recommend not to include a cut-off concentration. Analyses that use a very low or zero cut-off concentration for ozone therefore indicate that the human health impact of ozone is increasing; it is also increasingly being driven by exposures to ozone outside of the summer months, particularly in spring which is when the annual maximum in UK ozone occurs, and less by shorter-duration summer ‘episodic’ exceedances.

All areas of the UK have been compliant with the EU target value for the protection of vegetation for at least the last 12 years. The metric is based on a version of the AOT40 statistic not exceeding 18000 µg m^{-3}.hour per year, averaged over 5 years. The EU long-term objective for the protection of vegetation is AOT40 <6000 µg m^{-3}.hour each year. In 2018, which was meteorologically a relatively high ozone year, only some parts of Scotland and a few urban areas met this objective, with much of England and Wales having AOT40 values exceeding 9000 µg m^{-3}.hour. However, most parts of the UK did meet this long-term objective in the previous four years.

As with the assessment of the human health impact, other metrics exist for the assessment of the impact of ozone on vegetation and conclusions on the trend in the impact is sensitive to that choice. The stomatal flux-based POD_Y (phytotoxic ozone dose) metrics are now widely accepted as a better measure of vegetation damage than AOT40. These show continued exceedances of critical values and, in contrast to the declines shown for AOT40, little or no decline in the past 20 years.

The choice of metric to quantify human and vegetation exposure to ozone has consequences for policy actions to reduce these exposures. To reduce concentrations of ozone in excess of 70 µg m^{-3} (and higher) then reductions in NO_x and VOC emissions at the European and UK scales are likely to be effective. However, if the mean and/or lower concentrations of ozone better quantify the influence of ozone on health and vegetation (as recent thinking suggests), then controls of precursors at the hemispheric scale are required to reduce background ozone, which must also include action on methane emission reductions.

What are the drivers of current trends in UK ozone and what has been the influence of Europe-wide NO_x and VOC changes?

Most of the ozone experienced in the UK is a consequence of the hemispheric and global emissions of methane (to which the UK contributes) and of ozone generated from NO_x and VOC emissions outside the UK, including emissions from Europe and also beyond at hemispheric scale. Transport of ozone from the stratosphere also contributes to surface ozone in the UK, particularly in early spring. Approximately three-quarters of ozone in the UK may be considered as deriving from the ‘hemispheric baseline’ on average. The relative influences on UK ozone of the hemispheric baseline, of UK and continental VOC and NO_x emissions, and of the UK depositional sink, varies with time of year and the percentile of the ozone concentration being considered. As examples: dry deposition is greater in spring and summer; the higher the ozone concentration percentile being considered, the larger the influence of UK and continental emissions. This means that the values and trends of the various ozone impact metrics, which vary in the different portions of the ozone distribution and times of year they include, are differentially influenced by these drivers on UK ozone.

UK and total European emissions of NO_x have steadily declined since the 1990s but the declines in emissions of VOC have flattened since around 2010. The trends of reducing NOx and constant VOCs emissions are predicted to continue to 2030. The ratio of NO_x to VOC emissions was around 1.5 in the mid-2000s, but has since declined to a value of 1.1 due to the slower reductions in VOC emissions. The ratio is predicted to fall further to 0.75 by 2030. Constant-meteorology model simulations indicate that changes in UK and European anthropogenic NO_x and VOC emissions have resulted in little change to annual average ozone in rural areas and to increases in annual average ozone in the range 0.4 to 0.9 $\mu g\ m^{-3}\ y^{-1}$ in urban areas over the 2001-2015 period, the latter driven by the reductions in UK urban NO emissions. The same model simulations indicate that the Europe-wide NO_x and VOC emissions have led to little change in POD_1 and to an increase in SOMO35. These simulations quantify how changes in Europe-wide land-based anthropogenic emissions have influenced UK ozone. However, the actual trends in UK ozone have also been influenced by changes in other drivers.

The *in situ* production of ozone over most of the UK is transitioning away from the NOx-saturated chemistry that existed over much of central, eastern and southern England for the past 60 years. The increasing sensitivity to NO_x reflects the substantial reductions in emissions in these areas over the last 15 years or so. All other factors being equal, further NO_x emissions reductions in these areas will reduce ozone production more efficiently than would have been the case a decade or more ago.

Further reductions in ozone also require continued reductions in VOC. In the UK, as elsewhere, VOC emission profiles are increasingly de-coupled from energy and gasoline consumption and are now predominantly driven by industrial and domestic use of manufactured volatile chemical products. Achieving future reductions in atmospheric concentrations of VOCs will need additional interventions that are not reliant solely on further reductions from the extractive industries, fuel distribution or road transport.

In addition to the VOC mix changing, the photochemical ozone creation potentials of individual VOC compounds may also have changed since last quantification because of *inter alia* the change in VOC to NO_x ratios.

The lack of significant downward trend in high percentile concentrations of ozone in recent years may reflect a trend of increased vegetation water-stress during ozone episodes, i.e. a climate-ecosystem interaction. In episodes of elevated ozone in hot, dry conditions soil water deficit induces stomatal closure, reducing dry depositional loss of ozone to vegetation. The reduction in ozone deposition to vegetation in hotter and drier future UK summers may offset some of the gains generated from reductions in NO_x emissions.

As other air pollutants in the UK continue to decline it seems likely that the importance of ozone will grow, especially as its contribution to climate provides further motivation for control measures.

What are the projections for future surface ozone in the UK?

The future trajectory of surface ozone is tightly coupled to the socioeconomic pathways that are followed around the world and their associated climate and air quality related emissions. Ozone may continue increasing for the foreseeable future or it may peak in the next decade and start decreasing, depending on the pathway for a basket of precursor emissions. Whilst some key trajectories can be assumed to be downwards, such as NO_x from passenger cars, other sectors are far less certain. A critical driver of the future trend in baseline ozone is emission of methane on a global scale. Future shipping emissions of NO_x are also an important and uncertain determinant on both baseline ozone and on ozone in areas close to shipping activity.

Irrespective of anthropogenic ozone precursor emissions, as the climate warms and polar stratospheric ozone recovers, the contribution of downward transport of ozone from the stratosphere to the surface may increase.

Within the UK, actions necessary to achieve net zero greenhouse gas emissions by 2050 are predominantly anticipated to be of benefit to surface ozone since many actions require large-scale switching from fossil-fuel combustion to decarbonised electricity production and transport. A potential dis-benefit for future surface ozone relates to possibly increased biogenic VOC emissions from increased planting of forests and biofuel crops: selection of low-emitting species needs to be a key consideration.

Considering only the changes in ozone that would arise from the current European anthropogenic NO_x and VOC reductions agreed under the 2030 National Emissions Ceiling Directive, then further increases would be anticipated in (i) urban annual-average surface ozone, and (ii) the SOMO35 health burden metric (with very small increase in non-urban annual-average ozone). The vegetation impact metrics measured as AOT40 and POD_1 would be predicted to decrease. However, it is important to remember that the impacts on UK ozone from UK-only and continental European policy and actions will be superimposed on the concentrations of ozone that are consequent on all such actions on precursor emissions elsewhere globally, and on wider climate change effects (most of the ozone in the atmosphere over the UK is imported from external sources). As stated above, the net impact on UK ozone of all possible influences is not known.

How has ozone changed during the COVID-19 lockdowns?

The change in UK surface ozone concentrations as a response to the first COVID-19 lockdown implemented in the UK on 23rd March 2020 are hard to discern using observations alone because of the substantial effects of meteorological and transboundary influences. Preliminary analyses of measurements and models that endeavour to take account of these factors suggest no single direction of ozone concentration change, although a tendency for increases in surface ozone in urban areas, driven by the substantial reductions in traffic emissions of NO, leading to a shift towards ozone in the partitioning of urban O_x (sum of ozone and NO_2). These were most notable in central and south-eastern parts of the UK. The ozone response during lockdown may provide an analogue of a near-future UK atmosphere in which combustion-related transport emissions of NO_x have further declined as part of the transition to net zero carbon, but with other relevant emissions such as VOCs remaining broadly as now.

Is there an appropriate measurement programme in place to assess ground-level ozone impacts and trends?

The natural variability in ozone means that discerning trends is crucially dependant on the existence of consistent, high quality and long-time series of measurements. The UK already has a numerically and geographically extensive network of real-time ozone measurements, spanning the full range of site types from remote rural to kerbside. However, whilst the measurement of ozone in isolation can be sufficient to determine trends, it is essential that multi-pollutant measurement ‘supersites’ are retained or increased to help interpret those changes. The measurement of parameters such as photolytic fluxes would also be beneficial.

Daily lower troposphere ozone maps at a few km spatial resolution should be feasible in the future from satellites that currently provide column measurements of NO_2 and HCHO, in combination with modelling. Cloud cover will, as for other atmospheric composition parameters, mean that coverage will be highly weather dependant and this often limits measurements in UK winter.

Progress in improving metal-oxide and electrochemical sensors, and in data-processing algorithms, coupled with cost reductions, provides some prospect for reliable, spatially dense urban ozone sensor networks, albeit with concern over potential loss of transparent linkage between sensor signal and final readout and without the absolute measurement basis provided by current spectrophotometer based instruments.

The quantification of deposition fluxes of ozone is a considerably more complex challenge than the measurement of ozone concentrations. Depositional fluxes are currently measured routinely only at the Auchencorth Moss moorland site in central Scotland and over coastal water at Penlee Point in Cornwall. There is therefore a lack of measurement evidence to validate and/or improve the parameterisations used in the atmospheric chemistry and transport models as well as fluxed-based ozone impact metrics such as POD_1. There would be scope to develop an ozone deposition network as part of the UK’s work under Article 9 of the European National Emissions Ceilings Directive (2016/2284). Such a measurement network for ozone flux would need to cover ozone concentration and flux, water flux, as well as a number of ancillary meteorological and plant physiological parameters.

Recommendations

1. Ozone has multifaceted effects as a pollutant and there remains a critical need to maintain a monitoring network across the diverse geography and ecosystems of the UK, capturing rural, suburban and urban environments. The fast chemical reactions that couple ozone, NO and NO_2 requires an increased emphasis on measuring all three parameters at the same location. This is likely to be critical for the attribution of future ozone trends, and whether these are driven by regional / trans-boundary effects or more localised changes in UK NO_x emissions.
2. Further evaluation of trends in impacts of ozone on health and vegetation are required. There are several different metrics in use and these can result in different interpretations of both the magnitude and trend of impacts. Quantification of the latter is further complicated by the high sensitivity of some impact metrics to meteorological interannual variability. It is recommended that data analysis tools (for measurement data) and model diagnostics be established that routinely quantify these health and vegetation impact metrics. Model outputs should also be population-weighted for health metrics. COMEAP does not recommend the use of a concentration 'cut-off' for the quantification of short-term health impacts of ozone, and so a routine calculation of a 'SOMO-zero' metric is recommended.
3. Trends in ozone over the last two decades have been quantified in this report, but it has not been possible to establish quantitatively the underlying drivers of those changes. Further model simulations are required to evaluate the relative effects on UK surface ozone from recent changes in 'hemispheric baseline' conditions (the ozone flowing into the UK from the Atlantic), changes in UK precursor emissions, and changes in continental precursor emissions. It is likely that attribution of effects may well be different when considering different ozone metrics, for example annual average concentrations, objectives based on higher percentile concentrations, and SOMOx and POD_Y metrics. Without further detailed modelling analysis it remains unclear what fraction of ozone over the UK could be influenced directly by future UK actions to reduce precursors of NO_x and VOCs.
4. Related to Recommendation (3), AQEG highlights the potentially significant effects of hemispheric methane concentrations on UK ozone which require more quantitative evaluation. Methane acts as a source of peroxyl radicals for ozone generation both locally and at the hemispheric scale, and has indirect impacts, for example on oxidants which alter rates and concentrations of other atmospheric species. As a potent greenhouse gas methane also impacts on temperature-dependent drivers on ozone formation (emissions, rates of reactions, etc.).

5. The photochemical formation of ozone is dependent on precursor emissions of NO_x, VOCs and other trace gases. The impact of recent changes in the types of VOCs emitted in the UK and Europe (see AQEG report *VOCs in the UK*, 2020) requires further exploration, and a more detailed assessment of photochemical ozone creation potential (POCP) should be made to reflect current and future VOC emissions speciation. Metrics such as POCP that are used to evaluate VOC impacts (and by extension those prioritised for controls) should be extended to include not just impact on formation of ozone but also to impact on formation of peroxyacetyl nitrate (PAN) and secondary organic aerosol (SOA). Linking more closely the control of VOCs from a combined perspective of ozone and $PM_{2.5}$ is likely to be beneficial.
6. The reductions in urban NO_x observed in recent years have led to higher concentrations of ozone in the urban environment. Substantial temporary falls in urban traffic and NO_x during the COVID-19 pandemic has highlighted the scale of this effect for the future. To improve estimates of future human exposure to ozone in the urban environment will require improved spatial resolution in models to better account for reductions in NO_x emissions, the heterogeneity in NO_x distributions and the non-linear relationship of ozone with NO_x. This also applies to improving the representation of the high-resolution dispersion and chemical effects on ozone of ship NO_x emissions from shipping in UK coastal waters.
7. Dry deposition of ozone to vegetation is both a critical route for environmental harm and also a major control on surface ozone concentrations. A network of ozone deposition flux measurements would facilitate validation and/or improvement of the parameterisations used in atmospheric chemistry and transport models as well as quantification of fluxed-based ozone impact metrics such as POD_Y. There would be scope to develop an ozone deposition network as part of the UK's work under Article 9 of the European National Emissions Ceilings Directive (2016/2284). Such a measurement network for ozone flux would need to cover ozone concentration and flux, water flux, as well as a number of ancillary meteorological and plant physiological parameters.
8. Ozone is a pollutant that is influenced by processes that scale from the roadside to the hemispheric and its future trajectory in concentrations depends in part on greenhouse gas reduction strategies in the UK and globally. Further quantitative analysis is required to evaluate the potential impacts (positive and negative) of Net Zero GHG pathways on concentrations of ozone (and other air quality pollutants) over the UK. An example illustration of the need to coordinate the Net Zero and air quality agenda is the appropriate selection of low BVOC-emitting species for bioenergy/biofuel trees and crops (see AQEG report *Impacts of Net Zero on future air quality in the UK,* 2020).

9. The transboundary nature of ozone as an air pollutant is well recognised and this motivates international agreements (e.g. UNECE LRTAP, NECD etc.) for the control of emissions of precursors of NO_x and VOCs. There remains a critical requirement to coordinate future emissions reduction actions at the international level. Further modelling work to establish the reciprocal benefits of more ambitious UK and continental European ozone precursor emissions reductions is recommended.
10. Related to Recommendation (8), the future of ozone is also tied to uncertain large-scale changes in weather arising from climate change. Further analysis is required to establish the potential effects on ozone of changes in processes such as North Atlantic circulation, Rossby wave breaking, frequency and location of blocking highs and elevated summertime temperatures. Ozone is particularly sensitive to weather impacts which can influence the biogenic emission of VOCs, change dry deposition rates and affect emissions of NO_x from soils. There remains uncertainty over the future trends in stratospheric input of ozone to the troposphere in north-west Europe from the perspectives of recovery of the Arctic stratospheric ozone layer and as a result of the impact of climate change.

Contents

Chapter 1 - Introduction

Ozone is a minor but highly influential gaseous component of the atmosphere. In higher parts of the atmosphere (at heights between about 15 and 40 km – the stratosphere) ozone absorbs much of the sun's ultraviolet radiation and therefore prevents this harmful radiation reaching the ground. This is the 'ozone layer' (Figure 1). However, ozone in the air at the surface is of concern because of its effects on human health as well as on crops and ecosystems. Ozone in the lower atmosphere is also a greenhouse gas. Chemical reactions involving ozone influence rates of atmospheric chemical reactions, which in turn impact on the concentrations of other air quality and climate-change pollutants, and contributes to the conversion of gaseous compounds to detrimental particulate matter.

Although air quality policies have been implemented to reduce its concentrations, control of ozone is problematic because it is created in the atmosphere rather than being directly emitted from processes that can be regulated. The amount of ozone at any location is the net outcome of a large number of processes influencing its production, loss and transport that operate over a wide range of temporal and spatial scales, from very local to intercontinental.

This chapter provides a brief overview of the effects of surface ozone (also known as ground-level ozone), the processes determining its creation and removal, and the policy context for its control.

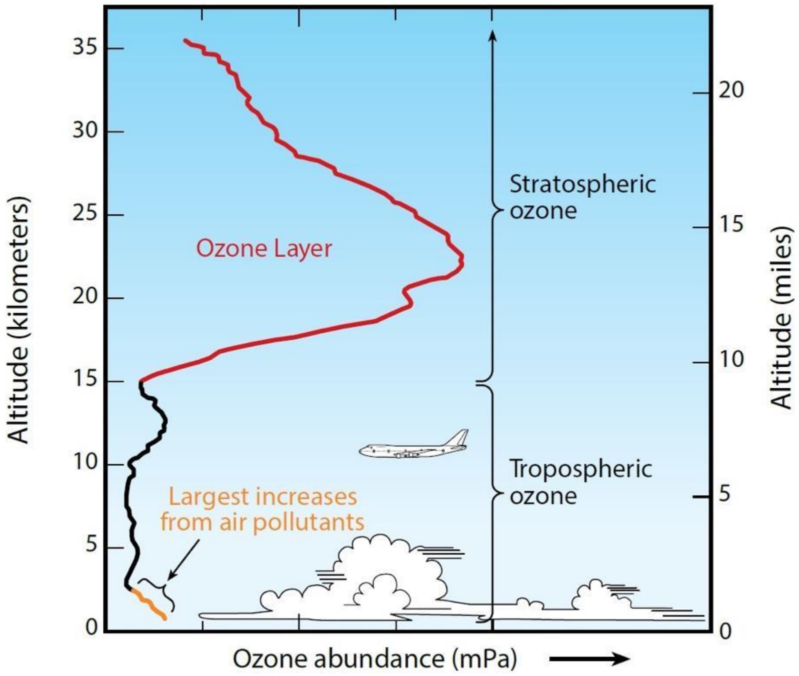

Figure 1: Abundance of ozone with altitude, showing relatively larger amounts between 15-40 km (the natural stratospheric 'ozone layer') and near the surface because of pollution. The latter is the subject of this report. Tick marks on the ozone axis are at 5 mPa intervals. Figure from WMO (2018).

1.1 The effects of ozone on crops, forests, ecosystems and people

1.1.1 Crops

Ozone is a powerful oxidizing agent and generates free radicals within and between plant cells. This necessarily requires access by ozone to the internal structure of plants, which occurs via stomatal apertures. Ozone uptake also occurs on the external surfaces of vegetation and there is some evidence that it accelerates the degradation of epicuticular wax structures, thus aging the protective outer surfaces of vegetation. However, the damage to vegetation occurs primarily within plants following stomatal uptake and leads to reduced carbon assimilation and increased respiration. The effects on ozone sensitive crops (e.g. wheat, soy bean) increase approximately linearly with the stomatal absorbed ozone dose above a threshold, thought to represent the free radical scavenging capacity of a crop. The free radical scavengers include ascorbate and glutathione among others, and variability in their supply within plant tissue has been shown to be an important regulator of sensitivity to ozone damage (Emberson, 2020).

Global yield losses for wheat due to ozone have been estimated in the range 4-15% (Van Dingenen et al., 2009), a range covering many of the recent estimates of wheat losses at regional scales (Emberson, 2020). While this scale of crop loss represents a substantial economic loss (globally 3.2 to 14 billion USD annually in recent years), the effects are not independent of climate. Drought and high temperatures, which correlate positively with elevated ozone episodes, also depress yields of major crops. Estimates of crop loss between 2000 and 2050 suggest that the effect of ozone will continue at levels similar to recent decades, with high temperatures having a similar scale of effect (Tian et al., 2011). However, it is important to note that effects of crop management have a greater effect on yield than ambient ozone, typically by a factor of two.

1.2.1 Forests

Forest productivity is also sensitive to ambient ozone, and some of the first observations of ozone effects on vegetation were identified in the San Bernardino Mountains of California (Haagen-Smit, 1952). The physiological effects of ozone on forest are similar to those on agricultural crops, with reduced net assimilation rates and dry matter productivity. Effects on root systems and root biomass appear to be very important and these make the trees much more sensitive to other environmental and biological threats, especially drought.

The practical difficulties in experiments with trees has led to much of the assessment being based on work with young trees. Buker et al. (2015) estimated 11-13%

reductions in annual biomass growth in response to ozone fumigation for European forest species and exposures to European summer ozone concentrations. For larger trees, open-air fumigation studies with ozone show reduced growth and net primary productivity in the order of −10 to −25% (Matyssek et al., 2010) for a range of forest tree species. Effects of ozone on forests at concentrations similar to those in central Europe and over much of the USA have been shown to reduce dry matter productivity at the −10 to −20% level. These reductions have offset effects of rising CO_2 concentrations and reactive nitrogen deposition, which have both been accelerating forest productivity. Using process-based models, the scale of the effects of enhanced CO_2 and N deposition on the productivity of northern hardwood forests in the USA were shown to be of a similar magnitude to the reductions in productivity due to ozone (Ollinger et al., 2002). Thus, ozone decreases the terrestrial carbon sink, which represents a second, indirect effect on climate, in addition to being a greenhouse gas itself (Sitch et al., 2007).

1.1.3 Other semi-natural ecosystems

Unlike agricultural crops and forests, which provide most of the field studies of long-term effects of ozone, the evidence for effects on other ecosystems is very limited. In a review of the subject, Fuhrer et al. (2016) showed that 40% of global terrestrial ecoregions were exposed to ozone above thresholds for ecological risks, and that the largest exposures were in North America, East Asia and Southern Europe, where there is field evidence of adverse effects of ozone. The assessments to date imply slow responses of the plant communities and subtle changes as ozone sensitive species are replaced by more ozone tolerant species, leading to overall productivity of the plant community changing little. However, the evidence to date shows that the range of interspecific ozone sensitivity observed in agricultural crops is similar to that present in natural plant communities, so that species casualties in a high ozone world are inevitable (Hayes et al., 2007). In addition, reduced species richness can lead to a reduction in certain ecosystem services as well as ecosystem resilience to other stresses (e.g. Mills et al., 2013).

1.1.4 Effects on human health

Like vegetation, human health effects of ambient ozone are generated by the damage caused by free radicals and the host reaction to the damage. Ozone causes oxidative damage to the cells and the lining fluids of the airways, thereby inducing immune-inflammatory responses in the lung. Lippman (1993) noted that evidence from epidemiological studies showed ambient exposures were associated with reduced lung function, asthma and premature mortality in the USA.

Epidemiological studies on the effects of ozone have used a range of metrics to characterise ozone exposure and results have been mixed. Whilst assessments show clear effects of ozone on human health, the scale of the effect is smaller than effects of $PM_{2.5}$ and PM_{10} and have attracted less attention for this reason.

In a recent review, Atkinson et al. (2016) noted that current evidence for impacts on health associated with long-term exposure to ozone was inconclusive, and the UK Committee on the Medical Effects of Air Pollutants does not currently recommend a concentration-response coefficient for quantifying long-term effects of ozone in the UK (COMEAP, 2015).

Evidence for short-term effects of ozone is stronger. COMEAP provides the following concentration-response coefficients for quantifying the mortality and hospital admissions associated with short-term exposure to ozone in the UK (COMEAP, 2015), with coefficients expressed as % increase per 10 $\mu g\ m^{-3}$ increase in daily maximum 8-hour running mean ozone, with no concentration cut-off.

- All-cause mortality (all ages): 0.34% with 95% confidence interval (CI) from 0.12% to 0.56%
- Respiratory hospital admission (all ages): 0.75% (CI: 0.3% to 1.2%)
- Cardiovascular hospital admission (all ages): 0.11% (CI: 0.06% to 0.27%)

Other organisations and regulatory authorities specify different guidelines and limit values for quantifying short-term health impacts (see Table 1 and Section 3.1).

1.2 Factors controlling surface ozone

Ozone is a unique pollutant in that it is not emitted directly into the atmosphere but is formed and removed from the atmosphere through a wide range of chemical reactions and physical processes, the timescales of which range from minutes to years. The ozone concentrations in the troposphere are therefore controlled by the balance between its sources and sinks. When these are out of balance, concentrations can change quite rapidly (on a timescale of hours or less). Processes controlling surface ozone were comprehensively described in previous Royal Society and AQEG reports on ozone (Royal Society, 2008; AQEG, 2009) and only the most important points are described here.

1.2.1 Chemistry

1.2.1.1 Ozone sources

Ozone produced in the stratosphere

At high altitudes, molecular oxygen is photolysed at wavelengths shorter than those which occur in the troposphere, and this produces oxygen atoms which undergo a three-body collision with an oxygen molecule and a non-reacting molecule (M) to form ozone

$$O_2 + h\nu \rightarrow O + O \quad \lambda < 243\ nm$$

$$O + O_2 + M \rightarrow O_3 + M$$

The peak concentration is at 25-30 km altitude, but some ozone from this source mixes down to the ground surface.

Ozone formed in the troposphere

Photolysis of nitrogen dioxide (NO_2) splits the molecule into nitric oxide (NO) and an oxygen atom:

$$NO_2 + h\nu \xrightarrow{J_1} NO + O(^3P) \qquad \lambda < 420\ nm$$

The atomic oxygen can then make ozone, but the ozone can also react with NO to reverse the process:

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2$$

As all three reactions are rapid, in daylight the rate of ozone formation is balanced by ozone removal,

$$J_1[NO_2] \quad = \quad k_3[O_3][NO]$$

from which $[O_3] = \frac{J_1\,[NO_2]}{k_3\,[NO]}$

This is termed the photostationary state and does not lead to net ozone formation. However, in the presence of carbon monoxide or other volatile organic compounds (VOC), further reactions occur.

Photolysis of ozone in the troposphere leads to the formation of the hydroxyl radical (OH) (as does photolysis of other molecules such as nitrous acid and formaldehyde):

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \qquad \lambda < 315\ nm$$

$$O(^1D) + H_2O \rightarrow 2OH$$

The OH radical can then react with carbon monoxide (CO), methane (CH_4) or other VOC to generate peroxyl radicals (radicals with the general formula RO_2, where R can be an H atom, a methyl radical CH_3, or larger organic radicals). Taking reactions with CH_4 and CO as examples:

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CO + OH \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

The peroxyl radicals (e.g. CH_3O_2 and HO_2) are capable of converting NO to NO_2 without direct consumption of ozone:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

This starts a chain of reactions which regenerate OH radicals without further ozone photolysis and perturbs the photostationary state towards higher ozone concentrations. The exact outcome of reactions of mixtures of VOC and NOx (NO + NO_2) are complex but, in general, the co-location of both sets of species maximises the potential for net ozone creation. Methane and CO react rather slowly with OH, having reaction half-lives of several years and months respectively, but are present in the atmosphere at much greater abundances than larger, more reactive VOC. Consequently, emissions of methane and CO predominantly control the ‘hemispheric baseline’ concentrations of ozone, whilst emissions of other VOC cause more rapid formation of ozone leading to ‘episodes’ of high concentration, which in Europe typically occur on a regional scale.

The direct reaction between NO_2 and alkene VOCs can also contribute to ozone generation but this route only becomes relevant at high concentrations of both species.

1.2.1.2 Ozone chemical sinks

Where emissions of NO are high, most notably close to fresh traffic emissions, the NO has the effect of shifting the photostationary state described above towards low ozone concentrations via the dominance of the reaction between NO and O_3. Ozone is therefore unusual amongst health-related air quality pollutants in having concentrations that are lower in urban areas (the so-called urban decrement) than in adjacent rural areas.

The production of the OH radical via the photolysis of ozone described above simultaneously acts as a chemical loss of ozone in the presence of water vapour. However, this only leads to net loss of ozone in very clean atmospheres, such as over oceans. In higher NO_x environments (which encompasses most of the northern hemisphere land masses) the ozone generated via the OH-initiated reactions described in the previous section more than offsets the ozone lost in the generation of the OH radical. In very high NO_x environments the reaction of NO_2 with OH is an important sink for OH, and so reduces the ozone generated via OH-initiated reactions; this is another cause of an ozone urban decrement.

1.2.2 Dry deposition

Ozone deposits to surfaces at a rate which can lead to substantial vertical gradients in concentration when vertical mixing is limited by atmospheric stability. Dry deposition is an important component in the overall budget of ozone and is discussed in more detail in Section 4.4.

1.2.3 Meteorology and climate

The tropospheric lifetime of ozone is typically several days or weeks. Concentrations in the UK are heavily influenced by the upwind baseline, either from the North Atlantic during westerlies, or continental Europe in an easterly circulation, i.e. by transboundary import – see next section. Dependent upon local meteorological conditions, surface ozone concentrations may be either decreased when UK sinks exceed the sources, or increased when photochemistry favours its formation. The large UK emissions of NO tend to have a major influence as a sink.

As well as determining the air mass reaching the UK, meteorology and climate indirectly influence ozone levels through many other processes (Doherty et al., 2017). For example, higher temperatures, particularly when coincident with high sunlight levels, increase the rates of the photochemical oxidation of VOC with NO_x that generate ozone. Biogenic volatile organic compound (BVOC) emissions from vegetation are strongly temperature dependent, and whilst BVOC emissions may be relatively small compared with anthropogenic VOC emissions on an annual basis, they can be very important during warm spells. When soil moisture is low, vegetation stomata may close in response and loss of ozone by dry deposition is reduced (e.g. Vieno et al., 2010).

Higher temperatures also increase the water vapour in the air (which has complex chemical influences on ozone) and increase emissions of methane from wetlands and NO_x from soils and the prevalence of ozone precursor gases from wildfires.

Local meteorological conditions influence the stability and hence rate of pollutant ventilation from the surface boundary layer, and climate change is likely to influence the number and persistence of ‘blocking’ high-pressure stagnation episodes that cause build-up of ozone (and other pollutants) from local sources of NO_x and VOCs.

1.3 Transboundary issues and the role of international actions

The consequence for policy of the range in timescales associated with the ozone budget is that concentrations of ozone in any one country are not controllable to any significant degree by actions in that country alone. There are three main contributions to ozone concentrations, namely (i) intrusions from the ozone-rich stratosphere, (ii) the tropospheric ‘hemispheric baseline’, (iii) ‘photochemical’ ozone generated from the well-known reactions of VOCs and NOx. Stratospheric intrusions are clearly uncontrollable but can on occasion contribute to elevated surface concentrations (Derwent et al., 1978; Colbeck and Harrison, 1985b). This is discussed further in Section 5.1.

The tropospheric hemispheric baseline, which comprises a large part of long-term average concentrations, is determined largely by global emissions of methane, and annual average surface baseline concentrations in the UK are in the range 30-40 ppb (60–80 µg m^{-3}) (see Section 2.1). The reason for the global spatial scale is because the lifetime of methane in the atmosphere is ~10 years so that methane is well mixed over the globe. Control of the tropospheric ozone baseline is therefore a hemispheric or global problem.

The photochemical ozone-generating reactions involving VOCs and NO_x have timescales ranging from minutes to days so that the spatial scale for ozone formed from these reactions is of the order of many 100s of kilometres, which from a UK perspective means emissions from much of Europe (but predominantly the north west) will potentially make contributions. Typical lifetimes of reactive VOCs range from about an hour for isoprene (emitted by some vegetation) to about 10 days or so for propane, with a range of other lifetimes in between. These reactions generate short-term peak hourly ozone concentrations which can add to the tropospheric baseline and reach total hourly concentrations of up to ~100 ppb (200 µg m^{-3}) during episodes typically characterised by high pressure systems over north-west Europe leading to easterly/south-easterly winds bringing ozone formed from precursors emitted in the rest of Europe (see Section 4.5). These episodes typically last for a few days and make little contribution to long-term average concentrations, i.e. to annual or summer means.

These scientific considerations are of fundamental importance for policy and legislation. The most obvious manifestation of this is in the EU Air Quality Directive

2008/50/EC (EC Directive, 2008) where ozone concentrations are governed by a non-mandatory 'Target Value' (TV)[1] as opposed to a mandatory 'Limit Value' (LV) as are pollutants like $PM_{2.5}$ and NO_2. Separate TVs exist for ozone in respect of its effects on human health and on vegetation. The details of the TVs, LVs and other metrics for the quantification of the effects of ozone are given in Table 1. In the context of the short-term impacts of ozone on health, the Committee on the Medical Effects of Air Pollutants specifically recommend against using a threshold concentration in health impact quantification (COMEAP, 2015).

These Target Values are consistent with a regional/Europe-wide approach to reducing ozone concentrations in that they focus on peak short-term concentrations above the tropospheric baseline. Peak short term concentrations of ozone in the UK have reduced significantly since the 1970s when hourly concentrations of ~200 ppb (400 µg m^{-3}) or more were observed (AQEG, 2009). As peak concentrations have declined, the magnitude of the tropospheric baseline clearly assumes greater importance. Moreover as NO_x concentrations reduce, long-term (e.g. annual or summer average) concentrations in urban areas increase and will tend towards the tropospheric baseline. There is still uncertainty over the health impacts of long-term ozone exposures. Whilst the WHO HRAPIE study recommended a concentration-response function for summer average ozone concentrations, albeit with a reduced confidence (WHO, 2013a), COMEAP currently conclude the evidence between long-term exposure to ozone and mortality is not convincing (COMEAP, 2015).

Although ozone concentrations are not controllable by any one country, national total emissions of precursor pollutants contributing to ozone formation are. This has been the method of reducing ozone concentrations in Europe via (i) the UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP) in the preamble to the Gothenburg Protocol (revised in 2012 and currently being considered for revision) and (ii) the National Emission Ceilings Directive (NECD, Directive (EU) 2016/2284 revised in 2016) in the EU. The targets for emission ceilings are linked to ozone concentrations via the IIASA GAINS integrated assessment model[2] which sets targets for exposures to pollutants based on health and environmental impacts and ultimately agreed in negotiation with parties to the CLRTAP Protocol and the NECD. Historically, the pieces of legislation which have done most to reduce ozone concentrations via the reduction of VOC and NO_x emissions are arguably the Euro standards Directives on vehicle emissions, particularly the introduction of three-way

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[1] The Directive defines a LV as '….a level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, ***to be attained*** within a given period and not to be exceeded once attained; while the TV is defined as 'a level fixed with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, ***to be attained where possible*** over a given period (AQEG 's emphasis).

[2] https://iiasa.ac.at/web/home/research/researchPrograms/air/GAINS.html

catalysts on petrol/gasoline vehicles and the Directives on the evaporative losses of vapour from the storage and distribution of petrol.

Table 1: Summary of air quality guidelines, target values and objectives for ozone.

For the protection of human health		
EU Target Value[a]	120 µg m^{-3} as maximum daily 8-hour mean	to be exceeded no more than 25 days per year, averaged over 3 years
EU Long-Term Objective	120 µg m^{-3} as maximum daily 8-hour mean	(no exceedances)
UK Objective	100 µg m^{-3} as maximum daily 8-hour mean	to be exceeded no more than 10 days per year
WHO Air Quality Guideline	100 µg m^{-3} as maximum daily 8-hour mean	(no exceedances)
WHO quantification of short-term impacts (REVIHAAP[b])	SOMO10 and SOMO35: the annual sum of the maximum daily 8-hour mean above 20 µg m^{-3} (10 ppb) and 70 µg m^{-3} (35 ppb)	
COMEAP[c] quantification of short-term impacts	Maximum daily 8-hour mean, full year, no threshold	
For the protection of vegetation and ecosystems		
EU Target Value[a]	18,000 µg m^{-3}.hours for the AOT40[d] metric accumulated over the hours 08:00-20:00 Central European Time in May to July	average per year over 5 years
EU Long-Term Objective	6,000 µg m^{-3}.hours for the AOT40[d] metric accumulated over the hours 08:00-20:00 Central European Time in May to July	(each year)
UK Objective	As EU Target Value	

[a] EU Target Values to be achieved by 1st January 2010.
[b] Review of Evidence on Health Aspects of Air Pollution (WHO, 2013a).
[c] Committee on the Medical Effects of Air Pollutants
[d] accumulated hourly ozone concentration in excess of 80 µg m^{-3} (40 ppb).

As noted above, the tropospheric ozone hemispheric baseline is now of growing importance. It is governed by global emissions of VOCs, particularly methane but there are few international agreements or policy instruments that address this issue. Ozone and methane are both greenhouse gases and the UNFCCC agreements in the Kyoto Protocol and the more recent Paris agreement both include methane but the problem with these instruments is that they do not address methane specifically, it is dealt with as just one part of the 'basket' of gases together, as 'CO_2 equivalents'. The conversion of methane emissions to a CO_2 equivalent via the Global Warming Potential incorporates the ozone formation potential of methane, but the targets in Kyoto and the ambitions in the Paris Agreement could in principle be met without reducing methane emissions significantly by acting on the other components in the 'basket'.

Regional air pollution agreements have also not included any significant actions on methane emissions. The Gothenburg Protocol notes in its preamble the importance of methane in the production of ozone, but no emission ceilings were included in the revised Protocol in 2012. This was because Parties noted that methane was already included in climate agreements and there was no appetite for including it in the Gothenburg Protocol. The EU National Emissions Ceiling Directive likewise stopped short of including an emission ceiling but did go further than the Gothenburg Protocol. A Declaration by the European Commission (note, not necessarily binding on the Member States) noted: “The Commission considers that there is a strong air quality case for keeping the development of methane emissions in the Member States under review in order to reduce ozone concentrations in the EU and to promote methane reductions internationally. The Commission confirms that based on the reported national emissions, it intends to further assess the impact of methane emissions on achieving the objectives set out in Art. 1 paragraph 2 of the NEC Directive and will consider measures for reducing those emissions, and where appropriate, submit a legislative proposal to that purpose. In its assessment, the Commission will take into account a number of ongoing studies in this field, due to be finalised in 2017, as well as further international developments in this area.”

There is now considerable interest in the so-called Short-Lived Climate Pollutants (SLCPs) which include ozone and methane. The Climate and Clean Air Coalition (https://ccacoalition.org/en) was set up by an initiative from the US in 2012. The CCAC is a voluntary coalition of countries and organisations including UNEP which “support fast action and deliver benefits on several fronts at once: climate, public health, energy efficiency, and food security.” This work covers methane as well as other SLCPs such as black carbon and HFCs.

The Target Values for ozone in the EU Air Quality Directive are based on World Health Organisation (WHO) Guidelines and the WHO is currently in the process of reviewing and potentially revising the air quality guidelines, including for ozone. No detailed information is available at present, but the outcome of the process will clearly be important for future UK and European policy on ozone.

Chapter 2 – Distributions and recent trends in ozone concentrations

2.1 Current spatial distribution of ozone across the UK and temporal & seasonal variability

2.1.1 Spatial variation in average ozone from AURN measurements

The 2016-2019 mean ozone concentration measured at several AURN sites across the UK is shown in Figure 2. A 4-year mean is calculated to average out the effect of inter-annual variation in meteorology on ozone concentrations. AURN sites were selected that are geographically dispersed across the UK and which have long-running time series (these sites are used in Section 2.3 to examine 20-year temporal trends in ozone). The Mace Head site on the west coast of Ireland is also included in the set of rural background sites as this site is often used to represent levels of ozone brought into the British Isles from the prevailing westerly wind direction.

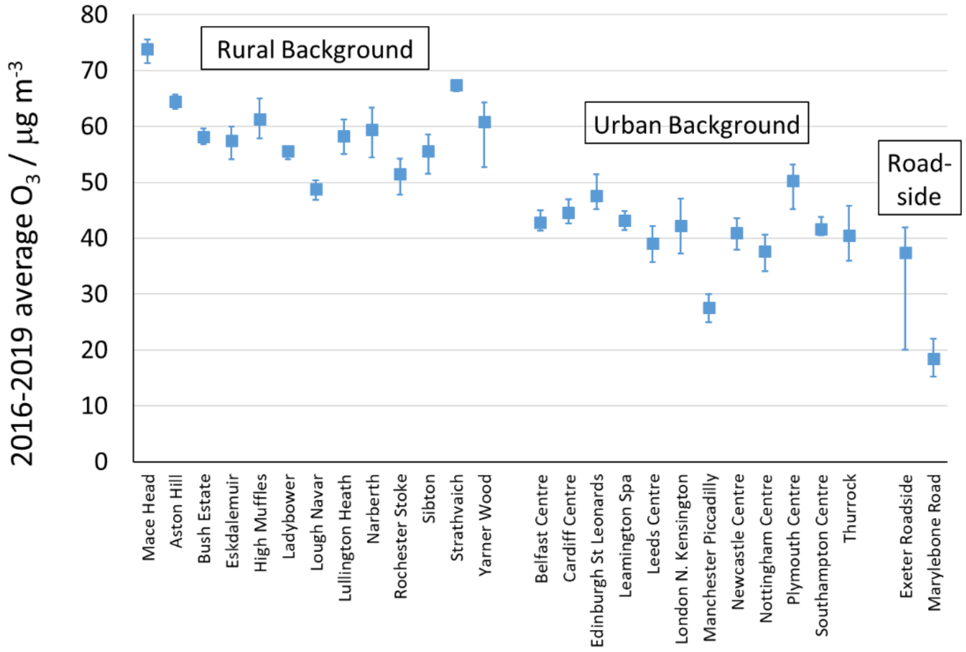


Figure 2: 4-year (2016-2019) mean ozone concentrations at selected AURN sites. The vertical bars extend to the minimum and maximum annual mean in the 4-year period.

Figure 2 shows a greater than factor 2 range in mean ozone concentration across the sites. Mean ozone concentrations decrease in the order rural background > urban background > roadside. Mean ozone exceeds 65 $\mu g\ m^{-3}$ at the remote sites of

Strathvaich and Mace Head in the far north and west, respectively, of the British Isles. In general, mean ozone concentration at the rural background sites is around 55-60 µg m^{-3}.

Mean ozone concentration at the urban background sites is around 40 µg m^{-3}, indicating a current urban decrement of around 10-15 µg m^{-3}. Ozone has not historically been measured at roadside locations because, unlike for most pollutants, ozone concentrations are lower at these locations than elsewhere due to the rapid chemical loss of ozone by reaction with traffic NO emissions. Mean ozone concentration at the London Marylebone Road site is currently around 20 µg m^{-3}.

Pollution roses for ozone measurements at four of the rural background sites, selected for geographic spread across the UK (Eskdalemuir, Aston Hill, Yarner Wood and Sibton), are plotted in Figure 3. The figure illustrates the dominance of the Atlantic sector (wind directions between southwest and northwest) as a source sector for ozone at each site, although highest hourly ozone concentrations at each site occur when wind is from the east.

Polar frequency plots for ozone at the Weybourne coastal rural site (Figure 4) confirm that despite the highest ozone concentrations coming from the east and north-east (left panel), the greater frequency of wind from the south-west means that the south-west makes a greater contribution to ozone overall at this sites (right panel). The highest concentrations generally occur in spring/summer anticyclonic conditions with slow moving air masses from continental Europe with enhanced build-up of emission and photochemical ozone production (see further seasonal analysis below).

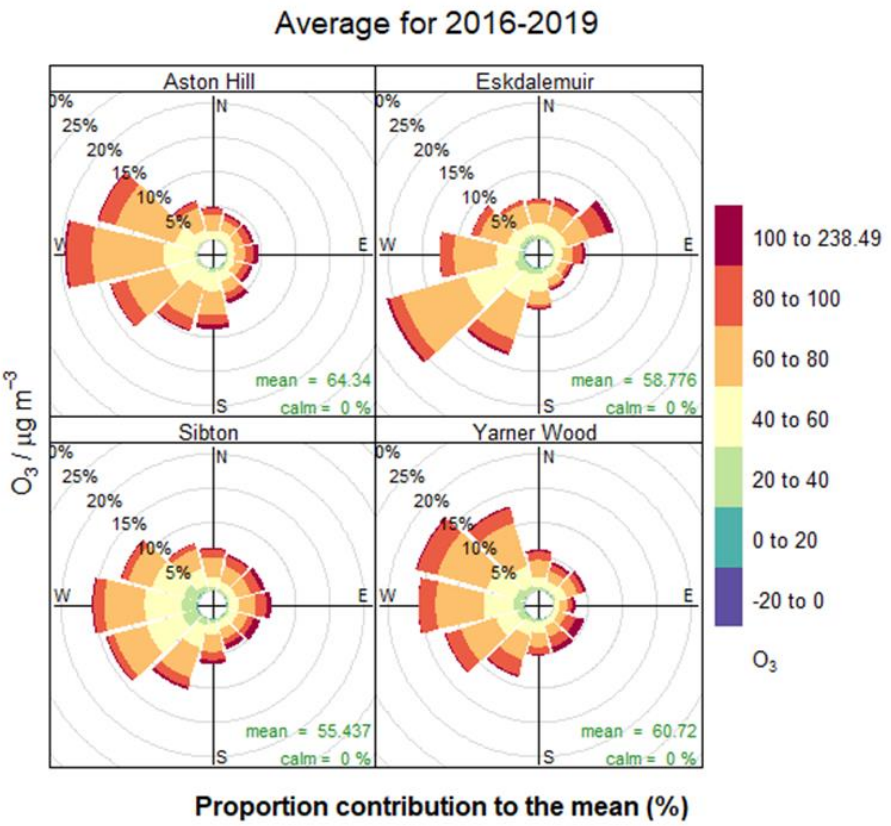


Figure 3: Pollution roses for ozone (µg m^{-3}) at four rural background sites for 2016-2019. The roses illustrate the proportion contribution of concentrations from different wind directions to the mean ozone concentration.

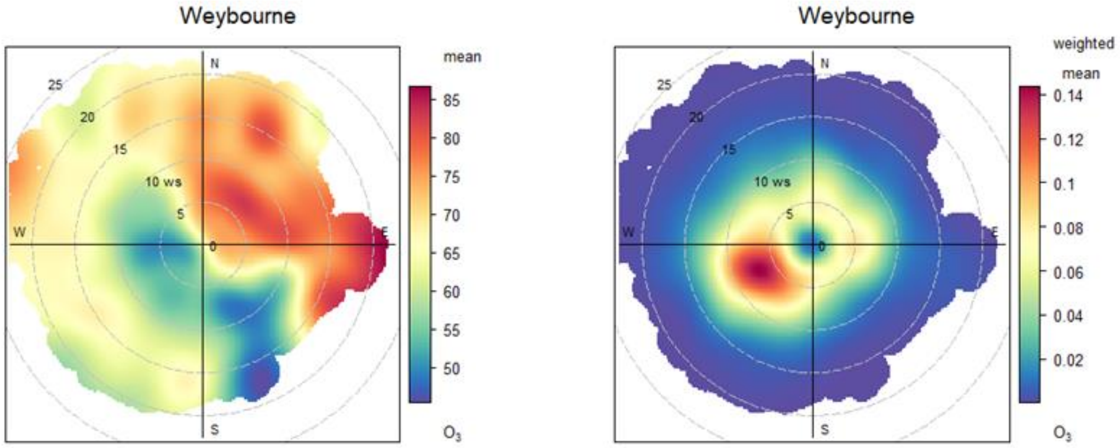


Figure 4: Polar plots of 2010-2020 mean ozone (left, µg m^{-3}) and weighted-mean ozone (right) at Weybourne. The latter is the product of the bin mean and the bin frequency divided by the total frequency.

2.1.2 Spatial variation in average ozone from the EMEP4UK model

To visualise the full spatial variation in surface ozone requires model simulations. Figure 5 shows modelled annual mean surface ozone over the British Isles for each year 2001 to 2015 mapped as the change in ozone from the 2001-2015 averaged ozone concentration. Simulations were undertaken at 5 km × 5 km horizontal resolution (and hourly temporal resolution) with the EMEP4UK atmospheric chemistry transport model based on the EMEP model version rv4.17 and WRF calculated meteorology version 3.7.1 (Vieno et al., 2010; Vieno et al., 2014; Vieno et al., 2016). Emissions for the UK were derived from the 2017 NAEI release, which included the 2015 spatial emissions field and country totals for previous years, which were used to rescale the 2015 spatial field. For the extended European domain in which the British Isles domain is nested the official EMEP emission fields for the years 2001 to 2015 were applied, whilst for shipping a fixed emission estimate for 2011 was used from the Finnish Meteorological Institute (Jalkanen et al., 2016). Boundary concentrations for the wider European domain were fixed at 2015 and static land cover was used as derived from the CEH 2015 and the EMEP land-cover dataset.

Like the measurements (Figure 2), the map of modelled 2001-15 mean concentrations (Figure 5) shows greater than a factor two spatial variation in ozone across the UK. Concentrations of >60 μg m^{-3} (30 ppb) are widespread over Scotland, Northern Ireland, Wales south-west England and the Pennines (except over urban areas), and exceed 72 μg m^{-3} (36 ppb) over the highest ground in these regions. Over the rest of rural England, mean ozone concentrations are in the range 52-60 μg m^{-3} (26-30 ppb). Upland areas tend to have the highest annual mean ozone concentrations since the greater vertical mixing at higher altitude (greater air turbulence) replenishes more of the ozone than is lost by dry deposition compared with locations at lower altitude (Coyle et al., 2002). This effect is particularly prevalent at night when vertical mixing is at its lowest.

The map reveals the clear decrements in mean ozone over major urban/industrial areas and transport corridors compared with the concentrations in their neighbouring rural areas, due to the rapid chemical removal of ozone by reaction with NO close to the sources of NO emissions. The urban decrement yields mean ozone as low as 40 μg m^{-3} (20 ppb) or less in the centre of the largest conurbations, consistent with the measurements. Measurement and models of higher spatial resolution intra-urban variation in ozone are presented in Section 2.2.

The mean concentration map in Figure 5 illustrates an important point about ozone in the UK that is not apparent from measurements and the Pollution Climate Mapping (PCM) model maps presented in Sections 3.1 & 3.2, which is that mean surface ozone over the UK is lower, and in most areas much lower, than over the surrounding sea. (Coastal locations receive this elevated ozone when air is onshore.) These results demonstrate that the hemispheric baseline is a major contributor to ozone concentration across the UK. Although UK emissions of CH_4, VOC and NO_x contribute to this ozone, on average the UK land surface (as elsewhere in Europe) is a net sink for ozone. This is because dry deposition of ozone to vegetation and other land surfaces is more efficient than over water and because the UK's NO emissions provide a chemical loss of ozone which exceeds the local ozone production from sources of VOC and NO_x. The implication of this is that future annual-mean concentrations of surface ozone in the UK will be principally determined by the magnitude of the baseline ozone, the magnitude of local NO emissions and the magnitude of dry deposition as determined by the climate and land cover, rather than by ozone generated solely over the UK.

The inter-annual 'delta' maps in Figure 5 also illustrate the considerable inter-annual variability in annual mean ozone, and also the variability of this inter-annual variability geographically across the UK, as revealed by the year-to-year variation in red and blue colours. Variability of ~12 $\mu g\ m^{-3}$ (6 ppb), i.e. ±6 $\mu g\ m^{-3}$ (±3 ppb) from the mean, is not uncommon; e.g. compare generally higher ozone concentrations in 2008 and lower in 2010.

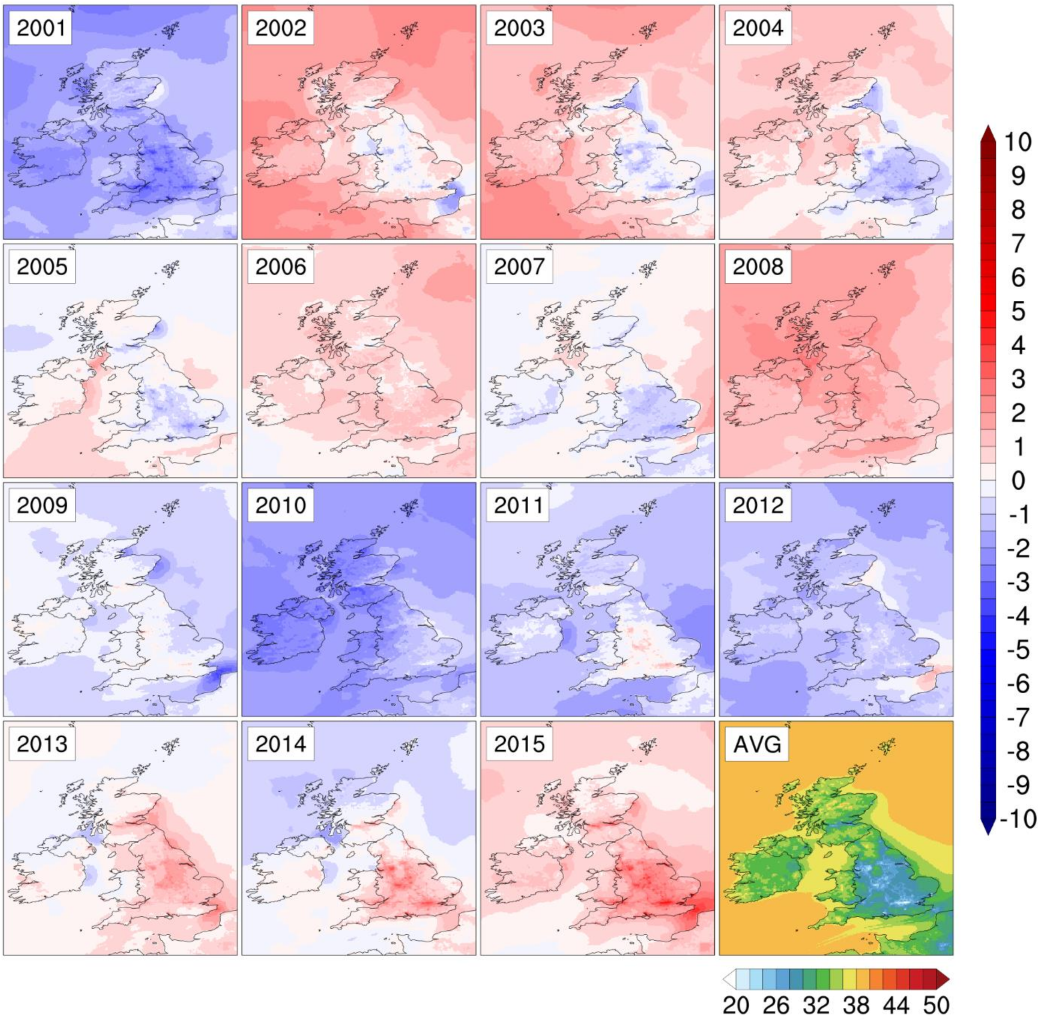


Figure 5: EMEP4UK-modelled annual mean surface ozone for 2001-2015 (with 2015 land cover and domain boundary conditions, and 2011 shipping emissions). Annual maps are shown as differences (right-hand legend) from the 2001-2015 average ozone concentration map shown in the bottom right corner. Units are ppb. For ozone, 1 ppb = 2.0 µg m^{-3}.

2.1.3 Monthly, daily and day-of-the-week variations in ozone

Figure 6 shows the 2016-2019 averaged hourly, monthly and day-of-week variations in ozone concentrations at example long-running rural and urban background AURN sites spread geographically across the UK. To better visualise relative differences between rural and urban ozone temporal distributions, Figure 7 presents the temporal variations as normalised plots. Both figures show that ozone concentrations exhibit strong seasonal and diurnal variation.

Seasonal variations

Maximum monthly mean ozone concentrations occur in spring, in April and May (Figure 6). At the urban background sites, concentrations are at their minimum during Nov-Jan, whilst at the rural background sites the period of lowest concentrations can extend from as early as late summer through to Jan, i.e. the spring-time maximum in ozone is of slightly shorter duration at rural sites than at urban sites (Figure 7).

Figure 7 also shows that, for these sites at least, the relative amplitude in the annual cycle of ozone is slightly smaller at rural sites than at background sites, extending from ~0.8 to ~1.25 times the annual mean at the rural sites, but from ~0.7 to ~1.4 times the annual mean at the urban sites. The greater relative seasonal amplitude at urban sites presumably reflects an enhanced chemical removal of ozone in urban areas in winter due to higher NO emissions in winter and lower average boundary layer. Since concentrations are on average higher at rural sites, the absolute seasonal amplitude in ozone concentration is similar across the sites, of the order of 25-30 µg m^{-3}.

Figure 6 illustrates seasonal variation in ozone across all wind directions. Figure 8 disaggregates the seasonal cycle of ozone at the Weybourne rural background site on the north coast of East Anglia by wind direction. Whilst most wind directions show the spring peak, ozone from the south-east shows a summer peak (and the east and north-east a secondary summer peak). Amplitudes of seasonal patterns are greatest in air from the south and south-east, in part caused by lowest winter concentrations, presumably arising from reaction of ozone with NO .

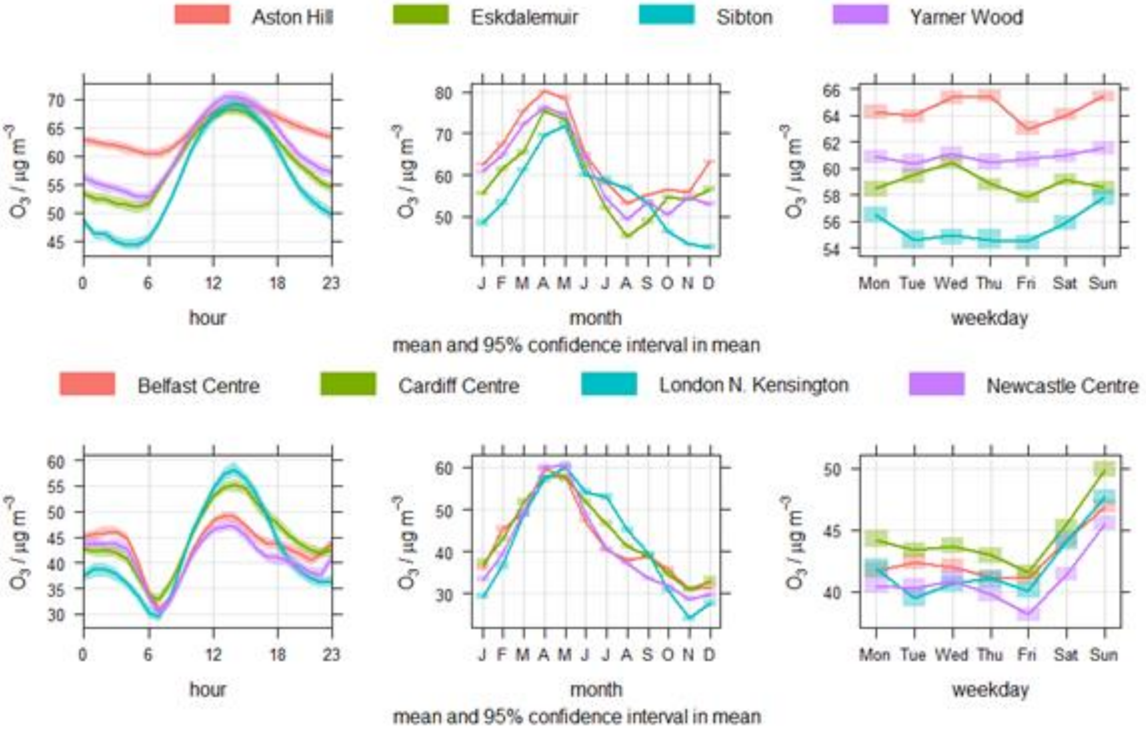


Figure 6: Hourly, monthly and day-of-week ozone concentrations at four example rural background (upper row) and four example urban background (lower row) AURN sites, averaged over 2016-2019.

The analysis of seasonal trends in ozone measured at sites across Europe by Boleti et al. (2020) (using a non-parametric time-scale decomposition methodology), Figure 9, illustrates how different the Apr-May maximum in ozone is in the UK and Scandinavia compared with the rest of Europe. Elsewhere in Europe, ozone concentrations start rising slightly later in the spring but continue increasing through June, remaining high until at least the end of July.

Boleti et al. (2020) also determined that the amplitude of the seasonal cycle of ozone at sites in their ‘north’ Europe cluster has decreased slightly over the 2000-2015 period of their data. The decrease in amplitude is a consequence of both small increases in the seasonal minimum and small decreases in the seasonal maximum, and amounts to ~0.29 ppb y^{-1} (0.58 µg m^{-3} y^{-1}) over this time period. They also determined a non-significant trend for the seasonal maximum at the ‘north’ sites to be reached 0.47 days earlier per year on average. However, the decrease in seasonal amplitude and the advancement in date of the seasonal maximum were in fact slightly smaller at the ‘north’ sites compared with the other European sites.

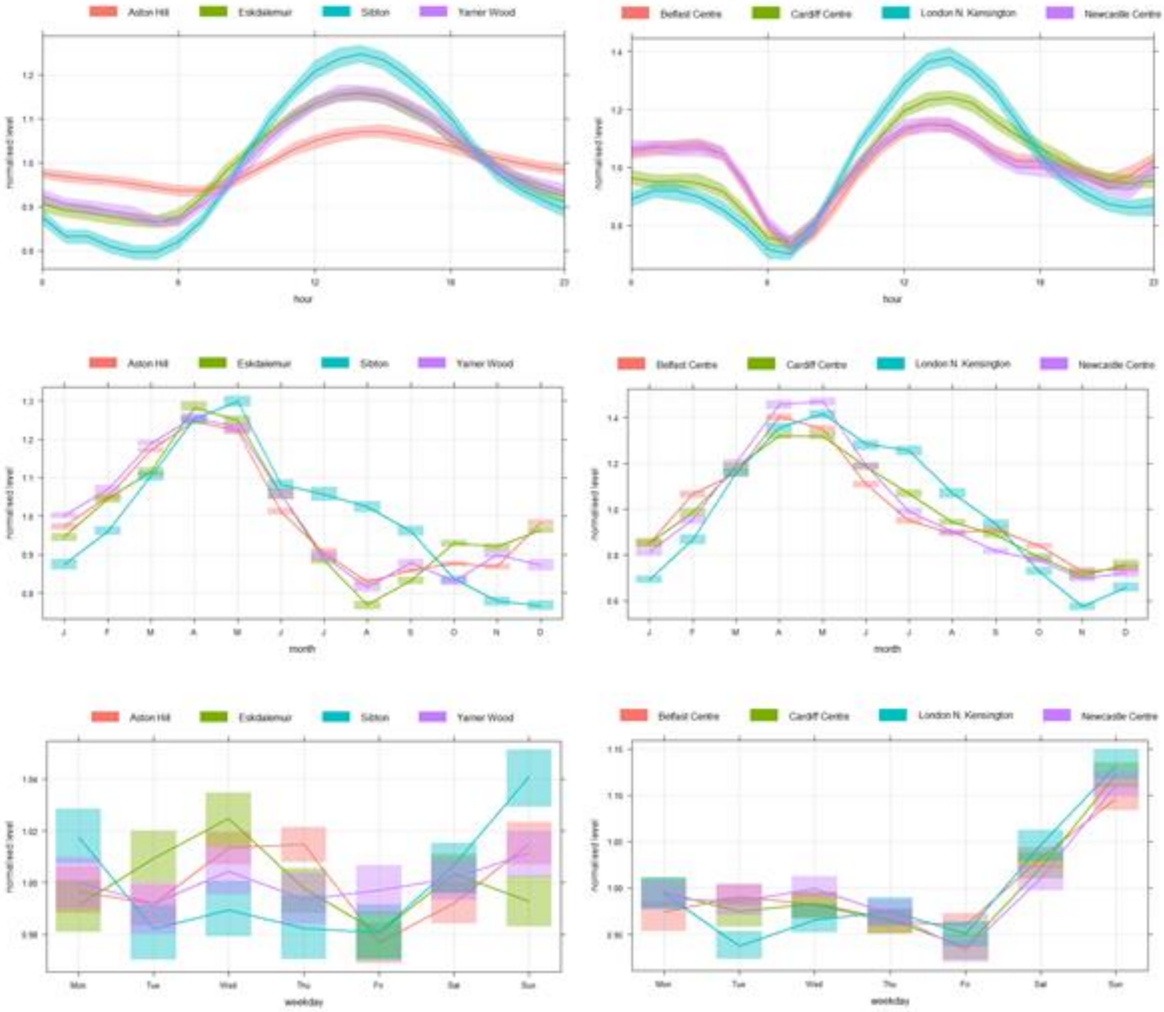


Figure 7: Comparisons of normalised hourly, monthly and day-of-week ozone concentrations between four example rural background (left-hand) and four example urban background (right-hand) AURN sites, averaged over 2016-2019.

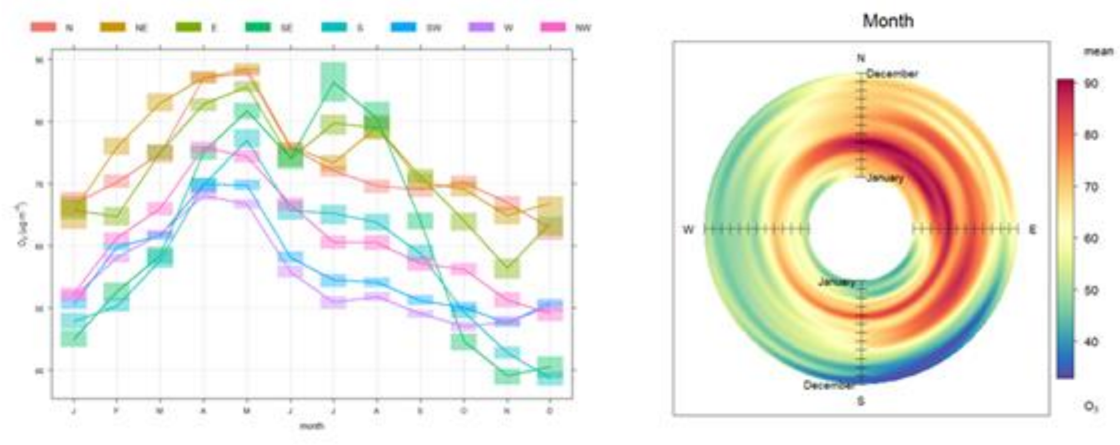


Figure 8: Seasonal cycles in ozone concentration as a function of wind direction at Weybourne (2010-2020) (µg m^{-3}), plotted as a time series for the eight 45° wind sectors (left) and as a polar annulus (right) with January at the inner edge and December at the outer edge.

The origin of the strong spring-time surface ozone maximum in NW Europe is not fully explained but is the net effect of the many factors that influence ozone concentrations (Monks, 2000; Butler et al., 2020). These effects include latitudinal dependence of stratosphere-to-troposphere exchange and precursor emissions, the predominantly westerly transport over an ocean surface with low depositional and chemical loss, and the timing of the new season vegetation growth that acts as a sink for surface ozone. The seasonality in source attributions of surface ozone is discussed further in Section 4.5.

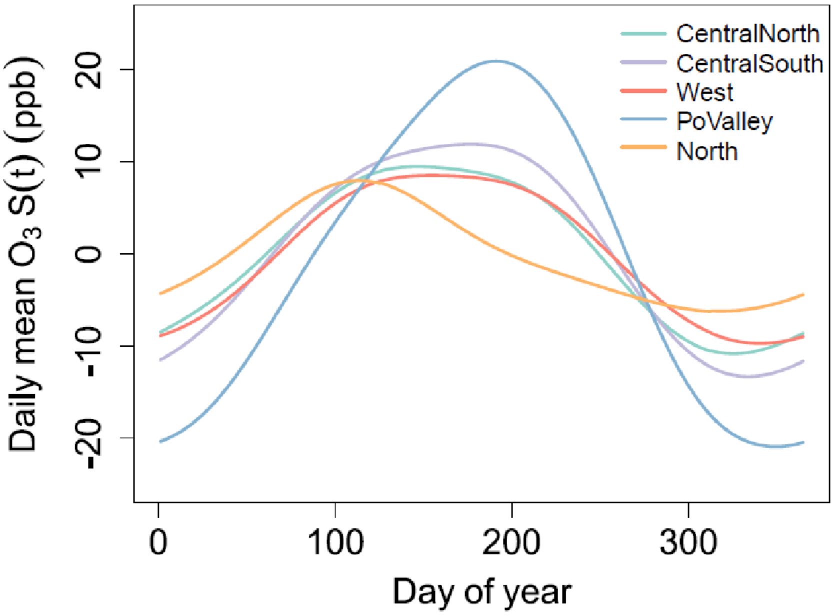


Figure 9: Seasonal cycles of measured daily mean European ozone disaggregated by geographical clusters identified by Boleti et al. (2020). The 8 sites from the UK in this analysis are in the 'north' cluster, which also contains sites in Scandinavia and the Baltic but not in the rest of continental Europe. April and May correspond to days 91 to 151.

Diurnal variations

Mean diurnal ozone profiles at UK sites also differ between rural and urban background sites, being broader and generally of smaller magnitude at rural than at urban sites (Figure 6 and Figure 7). Diurnal amplitudes at urban sites are ~15-20 μg m^{-3}. The diurnal cycle is particularly small at rural background sites at altitude, as exemplified by the measurements at Aston Hill (370 m) (amplitude <10 μg m^{-3}). This is because the generally windier conditions at elevation means greater vertical transport of ozone which offsets depletion of ozone by surface deposition, notably at night when vertical transport is generally lower (Coyle et al., 2002).

The Weybourne coastal site also demonstrates the effect of reduced surface loss on ozone diurnal cycles (Figure 10). The highest ozone concentrations at Weybourne derive from the on-shore N, NE and E directions, where ozone dry deposition to water is lower and the diurnal cycle is much weaker – the latter arising because the smaller diurnal temperature range of the sea surface means that shallow nocturnal boundary layers tend not to form so ozone loss at the surface is readily replenished.

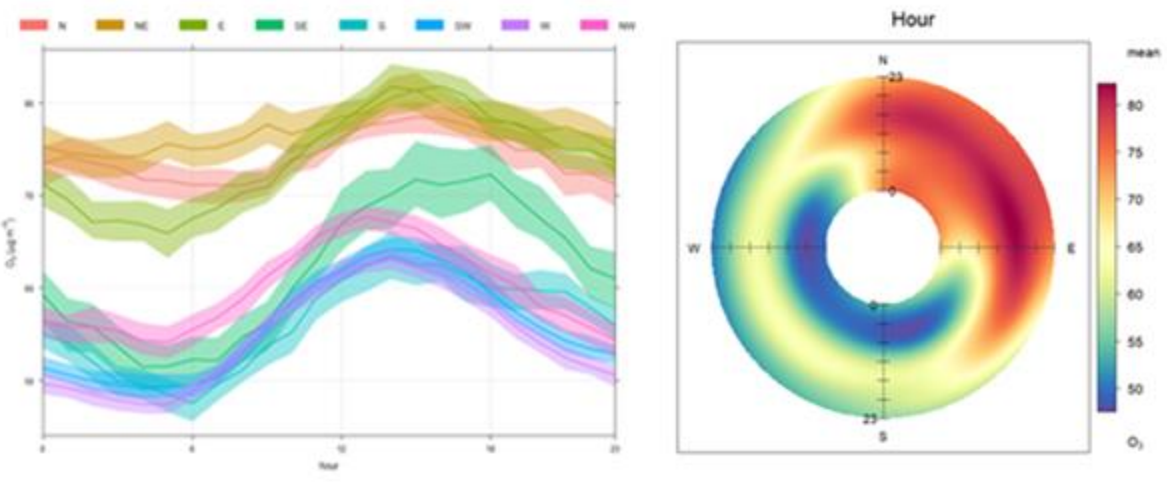


Figure 10: Diurnal cycles in ozone concentration as a function of wind direction at Weybourne (2010-2020) (µg m^{-3}), plotted as a time series for the eight 45° wind sectors (left) and as a polar annulus (right) with 00:00 at the inner edge and 24:00 at the outer edge.

In contrast, the diurnal cycle of ozone at urban sites is characterised by a predominant dip in concentration in early morning and a more rapid decline in early evening (Figure 7), driven by the combination of the urban cycle of NO_x emissions, coupled with the still shallow boundary layer during morning rush-hour (Kulkarni et al., 2015). When diurnal cycles at urban sites are examined by season (Figure 11) this bimodality of an additional early-hours peak is more obvious, particularly in winter when the nocturnal peak is of comparable magnitude to the afternoon peak at North Kensington and almost twice the magnitude at Marylebone Road.

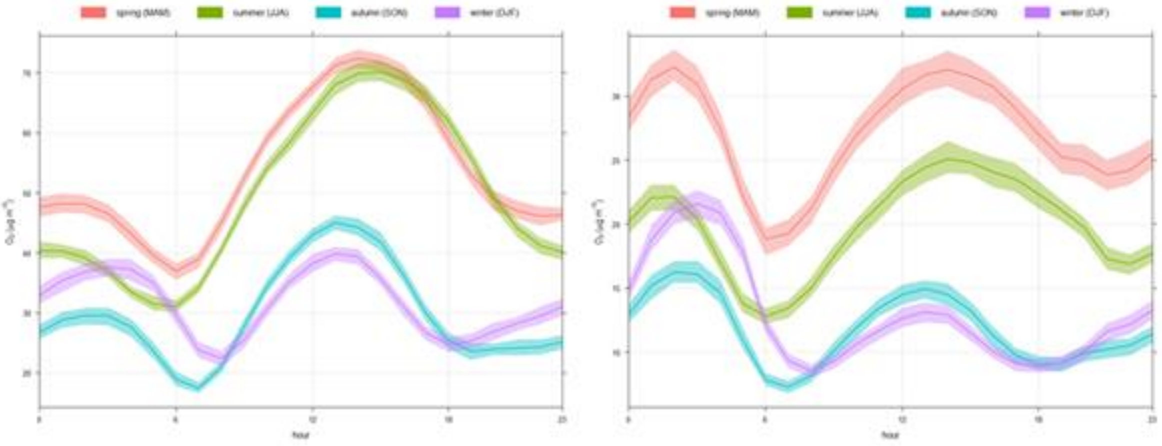


Figure 11: Diurnal cycles of ozone (2010-2020) by season. Left: North Kensington. Right: Marylebone Rd. Note scales are different.

Day-of-week variations

In terms of day-of-the-week trends (Figure 6 and Figure 7), the urban sites have higher ozone concentrations at weekends, especially Sundays, with concentrations exceeding those of weekdays by about 15% (or ~6 µg m^{-3}), whilst rural sites generally show no significant variation in ozone concentration across the week. The observation for urban areas again reflects weekday-weekend differences in NO_x emissions, particularly transport related.

2.2 Spatial variation in ozone within urban areas

The primary driver of ozone concentrations in an urban area is the ozone in the surrounding rural air transported inwards. Within the urban area the dominant influence on ozone concentration is its chemical removal by locally emitted NO which reduces concentrations relative to the rural background; local photochemical reactions and local emissions of NO_2 may counteract this effect to some extent.

As discussed elsewhere in this Chapter, the decline in NO emissions over recent decades is decreasing this chemical loss effect, resulting in increases in ozone concentrations in urban areas. The same effect was observed during the lockdown for the COVID-19 pandemic (AQEG, 2020a).

As the reaction between NO and ozone is relatively fast (timescales of minutes), its effects occur on relatively short distances and should lead to small-scale spatial gradients in urban ozone away from strong sources of NO, typically roads.

2.2.1 Measured intra-urban spatial variation in ozone

Whilst large cities may have several continuous analyser sites measuring NO and NO_2 (albeit many of these at roadside) these usually do not include ozone analysers. Consequently the intra-urban variation in ozone concentrations is not clearly apparent from measurements.

To investigate intraurban ozone, Lin et al. (2016) deployed ozone passive diffusion samplers at 30 different types of locations in Edinburgh in 2013. Spatial patterns in ozone were broadly temporally persistent over 6 repeat deployments in summer and winter. The intra-urban range in ozone was substantial, with decrements exceeding 30 µg m^{-3} at the most heavily-trafficked roadside sites compared with ‘background’ sites in suburban parks. Decrements at sites by urban ‘B’ roads and in residential areas were in the range 10-20 µg m^{-3}.

There was strong anti-correlation across the 30 sites between the magnitude of 'below background' decrement in ozone and 'above background' elevation in NO_2 as measured contemporaneously at the same sites by NO_2 passive sampler.

This study shows a larger range in intra-urban ozone decrement than can be captured by one or two network ozone analysers in an urban area or by atmospheric transport models (even where these can operate at 1 to 2 km spatial resolution).

2.2.2 Dispersion modelled intra-urban spatial variation in ozone

Figure 12 shows the annual mean ozone concentrations across London for 2018 and 2030 at a height of 2 m as calculated by the ADMS-Urban dispersion model (Hood et al., 2018). Emissions of NO_x and VOC for 2018 and 2030 are derived from the 2013 London Atmospheric Emissions Inventory; background concentrations are those measured upwind at Lullington Heath, Rochester, Chilbolton or Wicken Fen scaled to 2030 using Defra background maps for NO_x and the assumption of unchanged oxidant for ozone, bar a small change in primary NO_2. VOC emissions are assumed unchanged between 2018 and 2030. The map for 2018 shows strong spatial gradients in ozone associated with the major roads and between suburban and central London, the latter exceeding 20 µg m^{-3}.

The plots in Figure 12 show a marked increase in the annual mean ozone concentration in London in 2030, especially along major roads, with the central London decrement typically reduced by approximately 10 µg m^{-3}. The variation in ozone across the city is reduced.

Figure 13 shows instead the 97th percentile of the daily maximum 8-hour mean (i.e. the concentration which is exceeded ten times per year) for which the UK objective is 100 µg m^{-3}. Even in 2018, most areas of London are in exceedance (those coloured green to red). The figure shows that between 2018 and 2030 there are increases in both the 97th percentile concentration and in the area of London where the 97th percentile exceeds 100 µg m^{-3}, although the relative changes are smaller than for the annual mean.

Some insight into the causes of the changes in concentrations is provided by Table 2 which shows for concentrations (ppb) of each of NO_x, NO_2, O_3, Ox ($=NO_2+O_3$), primary NO_2 and locally-produced Ox, both the modelled annual mean and the hourly mean for the hour corresponding to the maximum hourly Ox concentrations at Bloomsbury and Marylebone Road in 2018. Both the annual mean and maximum hourly concentrations show the increases in ozone to be strongly associated with decreases in NO_x (NO) concentrations and therefore reduction in ozone titration; this increase in ozone is smaller than the decreases in NO_2 which also reflects the decreases in primary NO_2. For the simplified GRS chemical reaction scheme used in

ADMS, local Ox production due to photochemical reactions shows very little change on an annual mean basis whilst the maximum hourly locally-produced Ox shows some decrease (e.g. from 9.1 ppb to 6.6 ppb at Marylebone Road).

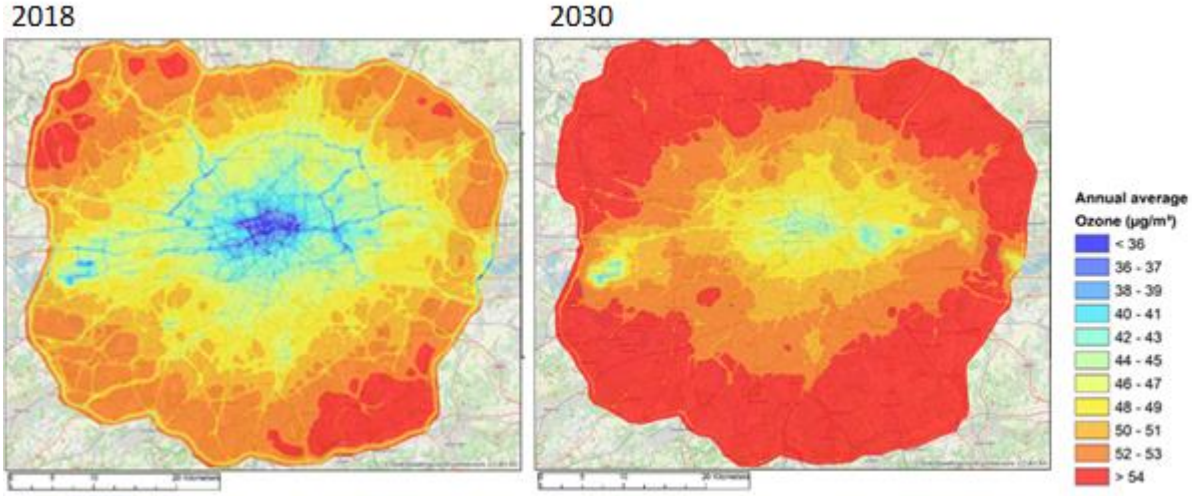


Figure 12: ADMS-Urban modelled annual mean ozone concentrations in Greater London (at 2m above ground) for 2018 (left) and 2030 (right).

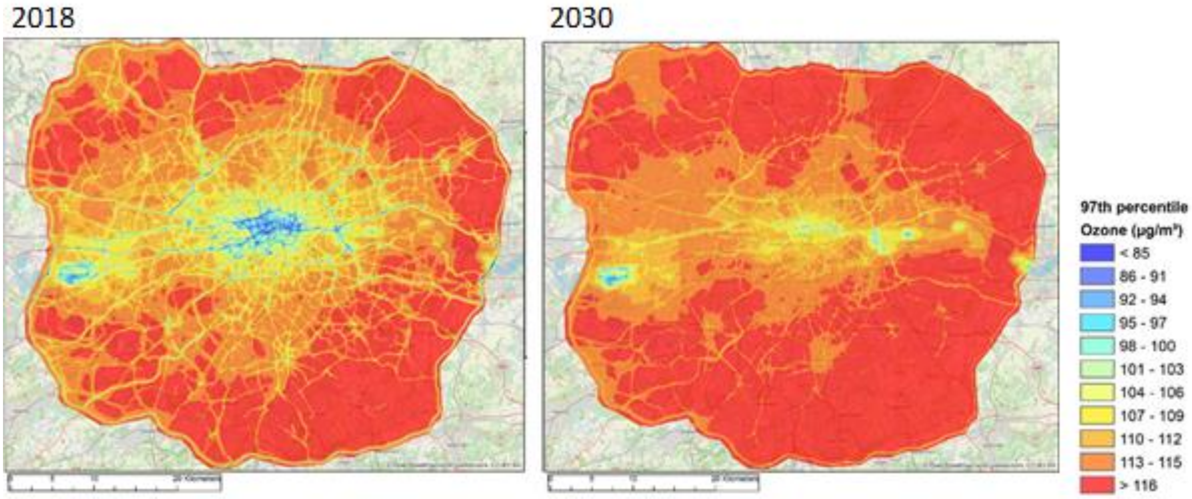


Figure 13: ADMS-Urban modelled annual 97th percentile of the daily maximum 8-hour mean ozone concentrations in Greater London (at 2m above ground) for 2018 (left) and 2030 (right). Areas coloured green through to red indicate exceedances of the UK objective of 100 µg m^{-3} for this percentile.

Table 2: Modelled annual mean and hourly mean concentrations corresponding to maximum hourly ozone concentrations (ppb) at a central London background site (Bloomsbury) and at a roadside site (Marylebone Road). Date of maximum concentrations (25/6/18 16:00).

Year	**Pollutant**	**Annual mean / ppb**			**Max. hourly mean for 25/6/18 16:00 / ppb**		
		Background	**Bloomsbury**	**Marylebone Road**	**Background**	**Bloomsbury**	**Marylebone Road**
2018	NO_x	4.7	38.0	99.0	4.2	34.9	152.2
	NO_2	4.0	21.6	37.1	3.7	28.6	80.9
	O_3	28.5	16.9	15.0	79.7	68.9	42.2
	Ox	32.5	39.4	53.4	83.4	97.5	123.0
	Primary NO_2	-	5.34	19.4	-	4.77	30.60
	Local Ox production	-	1.43	1.38	-	9.35	9.07
2030	NO_x	3.4	19.6	32.5	2.9	17.4	43.6
	NO_2	2.9	12.8	15.7	2.7	14.8	27.5
	O_3	28.7	21.7	21.5	79.8	75.7	68.2
	Ox	31.6	34.5	37.3	82.5	90.5	95.7
	Primary NO_2	-	1.57	4.30	-	1.37	6.60
	Local Ox production	-	1.26	1.25	-	6.61	6.59
Difference (2030 – 2018)	NO_x	-1.3	-18.4	-66.4	-1.3	-17.5	-108.6
	NO_2	-1.0	-8.7	-21.4	-1.0	-13.8	-53.4
	O_3	0.1	4.8	6.5	0.1	6.8	26.0
	Ox	-0.9	-4.8	-16.1	-0.9	-7.0	-27.3
	Primary NO_2	-	-3.77	-15.1	-	-3.4	-24.0
	Local Ox production	-	-0.17	-0.13	-	-2.74	-2.48

2.2.3 Population exposure to ozone using workday population density

Reis et al. (2018) investigated the impact on UK population-weighted exposure to outdoor ozone when considering the geographical differences in population density between place of residence and place of work. The latter data are a new product from the 2011 census. Hourly ozone was simulated using the EMEP4UK model at ~0.018° × ~0.018° (~2 km × 1.5 km) spatial resolution. UK population-weighted ozone concentrations were 62.3 μg m^{-3} and 61.9 μg m^{-3} based on residential and place-of-work population density. Assuming the working population were at their place of work on weekdays from 8 am to 6 pm and at their place of residence otherwise yielded population-weighted ozone concentration of 62.1 μg m^{-3}. The study therefore reveals that the population is exposed to about 0.3% lower ambient ozone concentration than is assumed when treating everyone as located at home. The decrease reflects the net movement of population into urban areas for work, where ozone is lower. The study was limited by the spatial resolution of the ozone modelling and of the aggregated population data.

2.3 Trends in UK ozone over the last 20 years from measurements

2.3.1 Trends in average ozone from measurements

Deseasonalised monthly mean ozone at 12 rural background sites, 12 urban background sites and 2 urban traffic (roadside) sites in the AURN with continuous measurements for the 20-year period 2000-2019 are plotted in Figure 14, Figure 15 and Figure 16, respectively. Figure 17 shows similar for the rural background site at Mace Head on the west coast of Ireland as this site is often taken to be representative of ozone brought into the British Isles from the prevailing westerly wind direction.

Sites were selected to cover the UK geographically, although in the case of urban background sites there were only a few other sites that could have been chosen which have time series for the full 20 year period. Other than the above criteria, the selection of sites was arbitrary. The Edinburgh St Leonards site is selected, even though it only started operation in November 2003, otherwise no urban background site in Scotland would be included. There are only two long-running AURN urban traffic sites measuring ozone, Exeter Roadside and London Marylebone Road.

The trend has been quantified using the non-parametric Theil-Sen method on the deseasonalised monthly means. The trend estimates are summarised in Table 3 with significant trends and their direction highlighted in colour for easier visualisation of patterns in the trends. (Trends are calculated for the full 20 years of data without consideration of whether there are periods of different trends.)

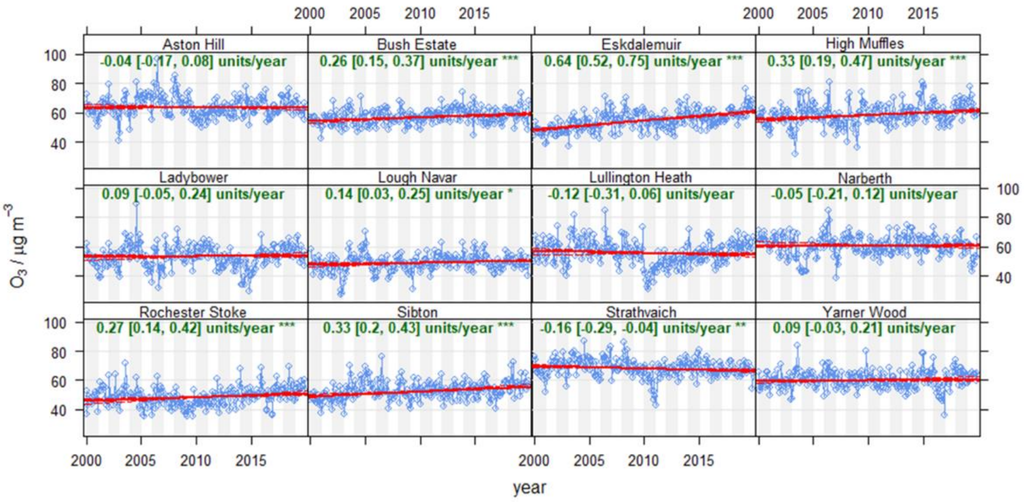


Figure 14: Deseasonalised trends in monthly ozone concentration at 12 rural background AURN sites, for the period 2000-2019.

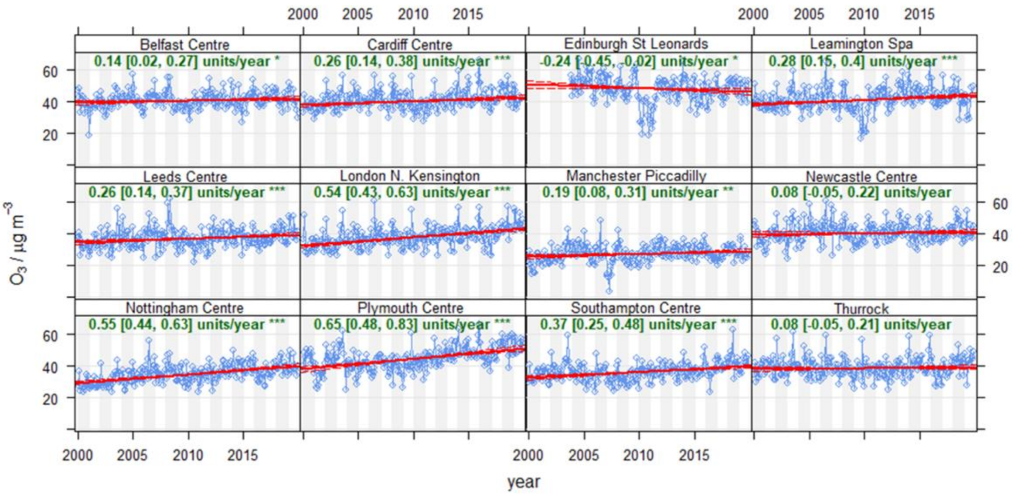


Figure 15: Deseasonalised trends in monthly ozone concentration at 12 urban background AURN sites, for the period 2000-2019.

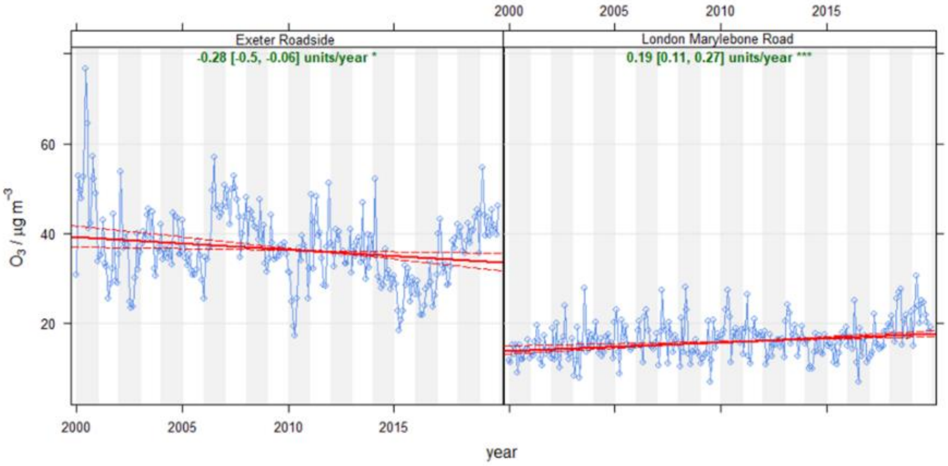


Figure 16: Deseasonalised trends in monthly ozone concentration at the two urban traffic (roadside) AURN sites, for the period 2000-2019.

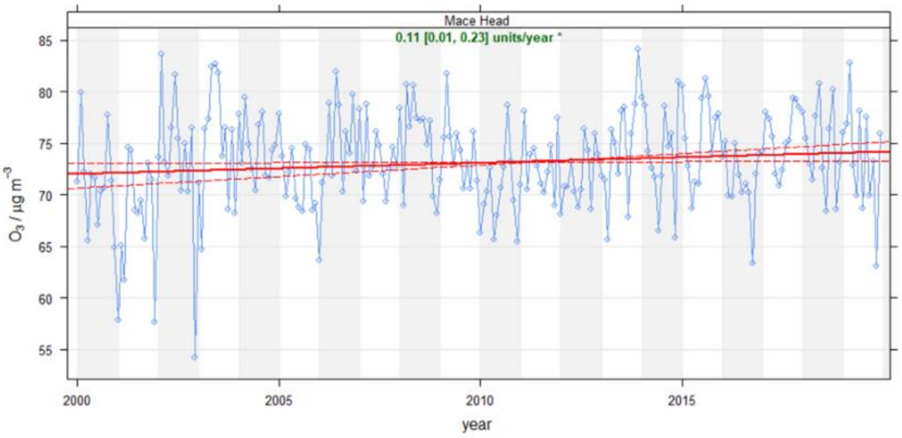


Figure 17: Deseasonalised trends in monthly ozone concentration at the Mace Head site, for the period 2000-2019.

Table 3: Magnitudes of Theil-Sen trends in $\mu g\ m^{-3}\ y^{-1}$ in various metrics of ozone concentration over the period 2000-2019 at a selection of AURN sites. Underlying data are hourly concentrations. Symbols denote significant trends at the following probability levels: *** = $p < 0.001$, ** = $p < 0.01$, * = $p < 0.05$ and + = $p < 0.1$. **Bold blue font** indicates significant **upward trend** at $p < 0.05$. **Bold red font** indicates significant **downward trend** at $p < 0.05$.

		Monthly means (deseasonalised)	Annual 50th %ile	Annual 25th %ile	Annual 99th %ile	Annual 99.9th %ile
remote	Mace Head	**0.11***	0.00	0.07	-0.26	-0.16
rural	Aston Hill	-0.04	0.02	0.04	-0.40	-0.18
	Bush Estate	**0.26*****	**0.22***	**0.21***	0.40	-0.02
	Eskdalemuir	**0.64*****	**0.66*****	**0.66****	0.59	0.64
	High Muffles	**0.33*****	**0.37***	**0.49****	0.00	-0.31
	Ladybower	0.09	0.12	0.26	-0.06	-0.87
	Lough Navar	**0.14***	0.23	0.06	0.15	0.19
	Lullington Heath	-0.12	0.00	0.07	-1.31 +	-1.77 +
	Narbeth	-0.05	-0.02	-0.08	-0.44	-0.35
	Rochester Stoke	**0.27*****	0.10	0.36 +	-0.64	-1.61
	Sibton	**0.33*****	**0.34***	**0.41***	-0.24	0.08
	Strathvaich	**-0.16****	-0.07	-0.06	-0.26	-0.33
	Yarner Wood	0.09	0.04	0.26	-0.33	-0.22
	Median, inc MH (max)	0.11 (0.64)	0.10 (0.66)			
urban back-ground	Belfast Centre	**0.14***	0.13	**0.33***	-0.15	-0.40
	Cardiff Centre	**0.26*****	**0.44****	**0.65*****	-0.52 +	-0.28
	Edinburgh St Leonards	**-0.24***	-0.15	0.04	-0.62	-0.07
	Leamington Spa	**0.28*****	**0.29***	**0.56****	-0.65	-0.85 +
	Leeds Centre	**0.26*****	**0.37***	**0.49****	0.01	-0.14
	London N. Kensington	**0.54*****	**0.67*****	**0.80*****	-0.24	0.31
	Manchester Piccadilly	**0.19****	**0.34***	**0.31****	-0.32	-0.53
	Newcastle Centre	0.08	0.04	**0.33***	-0.39	-0.41
	Nottingham Centre	**0.55****	**0.66*****	**0.63*****	0.19	-0.35
	Plymouth Centre	**0.65*****	**0.89***	**0.94****	0.33	0.78
	Southampton Centre	**0.37*****	**0.50***	**0.69*****	0.20	0.71
	Thurrock	0.08	0.00	**0.38****	-0.84 +	**-2.05***
	Median (Max)	0.26 (0.65)	0.36 (0.89)			
urban traffic	Exeter Roadside	**-0.28***	-0.25	0.15	**-1.35***	-1.87
	London Marylebone Rd	**0.19*****	**0.24***	0.05 +	-0.17	-0.68

Figure 14-Figure 17 show that even with deseasonalisation there is substantial monthly and annual variation in monthly ozone concentrations in all locations

reflecting the significant impact of climate and meteorology on a number of factors influencing ozone concentrations (chemical production, transport, and surface deposition to vegetation, in particular).

Including Mace Head, 7 of the 13 selected rural background sites show statistically significant increases in ‘average’ (deseasonalised monthly-mean) ozone concentration (at conventional $p < 0.05$ significance level) (Figure 14, Table 3). One site, Strathvaich, shows a statistically significant decrease in mean ozone. Table 3 also shows the Theil-Sen trend based on the 50th percentile of each year’s hourly values (i.e. the median hourly concentration each year) which is another way of representing a time series of ‘average’ ozone concentration at a given site. Using the annual 50th percentile, statistically significant upward trends are calculated for only 4 of the 13 rural background sites, the upward trends at the other 3 rural background sites that showed significant trends with deseasonalised monthly means no longer retaining statistical significance.

Overall, the analyses suggest there has been only moderate increases in average ozone concentration at rural background sites over the period 2000 to 2019. The median trend for the 13 rural background sites is 0.11 µg m^{-3} y^{-1} (based on deseasonalised monthly means), which equates to an increase of 2.2 µg m^{-3} over the 20-year period. The median trend for the 13 rural background sites based on the 50th percentile of hourly values each year is very similar at 0.10 µg m^{-3} y^{-1}. The trend at Mace Head, the site that best represents the baseline ozone around the British Isles, is similar to the median of the rural site trends. Using non-deseasonalised AURN data, Finch and Palmer (2020) similarly report only moderate increases in annual mean ozone at rural background sites over the period 1999-2019: mean ± sd increase of 0.16 ± 0.07 µg m^{-3} y^{-1} (n =22), not statistically significant.

Long-term trends at urban background sites are more consistent. Nine of the 12 urban background sites have statistically significant increases in deseasonalised monthly-mean ozone (Table 3). Edinburgh St Leonards shows a significant decrease but this is the only site in this analysis without a 20-year time series, and Figure 15 reveals potential issues with recorded concentrations around 2010. Table 3 also shows that 8 of the 12 urban background sites show statistically significant increasing ozone using instead the 50th percentile of annual hourly ozone.

Overall, the analyses provide strong evidence that average urban background ozone concentrations have increased over the period 2000 to 2019. The median trend in deseasonalised monthly means across the 12 sites is 0.26 µg m^{-3} y^{-1} which corresponds to a median increase over the 20-year period of 5.2 µg m^{-3}. The median trend across the 12 urban background sites based on the 50th percentile of hourly values each year is 0.36 µg m^{-3} y^{-1}, equivalent to 7.2 µg m^{-3} over the 20 years. Finch and Palmer (2020) report a mean increase in non-deseasonalised annual mean ozone for 1999-2019 across all AURN urban background sites of 0.47 ± 0.08 µg m^{-3}

y^{-1} (*n* =45, statistically significant). Trends at some of the urban sites indicate 20-year increases in mean ozone in excess of 10 µg m^{-3}.

There has also been a significant increase in mean ozone concentration at the Marylebone Road urban traffic site (Figure 16, Table 3), of the order of 0.2 µg m^{-3} y^{-1} or 4 µg m^{-3} over the period 2000 to 2019. Although this increase seems small, it needs to be noted that concentrations of ozone at this site are very low so an increase of 4 µg m^{-3} actually represents around a 25% increase in concentration over this period from a mean of ~16 µg m^{-3} in 2000 to the present-day mean concentration of ~20 µg m^{-3}. Ozone concentrations at Exeter Roadside have declined on average but the significance is low and Figure 16 shows that there is extremely large variability in ozone concentrations at this site.

Average rural background ozone concentrations predominantly reflect the average concentrations of ozone imported into the UK, which in turn are predominantly dependent on the hemispheric baseline to the west of the British Isles (see also the pollution roses in Figure 3). The trends in measurements at rural background sites described above suggest this contribution has increased modestly over the last 20 years. On the other hand, the increases in urban background (and roadside) ozone are principally driven by the decline in its chemical removal via its fast reaction with urban NO emissions, which have been declining, although a part of the increase in urban ozone will also be due to the small increases in rural background ozone.

A consequence of these trends is that the decrement in urban ozone concentrations relative to rural background ozone concentrations is getting smaller, and therefore the range in average ozone concentration spatially across the UK is also getting smaller. This characteristic can be observed in the EMEP model maps in Figure 5 which show the change in annual mean ozone each year relative to the 2001-15 mean. Although there is considerable inter-annual variability, the maps show that the increase in ozone has been larger in the urban areas and transport corridors than in more rural areas (darker blue colours over urban areas changing to darker red colours), which is explained by the greater absolute reductions in NO levels over the urban areas compared with the non-urban areas. Finch and Palmer (2020) report from an analysis of non-deseasonalised trends at AURN sites that the difference between urban and rural ozone has declined from 20 µg m^{-3} on average in 1999 to 12 µg m^{-3} in 2019.

2.3.2 Trends in percentiles of ozone from measurements

The 20-year time series of different percentiles of annual distributions of hourly ozone concentrations are plotted in Figure 18-Figure 20 for the 12 rural background, 12 urban background and 2 roadside sites examined previously. Table 3 presents the magnitudes of the non-parametric Theil-Sen trends in the 25th, 50th, 90th and

99.9th percentiles of annual concentrations, with significant trends and their direction highlighted in colour for easier visualisation of patterns in the trends.

Figures 18-20 demonstrate the positively skewed nature of annual distributions of hourly ozone concentrations. The 25th and 50th percentile concentrations have smaller difference in concentration than between the 99th and 99.9th percentile concentrations. The latter two percentiles are the concentrations for which, respectively, only 88 hours and 9 hours in a year have higher concentrations. These percentiles pick out trends in the magnitudes (and indirectly the number) of high concentration episodes.

Table 3 shows that the trends in the 25th percentile closely match the trends in the 50th percentile already discussed in the context of trends in ‘average’ ozone concentrations. The median and lower quartile concentrations of ozone have clearly increased over the period 2000-2019 at urban background sites (at 11 of the 12 sites selected), whilst corresponding increases at rural sites are in general smaller (and in many cases not statistically significant).

In respect of the 99th and 99.9th percentiles, Table 3 shows that there have been no significant trends (up or down) in these upper percentiles across all 27 sites examined (barring a couple of significant downward trends at Marylebone Road and Thurrock for 99th and 99.9th percentiles, respectively).

Inspection of Figures 18-20 show that trends in these high ozone percentiles vary between individual sites and, as expected, can be subject to large inter-annual variation. Finch and Palmer (2020) similarly report no statistically significant trend in non-deseasonalised annual maximum ozone on average across rural and urban background AURN sites for the period 1999-2019. Whilst their analyses showed that maximum ozone has decreased on average, there was very large inter-site variability in trends.

Even though there are no significant trends in the maximum and upper percentile concentrations of ozone, the fact that average concentrations have increased indicates that the magnitudes of the high concentration episodes above local background must have decreased slightly. Overall, however, the analysis suggests that there have not been large decreases in the magnitude and number of high ozone concentration episodes across the UK over the 20-year period 2000-2019. On the other hand, the magnitude of the peaks in ozone over the last 20 years are much smaller than those reported in the 1970-2000 period (PORG, 1997; ROTAP, 2012).

The recent work by Lin et al. (2020) provides evidence that the lack of strong recent downward trends in high percentile concentrations of ozone that might be anticipated from the reductions in NO_x and VOC emissions (Section 4.1) is due to a climate penalty. Using observations and Earth system model simulations for the period

1960-2018 they show that ecosystem-atmosphere interactions, especially reduced ozone removal by water-stressed vegetation, exacerbates ozone air pollution over Europe, offsetting much of the air quality improvements gained from regional emission controls. They predict a continuation of this feedback with the expected increasing frequency of hot and dry summers (see also Section 5.1).

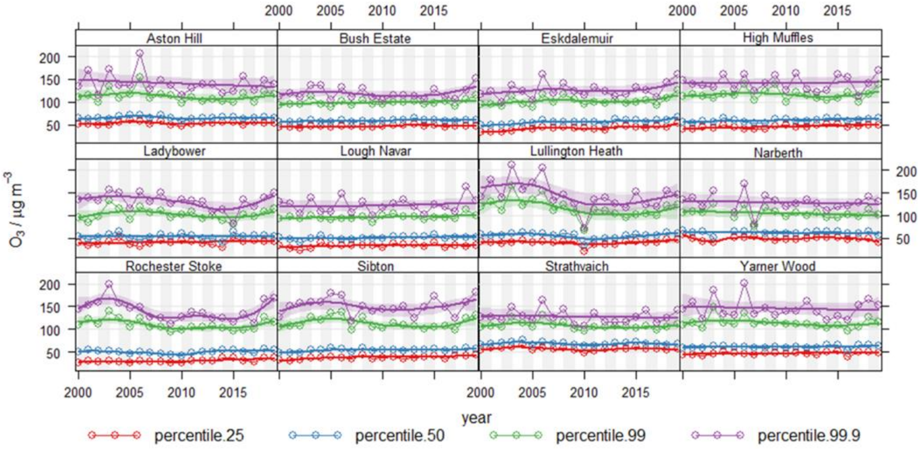


Figure 18: Time series of the 25th, 50th, 99th and 99.9th percentiles of annual hourly ozone concentration at 12 rural background AURN sites, for the period 2000-2019. The smoothed lines are to help visualise trends.

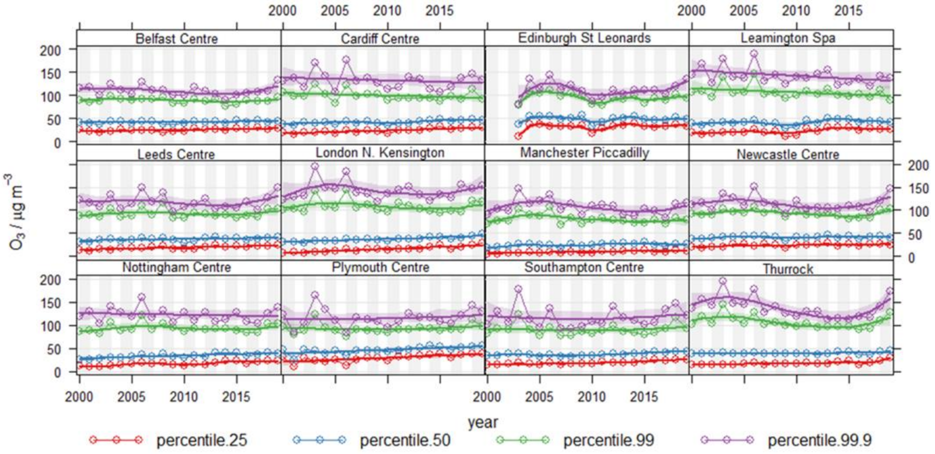


Figure 19: Time series of the 25th, 50th, 99th and 99.9th percentiles of annual hourly ozone concentration at 12 urban background AURN sites, for the period 2000-2019. The smoothed lines are to help visualise trends.

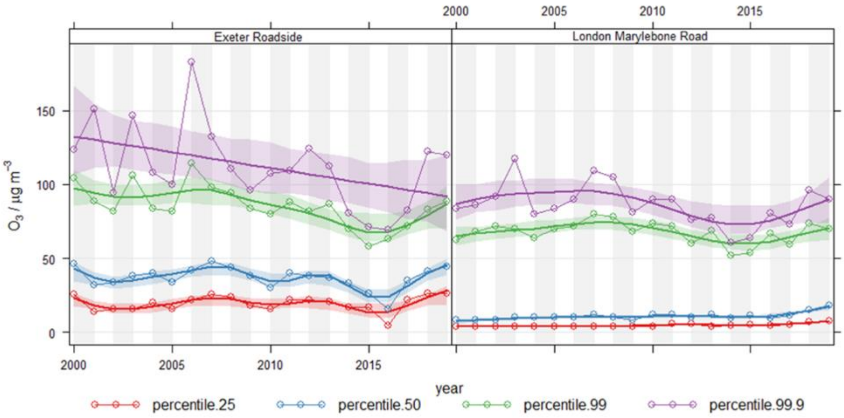


Figure 20: Time series of the 25th, 50th, 99th and 99.9th percentiles of annual hourly ozone concentration at the two urban traffic (roadside) AURN sites, for the period 2000-2019. The smoothed lines are to help visualise trends.

2.3.3 Trends in air-mass origin contributions to ozone at Mace Head and Lullington Heath

Figure 21 shows trends in ozone by air mass origin for two rural background sites with contrasting geographical positions in the British Isles: Mace Head on the Atlantic west coast of Ireland and Lullington Heath in East Sussex close to continental Europe. Air mass origins have been derived from Hysplit 4-day back trajectories run every 3 hours for the 20-year period 2000 to 2019. To simplify the analysis, back trajectories have been allocated to eight wind sectors (N, NE, E, …). A trajectory is allocated to a sector if it spends at least 50% of the time in that sector; otherwise it is considered ‘unallocated’.

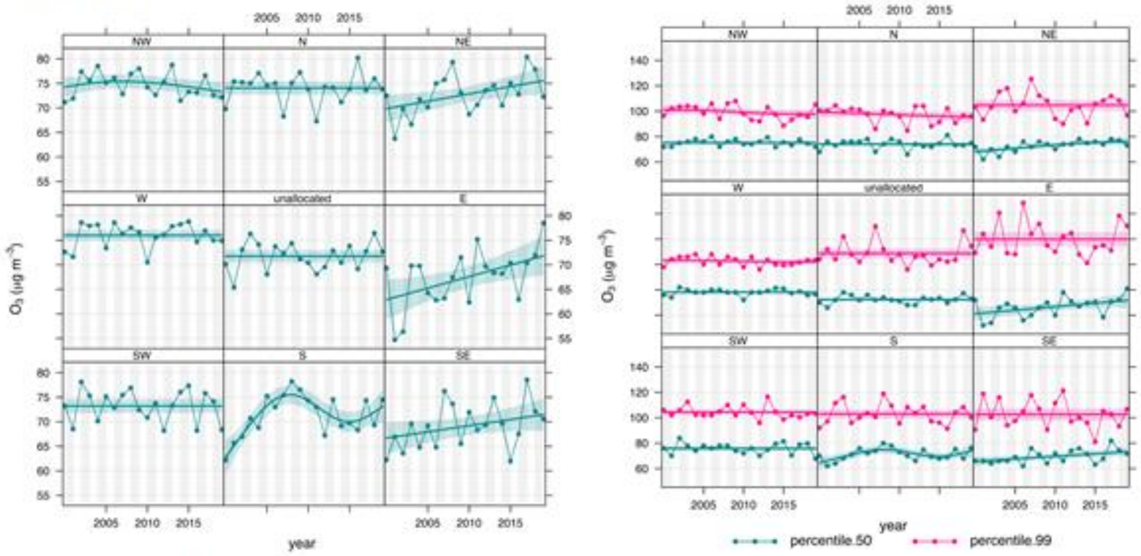
The figure shows that at Mace Head there no evidence of a trend in mean and median ozone over the past 20 years for non-European source directions (NW, W, SW) but a small increase in mean and median ozone concentrations in air mass sectors arriving from SE, E and NE. The small upward trend in average ozone at Mace Head shown in Table 3 and Figure 17 is therefore driven by increases in ozone from the direction of the UK and mainland Europe.

At Lullington Health, there is little evidence of change in mean and median ozone concentrations for any air-mass back-trajectory sector over the 20-year period (Figure 21). This is consistent with the absence of a trend at this site reported in Table 3, although it is noted that the majority of other rural background sites reported in Table 3 do show significant small upward trend in mean ozone.

In respect of trends in 99th percentile ozone concentrations, Figure 21 shows no significant trend for any air mass direction arriving at Mace Head, but some decrease in these concentrations in air arriving at Lullington Health from the easterly and north-easterly wind sectors (although this decrease appears to have levelled off in the last 10 or so years). The small downward trend in upper percentile concentrations reported in Table 3 for Lullington Health is therefore again driven by easterly air masses.

In summary, trends in the past 20 years in average rural background ozone are relatively modest, being slightly increasing in terms of average ozone and slightly decreasing in respect of highest percentile concentrations. The air-mass analyses (Figure 21) indicate these trends are driven by changes in ozone in continental rather than westerly (baseline) air. A tentative observation from Table 3 that increases in average ozone may be generally larger at rural (and urban) sites in the eastern part of the UK than in the western part, is consistent with this, and probably reflects both the greater influence in the east from changes in emissions in continental Europe and the greater reductions in NO_x levels in eastern areas where populations (and therefore emissions) are greater than in the west.

Mace Head



Lullington Heath

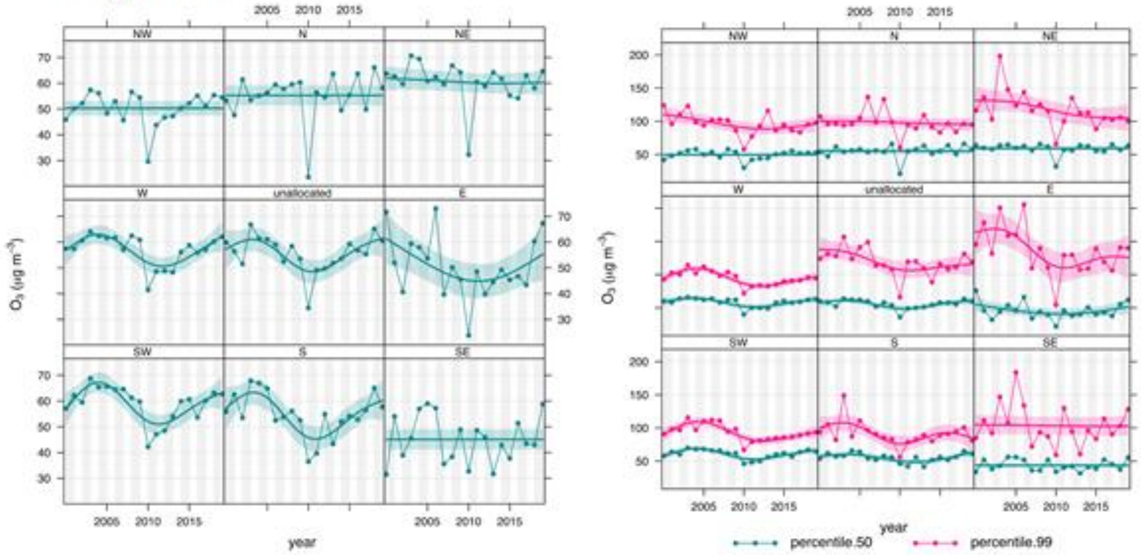


Figure 21: Trends in ozone concentration by air mass sector for 2000-2019 arriving at Mace Head (upper plots) and at Lullington Health (lower plots). Left hand panels show trends in mean ozone and right hand panels show trends in the median and 99th percentile of hourly ozone in each year. The smoothed lines are to help visualise trends.

2.3.4 Trends in average ozone due to emissions changes based on air quality modelling

Figure 5 in Section 2.1.2 shows the modelled ozone field as it is predicted to have changed between 2001 and 2015 in response to changing emissions and meteorology. However, the model allows the influence of terrestrial anthropogenic emission changes to be investigated in isolation by running the model over the various years with changing (UK and European) emissions, but the same meteorology, here arbitrarily chosen to reflect 2015. These model simulations are shown in Figure 22. Due to the setup of these modelling experiments (see Section 2.1.2), the results do not reflect additional changes due to changes in the hemispheric baseline, shipping emissions or land cover.

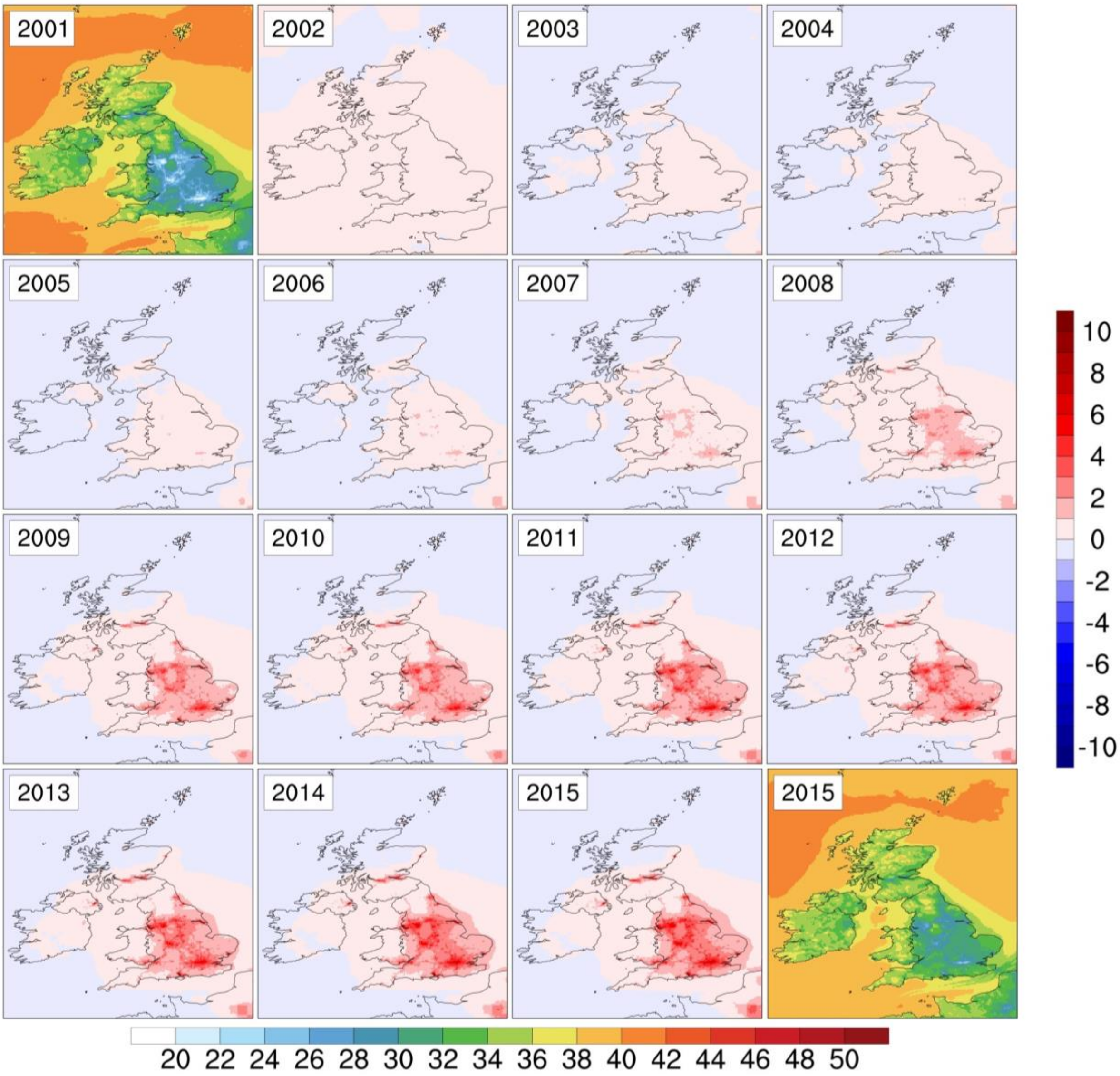


Figure 22: EMEP4UK modelled changes of annual mean surface ozone concentration (in ppb) compared with 2001, removing the effect of changing meteorology. All years are based on 2015 meteorology, 2015 Europe-external boundary conditions and 2011 shipping emissions in order to isolate the impact of land-based emissions changes in the UK and rest of Europe. The map of annual mean surface ozone for 2015 is also shown. Emissions data used in the model are described in Section 2.1.2. (EMEP version rv4.17; WRF version 3.7.1) For ozone, 1 ppb = 2.0 µg m^{-3}.

The model predicts that, without the interference of changing meteorology, ozone concentrations would have increased steadily over this period, with the largest increase seen in urban centres and along the major road network (Figure 22). This prediction is consistent with the measured trends being largest and statistically most significant at the urban sites. The close correlation of the pattern with NO_x sources suggests that it is driven mainly by a reduction in the ozone sink by reaction with NO as NO emissions have declined.

The magnitude of the modelled concentration changes in the urban areas are in the region of 3 to 6 ppb over 14 years, which equates to a trend of 0.4 to 0.9 µg m^{-3} y^{-1}, in line with the measurement-derived trends of Table 3. Comparison of the model results using fixed meteorology (Figure 22) and actual meteorology (Figure 5) shows the large additional role of meteorology in controlling the actual concentrations (interannual variations of a few µg m^{-3} y^{-1} is usual), which is why long time-series are needed to derive statistically robust trends from measurements.

2.4 Trends in ozone in the North Atlantic

Figure 23 shows the long-term trends in measured surface ozone at Mace Head for 1988-2020 compared with surface ozone at this location simulated for 1982-2017 by the UK Chemistry and Aerosol model (Archibald et al., 2020a). The model used CMIP5 historical emissions and Representative Concentration Pathway (RCP)8.5 scenario emissions after 2014.

Figure 24 presents ozone time series for a North Atlantic domain (45°-15° W; 40°-60° N) for lower tropospheric ozone column (in Dobson Units, DU) from the surface to 450 hPa (~6 km) derived from OMI satellite observations (Levelt et al., 2018), and for both UKCA modelled lower tropospheric ozone (surf to 450 hPa) and surface ozone. Satellite observations are only available from 2005. Nevertheless, these domain-averaged satellite and modelled data extend the information for ozone in the vicinity of Mace Head both horizontally (single location to large domain) and vertically (surface to lower troposphere).

As well as extending further back in time, the model simulation helps bridge the gap between the two types of observations by offering both surface versus lower troposphere data, and Mace Head versus North Atlantic.

The standard error of the least-squares linear trend estimate has been calculated from the standard deviation of the residuals (Wigley, 2006). The effect of autocorrelation has been included by using the lag-one autocorrelation coefficient to determine an effective sample size in the calculation of the standard error of the trend estimate (Santer et al., 2000; Wigley, 2006). Because of the high temporal variability of ozone, trend errors are generally large. A linear model may also not be the most appropriate fit.

Figure 23 shows that the observed linear trend in surface ozone at Mace Head is larger than the modelled trend, although both values are similar within the estimated error.

Figure 23 and Figure 24 together show that modelled surface ozone, averaged over the North Atlantic domain, is around 2 ppb (4 µg m-3) higher compared to modelled surface ozone at Mace Head, but that the trends in both are similar: positive but small. For the lower troposphere, the observed ozone trend is positive and larger than modelled trend (Figure 24).

Together the two figures indicate that the observed ozone in the North Atlantic lower troposphere has increased at a greater rate (5% per decade) than both the modelled surface ozone in the North Atlantic (around 1.5% per decade) and the observed surface ozone at Mace Head (about 0.5% per decade). Observations for the full tropospheric ozone column in the North Atlantic (not shown) also have significantly larger trend compared to surface values, with an increase of around 2 DU (or 5%) per decade. This suggests that tropospheric ozone in the North Atlantic is increasing faster than surface ozone. However, care is needed in these statements since the uncertainty estimates for the trends overlap. Also, all of Figure 21, Figure 23 and Figure 24 indicate essentially no trend in surface ozone from the Atlantic sector at Mace Head in time series since 2000.

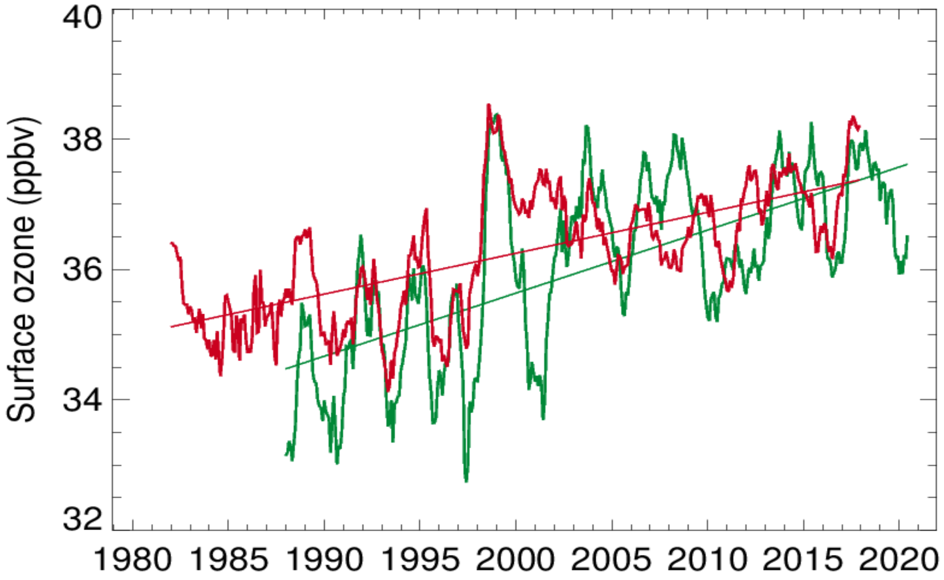


Figure 23: Surface ozone time series at Mace Head. Observed, green, (1988-2020) converted from mass mixing ratio data; modelled, red (1982-2017). Linear trends on the time series are for the full period of each dataset shown: observed (1.0 ± 0.4 ppbv/decade); modelled (0.6 ± 0.2 ppbv/decade). Linear trends calculated for the overlapping period of 1988-2017 are: observed (1.1 ± 0.4 ppbv/decade); modelled (0.6 ± 0.3 ppbv/decade).

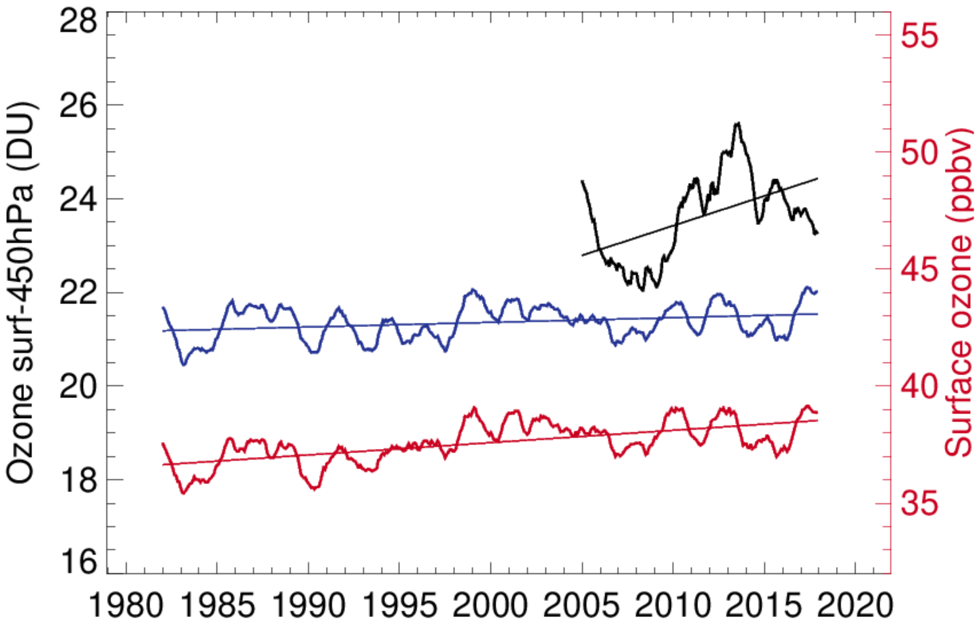


Figure 24: Ozone time series averaged over the North Atlantic domain (45°-15° W; 40°-60° N). In black: observed lower tropospheric (surf-450 hPa) ozone column in Dobson Units (DU) from OMI satellite (2005-2017), linear trend 1.2 ± 0.7 DU/decade. In blue: modelled lower tropospheric (surf-450 hPa) ozone column (DU), linear trend 0.1 ± 0.1 DU/decade. In red: modelled surface ozone (ppbv) (1982-2017), linear trend 0.5 ± 0.1 ppbv/decade. Linear trends calculated for the overlapping period of 2005-2017 are: observed lower troposphere (as above); modelled lower troposphere (0.3 ± 0.3 DU/decade); modelled surface (0.3 ± 0.6 ppbv/decade).

2.5 Observational trends at a wider spatial scale: European and hemispheric

Because ozone is a reactive gas, it must be measured in real time. Unlike longer-lived gases such as carbon dioxide, measurements cannot be constructed from air sample archives or ice cores, which hampers the ability to construct long-term trends of the gas. *In situ* measurements of atmospheric ozone were made in the late 19th century (Volz and Kley, 1988), but these measurements are regarded as highly uncertain by modern standards and do not agree well with model simulations (Hartmann et al., 2013).

The first measurements usable for the construction of long-term trends began around the mid-20th century and these proliferated in later years, motivated by studies in atmospheric chemistry, air quality, climate change and ecosystem damage (Tarasick et al., 2019). The richest historical datasets tend to exist within Europe, North America and East Asia (principally Japan and South Korea). Measurements at altitude are possible through differential absorption LIDAR, aircraft and balloon sondes. Measurements of tropospheric ozone are also possible using satellite data, although this covers a more historically recent period and is more representative of the atmospheric column rather than human exposure.

In 2014, the International Global Atmospheric Chemistry (IGAC) project initiated the Tropospheric Ozone Assessment Report (TOAR) to produce an assessment of global ozone concentrations and trends based on the peer-reviewed literature and generate a database of ozone exposure metrics at sites around the world (https://igacproject.org/activities/TOAR). The main database consists of measurements made from 1970 to 2015, which corresponds to the advent of UV absorption instrumentation that forms the basis of most modern *in situ* ozone monitors, such as those used in the AURN network (Schultz et al., 2017).

Ozone has a background concentration of around 20-60 ppb (40-120 µg m^{-3}) in the northern hemisphere, with concentrations increasing with altitude, corresponding to exchanges with the stratosphere (Jaffe et al., 2018). It also tends to exhibit a seasonal peak around spring or summer time (Carslaw, 2005), corresponding to the peak in photochemistry and troposphere-stratosphere exchange. Ziemke et al. (2019) produced an analysis of composite satellite products (augmented by model outputs) from 1979 to 2016 and showed a large amount of regional heterogeneity around the world.

Using instrumental data, Parrish et al. (2012) estimated that the northern hemispheric baseline concentrations approximately doubled between 1950 and 2000 due to increases in NO_x and VOC emissions, with a levelling off in Europe and North America subsequent to this in response to emissions controls (Figure 25).

Analysis by Derwent et al. (2018) of data from the Mace Head site showed that hemispheric baseline ozone concentrations representative of the westerly import to the UK increased substantially from 1987 to a peak of around 41 ppb (82 µg m^{-3}) in 2007 (Figure 26) but have not increased since. Whilst the fit to the baseline data in Figure 26 might suggest a small decrease in baseline ozone since 2007, this impression is a consequence of choosing to fit quadratics to the data, which is not justified and is visually misleading; and to 2016 being the last year of data available to that study. Years 2017 and 2018 had higher ozone than 2016. The trend analyses reported in Section 2.3.3 for data up to 2019 indicate there has been no significant trend in average ozone arriving from the west at Mace Head between the early 2000s and 2019.

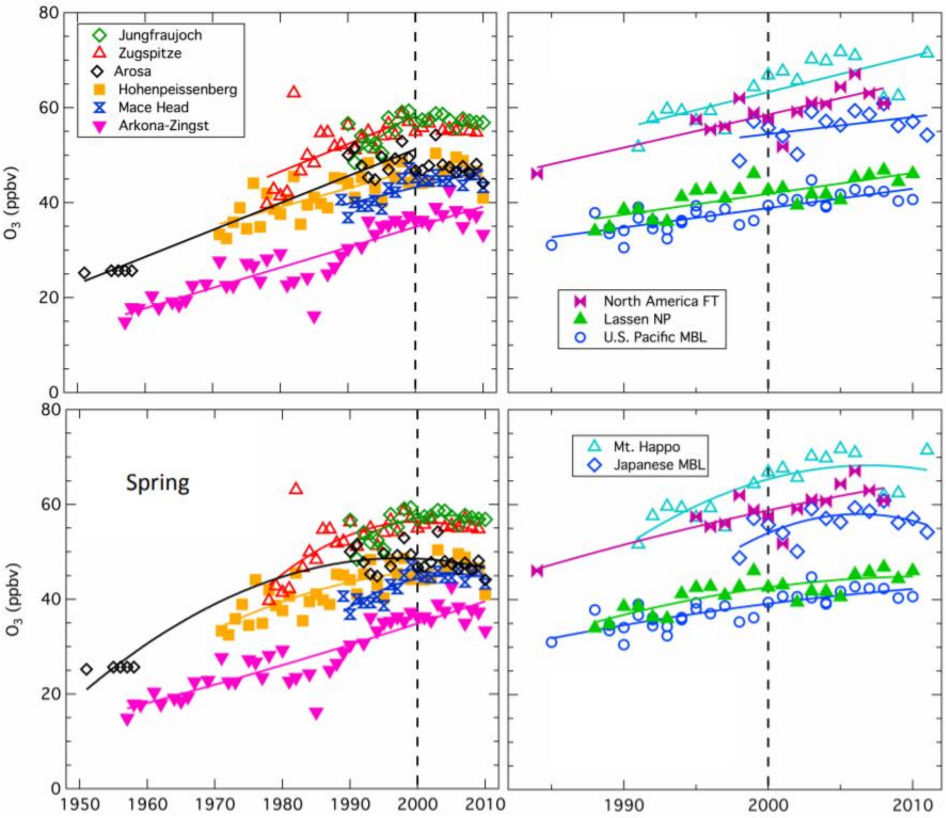


Figure 25: Long-term trends in springtime baseline ozone concentrations measured in Europe (left panels), North America (top right) and Japan (bottom right) (Parrish et al., 2012).

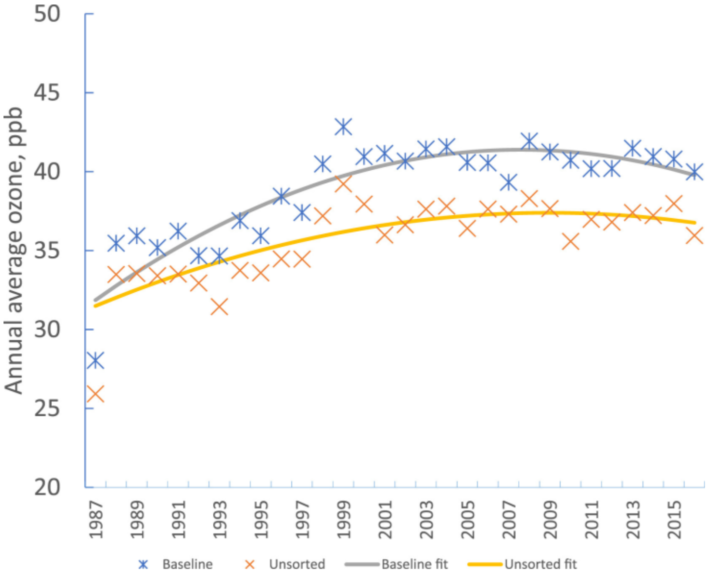


Figure 26: Annual-mean ozone at Mace Head, Ireland, 1987-2016. 'Hemispheric baseline' data are filtered to remove influences from Europe. Source: Derwent et al. (2018). AQEG consider that using quadratic curves to fit the data in this figure is not justified and is visually misleading.

Nearer sources of pollution, trends in ozone concentrations become harder to interpret because of the highly dynamic nature of its chemical interactions with NO_x. While NO_x and VOCs will form ozone through photochemistry, ozone will be locally consumed by NO when forming NO_2, so a local decrease in ozone may be due to an increase in pollution sources that contribute to an overall increase in the amount of ozone being produced regionally. As such, there can be a high diversity of trends at multiple sites within a given region. Because of this, scientists have turned to advanced data mining techniques to extract underlying trends from the data. As part of the TOAR, Chang et al. (2017) employed the Generalised Additive Mixed Model (GAMM) technique to rural background monitoring data in Europe, Eastern USA and East Asia between 2000 and 2015 (Figure 27). They found that average concentrations in Europe had not changed over the period, in contrast to eastern USA, which had decreased, and East Asia, which had increased. The deseasonalised trend analyses for UK rural background sites reported in Section 2.3.1 likewise show no or very small upward trends in average ozone between 2000 and 2019.

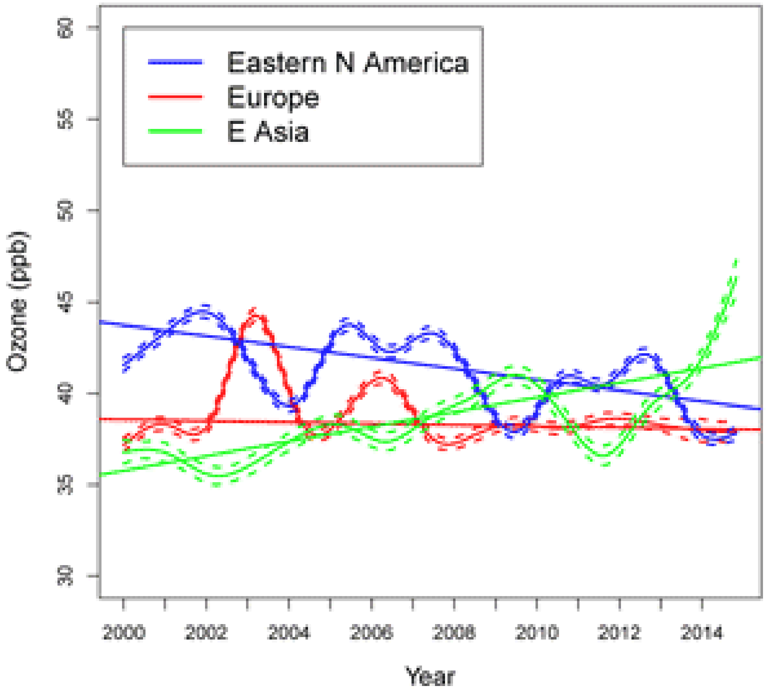


Figure 27: Time series of 2000-15 summertime daytime average ozone concentrations for Europe, eastern North America and East Asia determined using GAMM analysis (Chang et al., 2017).

Another analysis using the 2000-2015 period was performed by Boleti et al. (2020), who used a non-parametric time-scale decomposition methodology to extract underlying trends for individual monitoring sites across Europe and then grouped the sites using clustering. The eight UK monitoring sites included in this analysis were geographically clustered in the 'north' group alongside those in Scandinavia and the Baltic region. In addition, the sites were also clustered according to their pollution levels. Figure 28 shows that within the 'north' cluster, deseasonalised average ozone concentrations were decreasing slightly on average at rural sites but increasing at polluted sites. The increase in ozone at urban sites is as reported in Section 2.3. The range in trend at rural sites in the north cluster in Figure 28 spans negative and positive and only three of the 16 sites in this group are in the UK. The deseasonalised trend analysis on a larger group of 12 UK rural sites reported in Section 2.3 indicate that UK rural ozone has increased very slightly on average (~0.05 ppb y^{-1}) over the longer period 2000-2019.

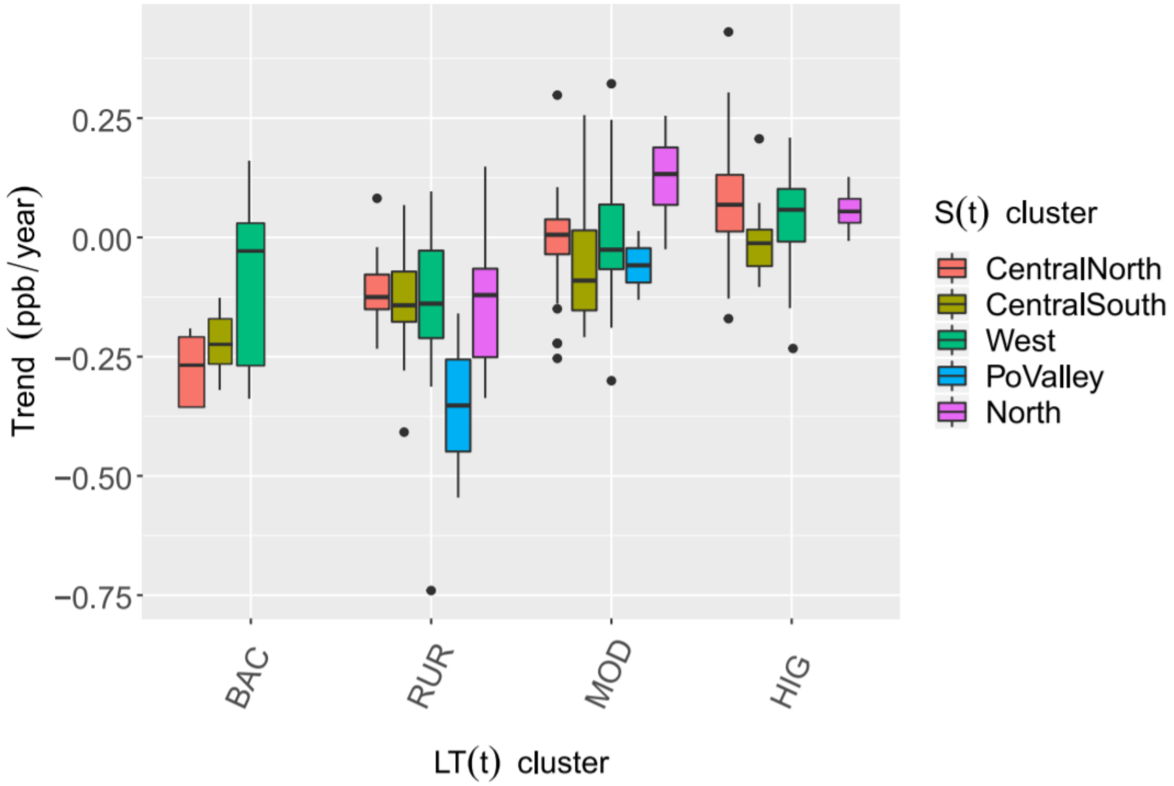


Figure 28: Trends in deseasonalised daily mean European ozone (2000-2015) according to the clusters identified by Boleti et al. (2020). Within the geographical classification clusters, 'BAC' refers to background, 'RUR' rural, 'MOD' moderately polluted and 'HIG' highly polluted. The 8 UK sites included in this analysis are all contained in the 'north' geographic cluster (3 of 16 'RUR', 2 of 4 'MOD' and 3 of 4 'HIG').

As well as overall concentrations, it is also of use to analyse trends of metrics of more relevance to acute and chronic human exposure. This is covered in detail for the UK in Chapter 3, but an analysis of this as part of TOAR was presented by Fleming et al. (2018), covering the period 2000-2014. The metrics used there were 4th highest daily maximum 8-hour ozone from Apr-Sep (4MDA8); number of days in the year with MDA8 > 70 ppb (140 µg m^{-3}) (NDGT70); annual sum of ozone MDA8 values over 35 ppb (70 µg m^{-3}) (SOMO35); and two further metrics (3MMDA1[3]; AVGMDA8[4]).

Within Europe, there was a slight downward trend in the exposure metrics for non-urban sites, but less so for urban sites (Figure 29). At urban sites, there was little or no trend (for the 2000-2014 period) for the exposure metrics with no concentration cut-off (e.g. AVGMDA8) or relatively low cut-off (e.g. SOMO35). These findings from the TOAR project are consistent with the 20-year trends in 'average' and lower percentile ozone concentrations at UK rural and urban background sites presented in Section 2.3 of this report.

In contrast, North America showed generally downward trends and East Asia was flat for non-urban sites and slightly upward for urban sites. It is important to note, however, that beyond these headline statements there is large variability in trend between sites in each region. It is also worth noting that in contrast to the aforementioned daytime average concentrations, Chang et al. (2017) also reported a downward trend in exposure metrics for Europe after GAMM analysis, in particular in NDGT70.

In summary, the long term-trends of ozone in the UK, in line with the rest of Europe, have been largely flat since 2000, after a sustained increase from the mid-20th century. The baseline mean concentration is around 35-40 ppb (70-80 µg m^{-3}) (depending on how it is defined) with individual sites showing local positive and negative variations from this. The most evident increases in mean concentrations are at polluted sites. While a decrease in health exposure metrics since 2000 can be seen for Europe in some analyses, these are very slight or non-existent for urban areas and for low concentration cut-off metrics. Contrasts can be seen with other areas in the northern hemisphere mid-latitudes that also have good historical data coverage; concentrations have declined more significantly since 2000 in North America, while concentrations in East Asia continue to increase.

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[3] Annual maximum of the 3-month running mean of daily maximum 1-hour ozone. Used by the Global Burden of Disease project but not routinely used in Europe.

[4] Mean of the daily maximum 8-hour ozone from April to October.

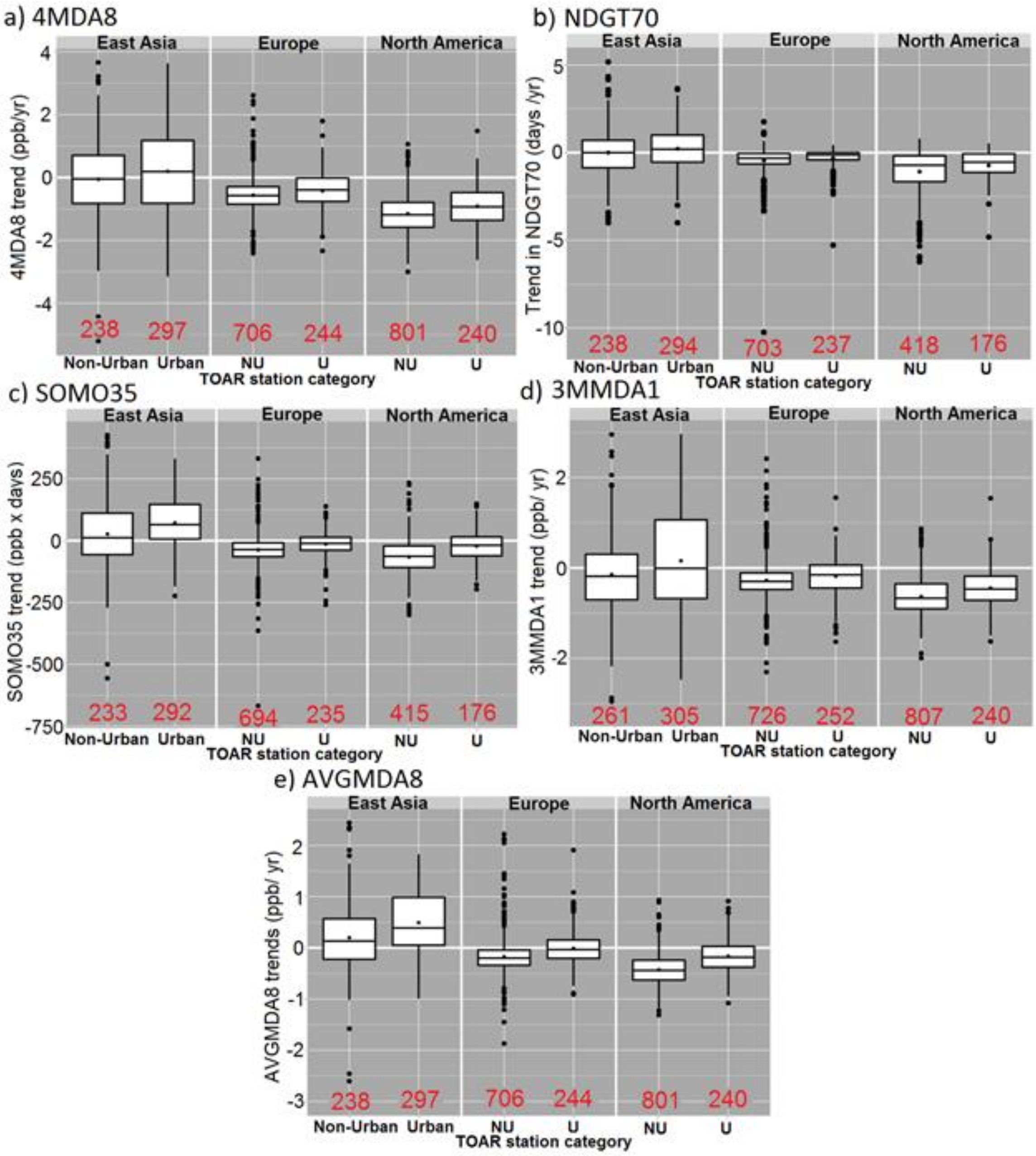

Figure 29: Trends in ozone exposure metrics (2000-2014) at rural and urban sites in East Asia, Europe and North America (Fleming et al., 2018).

2.6 Trend in total oxidant at London Marylebone Road

It is useful to consider the trend in total oxidant, Ox = O_3 + NO_2, to understand how local and regional changes in ozone and NO_2 have changed in urban areas. Using the approach of Clapp and Jenkin (2001), the total oxidant concentrations at Marylebone Road have been partitioned between a local NOx-dependent component and a regional background component. The local component that depends on NO_x

concentrations provides an estimate of the Ox that is related to directly emitted NO_2 from road vehicles. The regional component can be thought of as the regional background ozone contribution.

Figure 30 shows that the local oxidant contribution (shaded green) has decreased over time, with an accelerated decrease through 2019 and 2020, in part affected by reduced road traffic due to COVID-19 (see also Section 2.7). This decrease shows that vehicle emissions of directly emitted NO_2 have decreased considerably over this time, reflecting effective emissions control. On the other hand, the regional contribution has been largely invariant, consistent with the findings elsewhere in this report that suggest only minor changes in regional background ozone contributions. Overall, however, there has been a reduction in total Ox over the past 20 years, which will likely be reflected at other urban site locations.

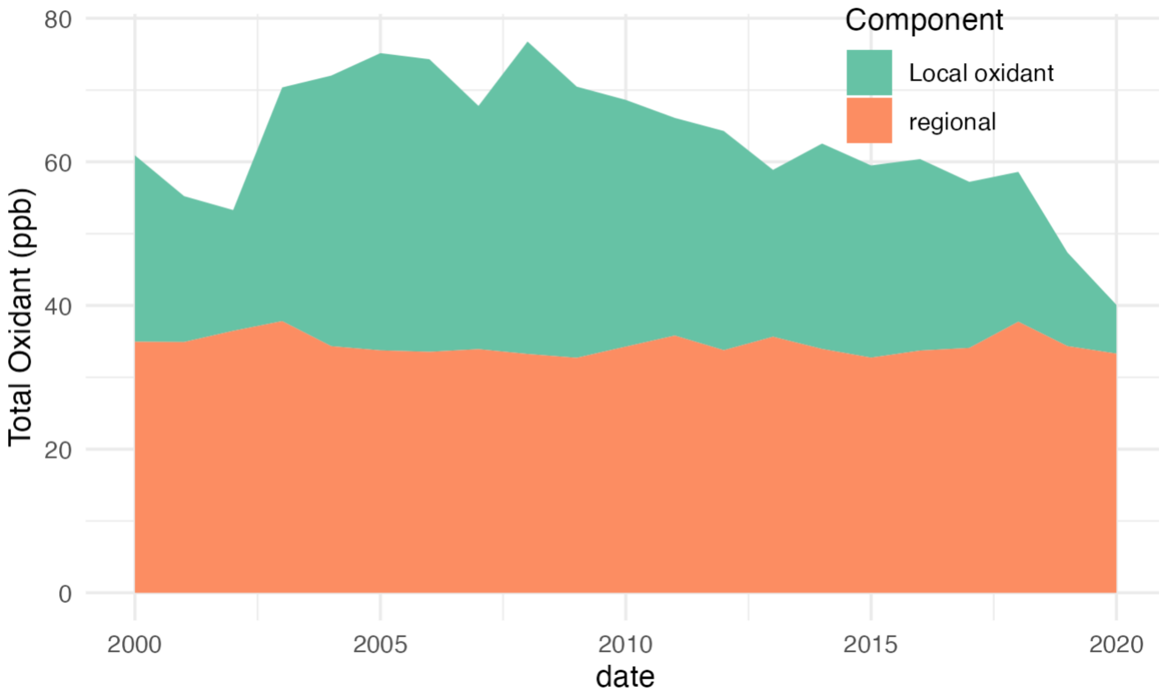

Figure 30: Trend in total Ox from 2000 to the end of 2020 at Marylebone Road, London. The local oxidant contribution can be thought of as that made by directly emitted NO_2 emissions from road vehicles and the regional component corresponds to the regional ozone contribution.

2.7 Changes in ozone arising from the COVID-19 lockdown

The global COVID-19 pandemic in 2020 resulted in unprecedented restrictions or ‘lockdowns’ on populations at national scale in the UK and elsewhere in order to limit the spread of the disease. This resulted in substantial reductions in many activities responsible for air pollutant emissions, notably transport and parts of the industrial and commercial sectors. The UK government advised against all nonessential travel and contacts on 16th March 2020, closed schools, pubs and restaurants on 20th March and announced full lockdown on 23rd March. Neighbouring countries implemented similar lockdowns in the days immediately prior to the UK lockdown.

In April 2020, Defra issued a call for evidence for the impact of the lockdown on air pollutant emissions, concentrations and population exposures, with a submission deadline of 30th April. AQEG synthesised this evidence into a report (AQEG, 2020a). AQEG’s initial conclusions relate only to changes in UK air quality in the first few weeks of the first lockdown. It is also important to highlight that UK air quality was negatively influenced by a significant change in meteorology between the weeks preceding and following the lockdown (from predominantly westerly to predominantly easterly air masses), in addition to changes, both positive and negative, arising from responses to COVID-19. Disentangling responses of ozone, as a secondary pollutant, to the lockdown from meteorological and seasonal influences is particularly challenging and will require sophisticated chemical-transport modelling, informed by observations and revised emissions inventory data.

The most pronounced changes in UK air quality during lockdown were in the urban environment, notably for NO and NO_2, driven by the very substantial reductions in traffic emissions. Once weather effects are accounted for, mean reductions in urban NO_x averaged over the first few weeks of lockdown were typically 30-40% (AQEG, 2020a). As a consequence of reduced chemical removal by NO, increases in ozone were apparent at many urban monitoring stations, particularly roadside. Analyses for London have in fact shown that the concentration of Ox (= O_3 + NO_2) increased immediately following lockdown due to the incidence of several ozone episodes associated with winds from continental Europe coupled with high temperatures. The interest in Ox arises because of its potential role in oxidative stress and potential adverse health effects (Williams et al., 2014).

Changes in rural ozone have been harder to discern since transboundary contributions are not always accounted for by local meteorological normalisation. Analysis of measurements and models suggest no single direction of change although a tendency towards very modest increases (a few µg m^{-3}) compared with business as usual in central and south-eastern parts of the UK.

These preliminary findings for the UK have been supported by subsequent more extensive trend analyses. Grange et al. (2020) applied machine learning models to NO_2 and O_3 data from 246 ambient air pollution monitoring sites in 102 urban areas in 34 European countries between February and July 2020. Concentrations of NO_2 were on average 34% and 32% lower than expected for traffic and urban-background sites, respectively, while ozone concentrations were 30% and 21% higher. Total oxidant Ox changed little. Likewise, Shi et al. (2021), applying a deweathering machine learning technique to pollutant concentrations in 11 cities globally, including London, similarly conclude that changes in pollutant concentrations following initial COVID-19 lockdowns were not as large as early reports might have suggested. Whilst urban NO_2 concentrations declined, ozone concentrations increased, with little impact on Ox.

The response of air quality to lockdown may provide an analogue of a future UK atmosphere in which combustion-related transport emissions have substantially declined as part of the transition to net zero carbon. The indication is there will be widespread increases in urban ozone unless additional mitigation measures are introduced, for example on VOC emissions.

Chapter 3 – Recent spatial and temporal trends in measures of ozone impacts

A number of metrics to quantify the impacts of ozone on human health and vegetation have been derived from evidence on the concentrations and averaging times, and season(s) of exposure, that lead to adverse effects. Different metrics exist to cover different aspects of impact, for example on human health from short-term or from long-term exposure, or on specific types of vegetation. In addition, different authorities also sometimes derive different variants of metrics to quantify the same impact. Impact metrics pertaining to the UK are summarised in Table 1.

Due to their emphasis on different aspects of ozone concentration distributions, the spatial pattern of the metrics in Table 1, and the spatial pattern of their changes in time, do not necessarily follow those for mean concentration of ozone.

None of the impact metrics can be measured directly and therefore they must be inferred from concentration values, and, in some instances of flux-based metrics, from other variables in addition. Also, whilst these metrics can be calculated for individual monitor sites, assessment of the impacts on population and vegetation over large areas requires model interpolations or simulations.

3.1 Trends in human health impact metrics

The health impacts of short-term exposure to ozone are usually quantified using a version of the daily maximum 8-hour running mean ozone concentration. COMEAP (2015) recommend not to apply any cut-off (or threshold) to this value, i.e. all such ozone concentrations contribute to the impact quantification. In contrast, the EU and the WHO specify assessments that include a number of cut-off concentrations (Table 1). Metrics with cut-off concentrations have been most widely used.

3.1.1 Spatial and temporal trends in health impact metrics for EU compliance reporting derived from the PCM model

The EU target value and long-term objective for quantifying acute effects on human health are based on number of days in the year in which the maximum daily 8-hour mean ozone exceeds 120 µg m^{-3}. This metric tends to be sensitive to the extent and persistence of photochemical episodes of ozone.

The UK data for EU compliance reporting are derived from the measurements-based Pollution Climate Mapping (PCM) model. Details of the empirical methods used to derive the maps are described in Brookes et al. (2019), but include interpolation of monitoring data from rural monitoring sites and adjustments for altitude and urban

NO$_x$. As the PCM model is periodically updated, the methodology used for contemporary and historic maps may not be exactly the same.

The EU TV is ≤25 days per year exceedances of 120 µg m^{-3} maximum daily 8-hour mean, averaged over 3 years. Figure 31 shows that all parts of the UK were compliant with the TV in 2018; the greatest number of exceedances averaged over 2016-18 being in the range 6-10 days, in southern and eastern England (but less so in urban areas) and in mid-Wales.

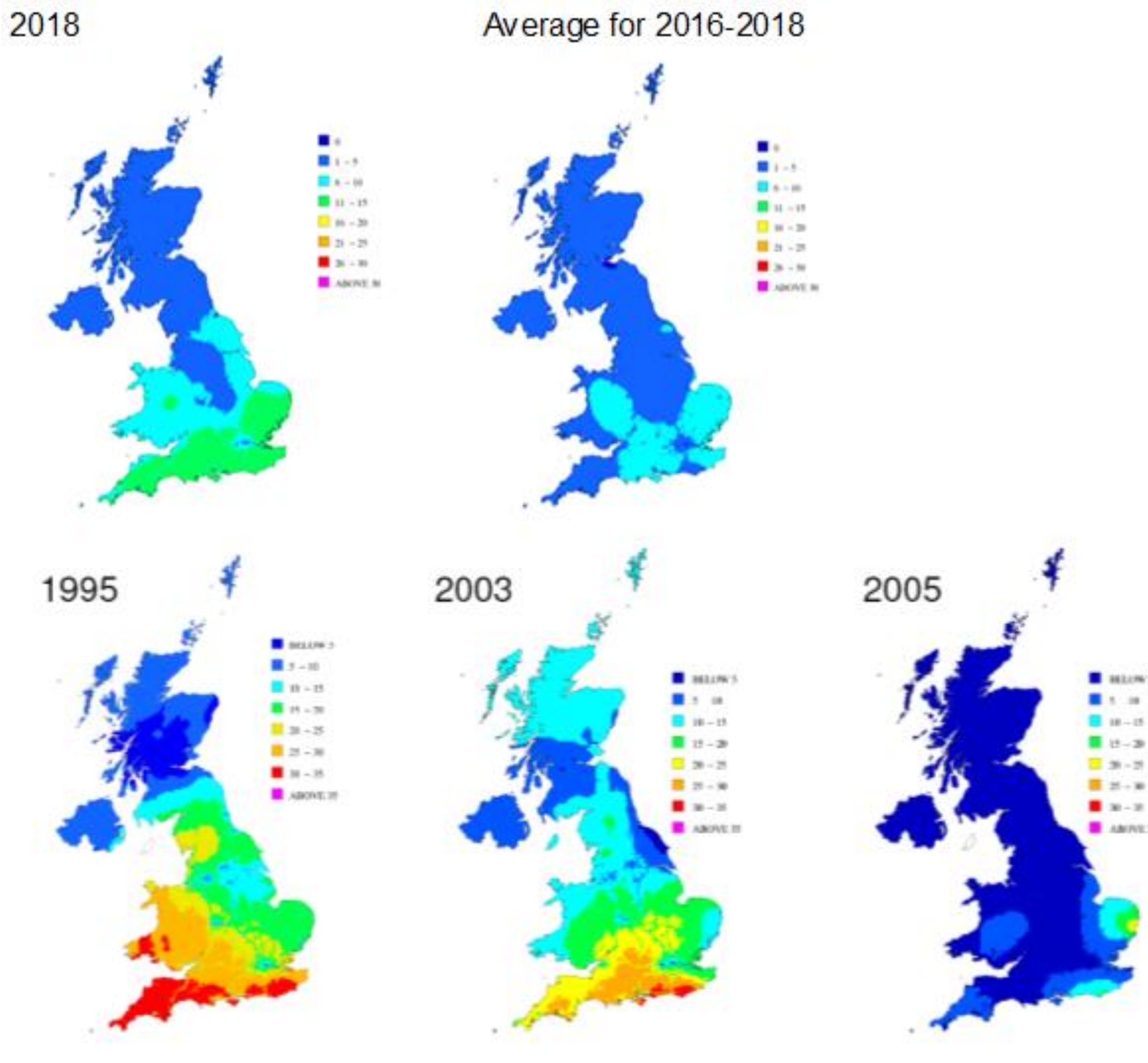

Figure 31: PCM model maps of number of days in the year with daily maximum 8-hour mean ozone concentration >120 µg m^{-3}. Upper row left is for 2018, upper row right is the mean for 2016-18 (source: Air Pollution in the UK 2018 (Defra, 2019)). The maps for 1995, 2003 and 2005 are as presented in the AQEG 2009 report on ozone (AQEG, 2009). Note that the colour scale is slightly different for these latter maps.

Figure 31 also presents the mean number of exceedance days in 2018 alone (the latest maps available) and shows that exceedances in 2018 were greater than for the 2016-18 mean. Greatest exceedances reached 11-15 days, again in the south of England, East Anglia and mid-Wales, but with clear urban decrements, particularly around Greater London. The rest of England and Wales, Northern Ireland and Scotland had 10 or fewer days with ozone >120 µg m^{-3}. The differences between 2018 and the 2016-18 mean illustrate the meteorologically-driven inter-annual variability in surface ozone concentrations and that ozone concentrations in 2018 were the highest the UK experienced for some years.

The UK has been compliant with the EU target value for the last 5 years (Table 4), and at least as far back as 2007 – source: UK annual air quality reports.

The EU long-term objective for the protection of human health from ozone is for no exceedances of 120 µg m^{-3} daily maximum 8-hour ozone concentration. Figure 31 shows that none of the 43 UK zones and agglomerations were compliant with this long-term objective in 2018, although variable numbers of urban agglomerations (and parts of Scotland) have been compliant with this long-term objective over the last 5 years (Table 4). For the 10 years prior to 2014, none of the zones (or almost none of the zones) were compliant with the long-term objective.

However, the maps for earlier years in Figure 31 demonstrate that over the long term there has been reduction in numbers of days of exceedances of 120 µg m^{-3} even though zero exceedances is not yet achieved everywhere. In 1995 and 2003, there was almost no, or only a very small, area of the UK with fewer than 5 exceedances, whilst substantial parts of southern England and Wales experienced 25 or more days of exceedance, in violation of the EU target value. The reduction in exceedances is due to less intense photochemical ozone episodes, including transboundary events, brought about by pan-European reductions in emissions of VOC and NO_x.

Table 4: Compliance for the years 2014 to 2018 of the 43 UK zones (which comprise 28 urban areas and 15 non-agglomeration areas) with EU target values and long-term objectives for the protection of health and vegetation against ozone. A zone is non-compliant if anywhere in the zone is non-compliant. Data from annual *Air Pollution in the UK* reports.

Year	**Compliance with protection of health**		**Compliance with protection of vegetation**	
	EU Target Value	**EU Long-Term Objective**	**EU Target Value**	**EU Long-Term Objective**
2018	All compliant	No zone compliant	All compliant	5 zones compliant: North East Scotland, Central Scotland, and Glasgow, Belfast and Preston urban areas
2017	All compliant	9 zones compliant: Highland, North East Scotland, Central Scotland, Scottish Borders, North East, and Glasgow, Edinburgh, Tyneside and Teesside urban areas	All compliant	All compliant
2016	All compliant	1 zone compliant: Edinburgh urban area	All compliant	All compliant *except* 5 zones: North East, Yorkshire & Humberside, West Midlands, South Wales, and North Wales
2015	All compliant	No zone compliant	All compliant	All compliant *except* 1 zone: Eastern
2014	All compliant	11 zones compliant: Edinburgh, Blackpool, Preston, Greater Manchester, Liverpool, Birkenhead, Bristol, Brighton-Worthing-Littlehampton, Southampton, Cardiff and Swansea urban areas.	All compliant	All compliant *except* 3 zones: Eastern, South East, and East Midlands

3.1.2 Spatial and temporal trends in EMEP4UK-modelled SOMO health impact metrics

The metric recommended by the WHO to assess the impact of short-term exposure to ozone on human health is SOMO35, which reflects the amount of ozone the human body is thought not to be able to detoxify and is defined as the annual sum of the daily maximum of 8-hour running mean concentration over 35 ppb (70 µg m^{-3}) and is expressed in ppb. days or µg m$^{-3.}$ days. This metric is also used by the European Environment Agency. The WHO REVIHAAP project (WHO, 2013a) additionally recommend quantification of the short-term human health impacts of ozone using an analogous metric, SOMO10, which has a concentration cut-off of 10 ppb (20 µg m^{-3}) and is therefore closer to the recommendation of COMEAP (2015) not to include any cut-off.

Figure 32d shows the change in SOMO35 across the UK between 2001 and 2015 as simulated using the EMEP4UK model for constant 2015 meteorology. Whilst purely based on the changes in anthropogenic emissions, the mean ozone concentration field shows an upward trend throughout the country (Figure 22), the human health impact is predicted to have increased only in the heavily urbanised parts of the country but decreased in remote areas (Figure 32d). This is because SOMO35 only reflects changes in daily maximum 8-hour running mean concentration above 70 µg m^{-3} and not changes in means.

The increases in urban ozone brought about by the decline in the ozone sink by reaction with NO have increased instances of urban concentrations now exceeding >70 µg m^{-3}; on the other hand, in most rural areas, where ozone already exceeds 70 µg m^{-3}, the small downward trend in SOMO35 is driven by the small decreases in highest ozone concentrations brought about by decline in intensity of photochemical episodes. Absolute SOMO35 values remain greater in rural areas than in urban areas (Figure 32a).

Due to the association of the population with urban areas, the effect of the geographical variations in changes in SOMO35 illustrated in Figure 32d has been to increase the UK population-weighted mean SOMO35 by about 25% between 2001 and 2015. However, it must be emphasised again that this value relates only to change in SOMO35 due to changes in pan-European anthropogenic terrestrial emissions in that period and does not include changes in SOMO35 due to changes in baseline ozone. Simulations where this is included suggest considerably less change in SOMO35 over this period. Neither does Figure 32d reflect variations in SOMO35 arising from interannual variation in meteorology. In reality, the impact metrics will be subject to similar meteorologically driven year-to-year variability as illustrated in Figure 5 for annual mean ozone concentration.

The trend in SOMO35 is different to the trend in EU long-term objective because the cut-off concentration in SOM35 is considerably lower than the threshold of 60 ppb (120 µg m^{-3}) used in the latter which is only affected by changes in ozone concentrations on the very few days in a year that exceed this higher concentration.

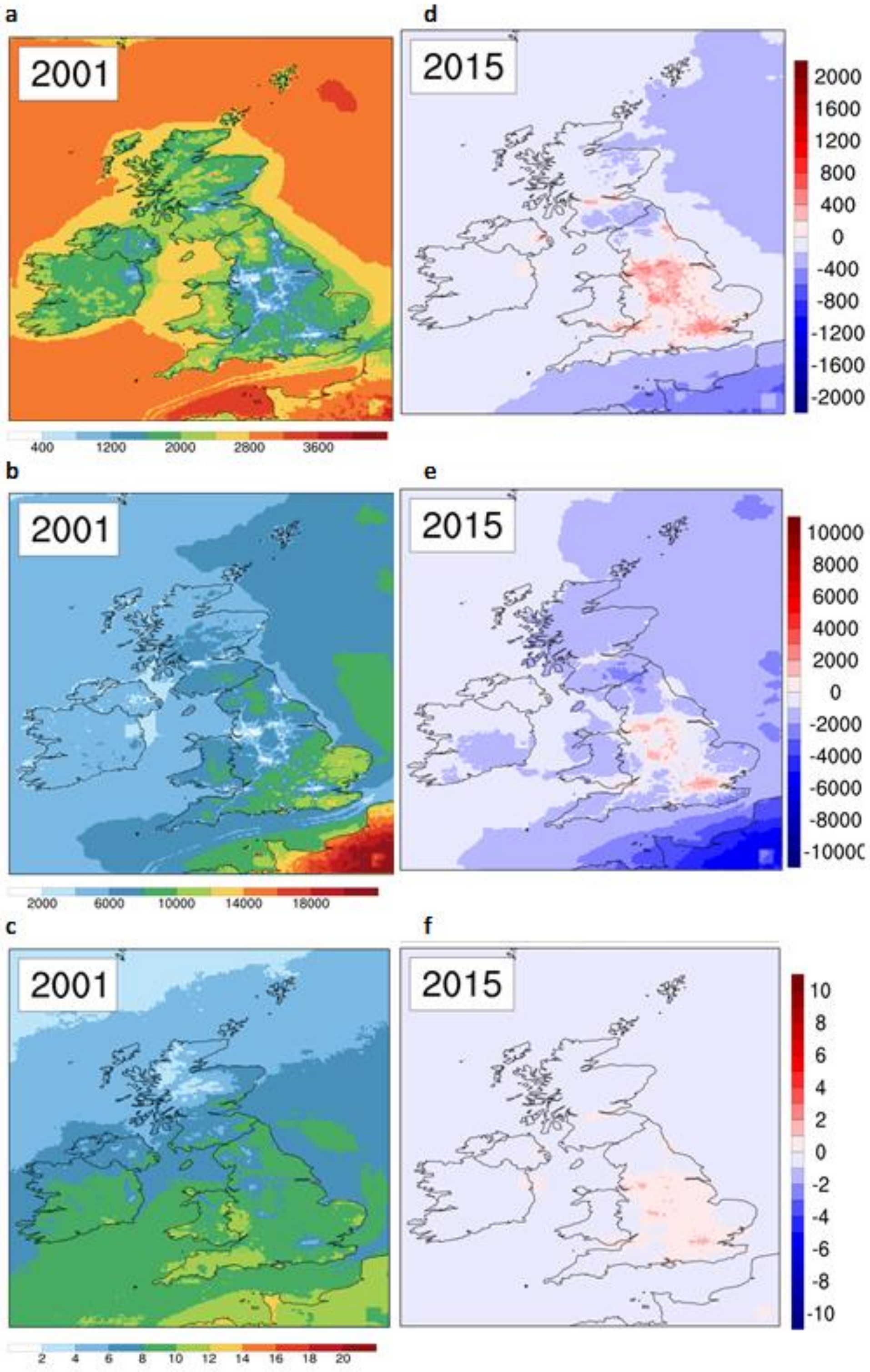

Figure 32: EMEP4UK-modelled changes in ozone impact metrics for 2015 compared with the value of the metric in 2001, removing the effect of meteorology. Row (a) & (c): SOMO35 for human health (ppb days); row (b) & (d): AOT40 for forests (ppb h); row (c) & (f): POD_1 for deciduous forest (mmol m^{-2} y^{-1}). For ozone, 1 ppb = 2 µg m^{-3}. The simulations use 2015 meteorology, 2015 Europe-external boundary conditions and 2011 shipping emissions in order to isolate the impact of land-based emissions changes in the UK and rest of Europe. Emissions data are described in Section 2.1.2. (EMEP version rv4.17; WRF version 3.7.1)

3.1.3 Trends in seasonal contributions to SOMO metrics at Harwell and Auchencorth

At Harwell, the majority (~90%) of SOMO35 accumulation occurred in spring and summer but with a significantly decreasing contribution from summer months (-1.2 % y^{-1}) between 1990 and 2013, and a significantly increasing contribution from spring months (+1.1 % y^{-1}) (Figure 33) (Malley et al., 2015). Contribution to SOMO35 from spring months was greater at Auchencorth than at Harwell.

For SOMO10, about one-third of the SOMO10 value derives from autumn and winter seasons and (at Harwell) there has been a small, but significant, decrease in contribution from summer (-0.4 % y^{-1}) and a significant increase in contribution from winter (+0.3 % y^{-1}).

Irrespective of whether a 70 µg m^{-3} (35 ppb) or a 20 µg m^{-3} (10 ppb) threshold is selected, the extent and annual timing of the human health impact of ozone in the UK as quantified by a SOMO metric is increasingly driven by more frequent, modest exceedances of the respective threshold outside of summer months, particularly in spring, because of the maximum in hemispheric baseline ozone over the UK in spring, and less by short-lived summer-time extreme episodic exceedances. When not including any threshold, as recommended by COMEAP, then short-term effects of ozone are also important in autumn and winter.

The trends in health metrics discussed above clearly have policy implications. For reducing exposures to ozone in excess of 100 or 120 µg m^{-3} (and also in excess of 70 µg m^{-3}), then controls at the European and national scales can be effective. However, if the mean or lower percentiles are important, then controls at the hemispheric scale are required, particularly under the current circumstances where decreasing urban NO is leading to increases in urban ozone to approach that of neighbouring rural levels.

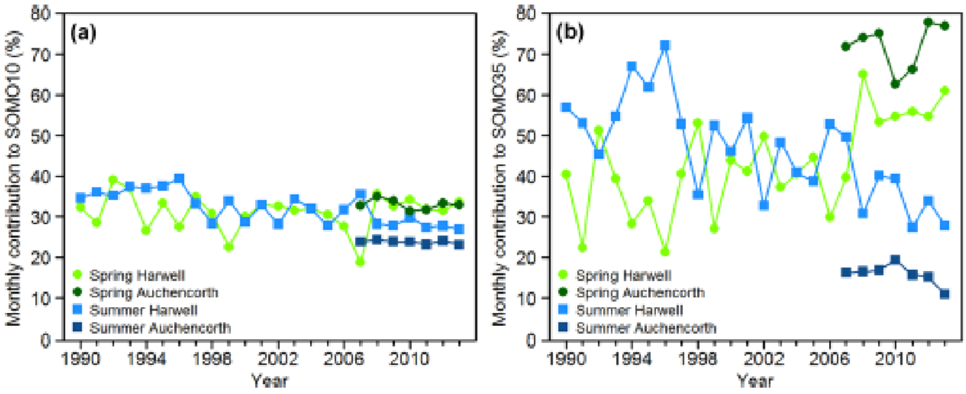

Figure 33: Relative annual contributions from spring (MAM) and summer (JJA) to (a) SOMO10 and (b) SOMO35 (Malley et al., 2015).

3.1.4 EMEP4UK-modelled trends in long-term health effects

The evidence for impacts on health associated with long-term exposure to ozone is inconclusive (Atkinson et al., 2016) and COMEAP do not currently recommend a concentration-response coefficient for quantifying long-term effects of ozone in the UK (COMEAP, 2015).

The Health Risks of Air Pollution in Europe (HRAPIE) project recommend quantification of respiratory mortality from long-term exposure to ozone using the mean of the daily maximum 8-hour mean ozone concentration >70 µg m^{-3} across the period April to September (WHO, 2013b). This metric is proportional to a SOMO35 metric, but for a 6-month period rather than the full year.

When using the HRAPIE quantification, Carnell et al. (2019) showed using EMEP4UK model simulations of historic ozone distributions across the UK (coupled with historic population distributions, but with a fixed meteorology to remove the impact of inter-annual meteorological variability) that UK-wide respiratory mortality attributable to long-term exposure to ozone increased by about 54% from 1970 to 1990 but by 2010 had decreased again such that in 2010 attributable mortality was 17% higher than in 1970. The decrease between 2000 and 2010 was 14%.

These studies illustrate the different trends that are derived when considering different versions of health-related metrics or different locations. Metrics with higher ozone cut-offs such as the EU objective have declined in value. In contrast, the SOMO35 metric has increased in urban areas (Section 3.1.2), but shows a small decrease at rural sites like Harwell (Section 3.1.3). The reason why the Carnell et al. (2019) study suggests a small decrease in health-related ozone burden between 2000 and 2010 compared with the increases implied by the model simulations shown in Figure 32d is that the former analysis uses daily ozone concentrations in Apr-Sep only whilst the latter includes daily concentrations across the full year. The analysis of Malley et al. (2015) indicates that increasing ozone concentrations in autumn and winter are an increasing contribution to full-year SOMO35 exposure.

3.2 Trends in vegetation impact metrics

3.2.1 Spatial and temporal trends in vegetation impact metrics for EU compliance reporting derived from the PCM model

The EU target value for the protection of vegetation from ozone is based on the AOT40 statistic; specifically that the accumulated hourly ozone concentration in excess of 80 µg m^{-3} (40 ppb) for the hours 08:00-20:00 Central European Time for May-July does not exceed 18000 µg m^{-3}.h per year, averaged over 5 years (Table

1). The threshold is the concentration below which plants can neutralise the effect of ozone.

The Pollution Climate Mapping (PCM) model is used for UK compliance reporting. The PCM maps in Figure 34 show that all areas in the UK met this objective, and also in 2018 specifically, which had higher ozone than in recent years. In 2018, this AOT40 metric ranged from <6000 μg m^{-3}.h across nearly all of Scotland and Northern Ireland, to more than 9000 μg m^{-3}.h over most of England and Wales, with clear decrements over large urban areas and major transport corridors, reaching 15000 μg m^{-3}.h in one very localised area in southern England. The average AOT40 metric over the five years 2014-2018 shows a clear NW to SE increase, with highest values in East Anglia, but no part of the UK had AOT40 exceeding 9000 μg m^{-3}.h (Figure 34).

The target value for vegetation has been met everywhere in the UK for the last 5 years (Table 4), and at least as far back as 2007 – source: UK annual air quality reports.

The EU long-term objective for the protection of vegetation is AOT40 <6000 μg m^{-3}.h each year. In 2018, only five zones and agglomerations met this long-term objective: North East Scotland, Central Scotland, Glasgow Urban Area, Belfast Metropolitan Urban Area and Preston Urban Area. However, Table 4 shows that most of the UK met this long-term objective for vegetation in the previous 4 years, illustrating again the existence of large inter-annual variability in ozone levels across the UK. In years prior to 2014, larger numbers of zones did not meet this long-term objective.

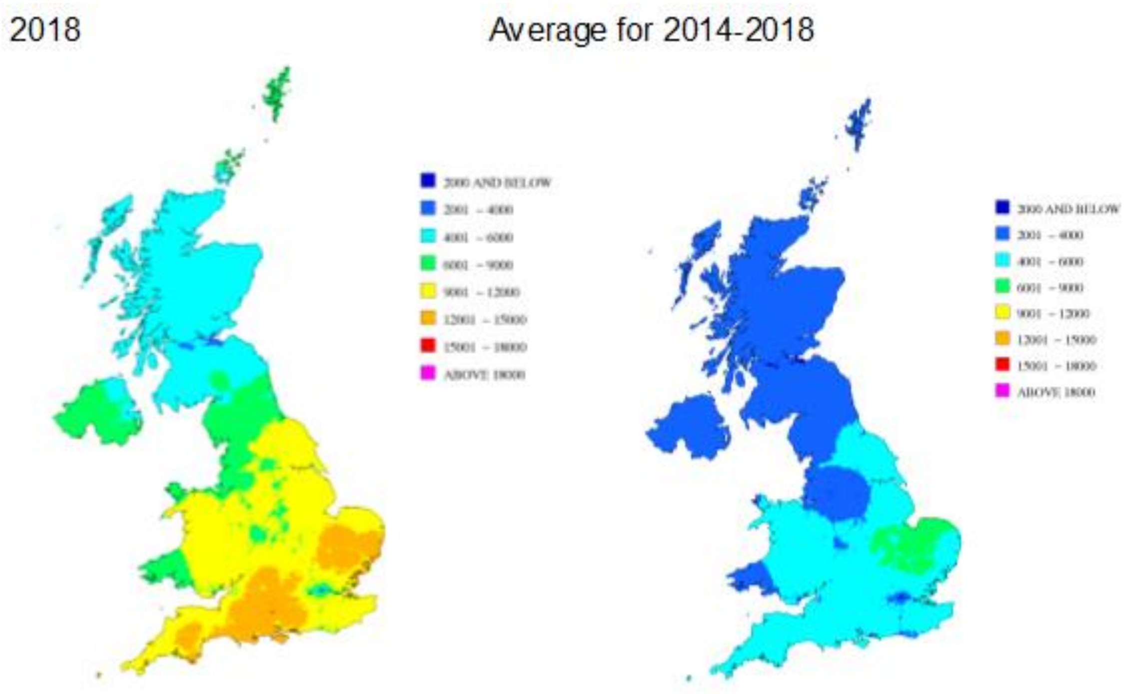

Figure 34: PCM model maps for the AOT40 metric for the protection of vegetation (units: µg m^{-3}.h). This metric is the accumulated hourly ozone concentration in excess of 80 µg m^{-3} (40 ppb) for the hours 08:00-20:00 Central European Time for the months of May to July. Left map is for 2018 and right map is the mean for 2014-18. From *Air Pollution in the UK 2018* (Defra, 2019).

3.2.2 Spatial and temporal trends in EMEP4UK-modelled AOT40 and POD$_1$ vegetation metrics

Figure 32e shows the change in EU-defined AOT40 across the UK between 2001 and 2015 as simulated using the EMEP4UK model for constant 2015 meteorology. The AOT40 metric has a more widespread spatial trend than the similar cut-off based SOMO35 metric for health (Figure 32d), with increases only over the heavily urbanised areas and decreases in rural and remote areas. Given that the bulk of vegetation is associated with the latter areas, it is anticipated that UK-wide impacts of ozone on vegetation, when quantified via AOT40, have decreased over this time period. The EMEP4UK and PCM model maps are consistent on small downward trends in AOT40. This is driven by the small decreases in highest ozone concentrations brought about by decline in intensity of photochemical episodes.

The extent of AOT40 increase in urban areas is smaller than for SOMO35 (Figure 32e vs. Figure 32d) because the general increase in ozone concentrations in urban areas is sufficient to exceed the cut-off for SOMO35 but less often the higher cut-off for AOT40.

More recently the phytotoxic ozone dose (POD_Y) above a threshold flux *Y* has been developed as a flux-based (rather than concentration-based) measure of ozone impact on vegetation to more accurately reflect the reality that only the ozone that enters the inside of the leaves actually does the damage. POD_Y is a species-specific, modelled, accumulated stomatal uptake over a fixed time period related to the species growing season. It is based on hourly variations in temperature and water vapour pressure deficit, photosynthetically-active radiation (PAR), soil water potential, ozone concentration and plant phenology, and is calculated from these variables using the DO_3SE model (Emberson et al., 2000).

The metric POD_1 (in mmol m^{-2} y^{-1}) is used for forest trees and represents the accumulated stomatal flux exceeding 1 nmol m^{-2} s^{-1}. It is linked closely to changes in daytime concentration only as plants only take up ozone during daytime stomatal opening. The EMEP4UK data do not show areas of significant decrease in this flux-based POD_1 metric between 2001 and 2015 (Figure 32f) and thus present the conclusion of no change in vegetation impact compared with the impression of a decrease derived from the AOT40 metric (Figure 32e). The EMEP4UK data also indicate there is widespread exceedances across the UK of the 4 mmol m^{-2} y^{-1} critical value for POD_1 for deciduous forest (even allowing for the caveat in the following paragraph).

It should be noted again that the 2001 baselines and the changes shown in Figure 32 are calculated using static meteorology (year 2015) and other fixed variables so as to isolate the changes associated with European anthropogenic terrestrial emissions. Consequently the absolute values in a given year would be different than shown because of differences in meteorology and other model conditions.

3.2.3 Trends in vegetation impact metrics from measurements

Malley et al. (2015) compared trends in AOT40 and POD_Y for crops and trees at Harwell for 1990-2013 (Y = 1 nmol m^{-2} s^{-1} for trees and 6 nmol m^{-2} s^{-1} for crops). The crop-relevant AOT40 value significantly decreased between 1990 and 2013, with a median decrease of -3.6 % y^{-1}, from a mean vaue of 6530 ppb.h (13060 µg m^{-3} hour) during 1990-1993 to a mean value of 2620 ppb.h (5240 µg m^{-3} hour) during 2010-2013 (Figure 35). (The critical value of AOT40 for crops is 3000 ppb.h (6000 µg m^{-3} hour).)

In contrast, for all of wheat and potato crops, and pine and beech trees, there was no significant change in POD_Y values between 1990 and 2013, and for all soil types investigated (Figure 36). For the trees, the POD_Y values at this location substantialy exceed the critical values of 4 and 8 mmol m^{-2} y^{-1} for beech and pine, respectively.

The POD_Y metric does not follow the decrease in regional photochemical ozone production captured in the crop AOT40 metric because POD_Y takes account of other factors that reduce plant stomatal conductance and hence accumulated ozone uptake, such as low soil water potential and changing plant phenology.

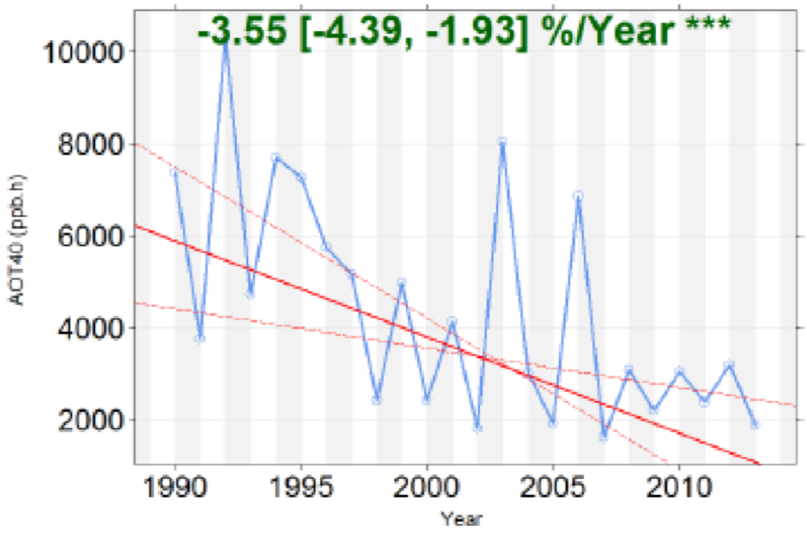

Figure 35: Crop-relevant AOT40 values (May to July) at Harwell for 1990 to 2013. The Theil-Sen estimate of median trend (shown in red) is -3.6 % y-1 (p = 0.001) (Malley et al., 2015).

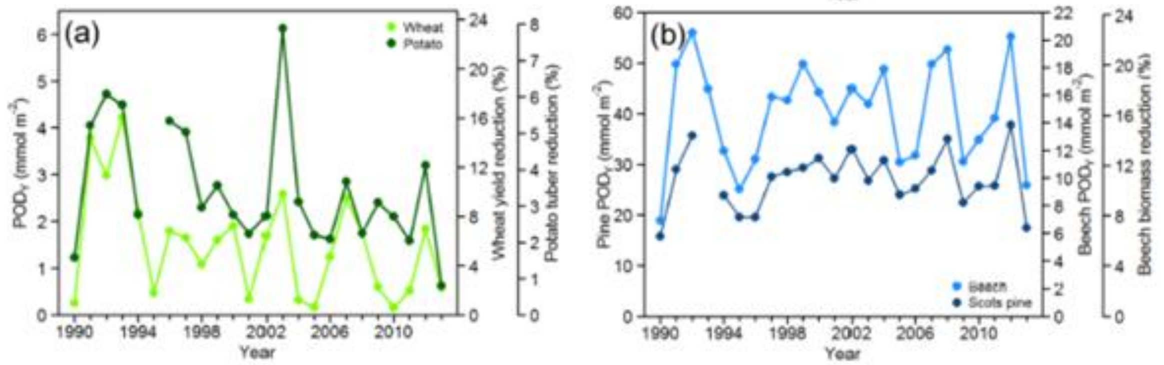

Figure 36: Impact of ozone characterised by the POD_Y metric (and associated response) for (a) wheat (grain yield reduction) and potato (tuber weight reduction, and (b) beech (biomass reduction) and Scots pine at Harwell for 1990-2013 (Malley et al., 2015).

As part of the TOAR global assessment based on the analysis of non-urban ozone network data Mills et al. (2018) concluded that all sites in the UK showed a downward trend in AOT40 over the period 1995 to 2014.

By contrast, they found significant upward trends in M12 for wheat, another vegetation metric which is the mean daytime ozone concentration over a 3-month growing season. This metric follows the behaviour of average rather than higher percentile daytime summer concentrations, the former of which has increased in many locations.

The analyses of measurements therefore demonstrate, as was the case for the EMEP4UK model (Section 3.2.2), that the conclusion of whether the impact of ozone on vegetation has decreased depends on the chosen metric. Scientific understanding is that POD_Y is the more biologically-relevant metric, in which case both measurements and model indicate that the impact of ozone on vegetation in the UK has changed little over the period 1990-2015.

The policies required to substantially reduce exposure of vegetation in the UK to damage from ozone, like those for human health where low threshold is assumed, are those that act to reduce hemispheric baseline ozone concentrations.

Chapter 4 – Controlling factors on UK ozone

4.1 Recent trends in ozone precursors emissions

The trends in ozone precursor emissions of NO_x and non-methane volatile organic compounds (NMVOCs) from anthropogenic sources over time are provided in emission inventories reported by individual countries. The National Atmospheric Emissions Inventory (NAEI) provides the UK's official inventory as annual mass emission rates of pollutants by source sector from 1970 up to the latest inventory year (currently 2018) and projected forward to 2030 (NAEI, 2020). The NAEI is updated annually to provide a consistent time-series in emissions over this period using the same methodologies. The emissions are derived from sector-specific emission factors and activity data or provided directly by industry plant operators and regulating bodies. As well as providing national emission totals, the NAEI provides spatially resolved emission maps for the UK for the latest inventory year at 1 km x 1 km resolution. These are crucial inputs to chemical transport models of ozone formation and removal.

Details on the methods used in the NAEI have been reported in previous AQEG reports (e.g. AQEG, 2020b) and in the UK's annual inventory report (NAEI, 2020) and are not repeated here.

The NAEI provides the official national totals in emissions for reporting under the revised EU Directive 2016/2284/EU on National Emissions Ceilings (NECD)[5] and the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (CLRTAP)[6]. Both the NECD and the Gothenburg Protocol to the UNECE CLRTAP set 2010 emissions ceilings for NMVOCs and NO_x. The Gothenburg Protocol was revised in May 2012 to set more stringent emission reduction obligations from 2020. The revised NECD sets commitments for 2020 (in line with Gothenburg Protocol obligations) and 2030. Emission reporting to the NECD and CLRTAP follows guidelines that aim to ensure inventories for all countries are produced on a consistent basis and therefore provide inventory data that are

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[5] See https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32016L2284&from=EN for Information on the new NEC Directive (2016/2284/EU).

[6] See http://www.ceip.at/ms/ceip_home1/ceip_home/reporting_instructions/reporting_programme/ for reporting requirements of estimating and reporting emissions data under the CLRTAP

comparable. They also provide the baseline inventory data for tracking progress towards emission reduction targets.

Figure 37 shows the time series in NO_x and NMVOC emissions from sources in the UK from 1990 to 2018 and projected to 2030. These charts show there have been significant reductions in emissions of both these ozone precursors since 1990, largely driven by regulation in vehicle emissions. Decreasing use of coal along with regulation and technological improvements in combustion plant have also contributed to reductions in NO_x emissions. Controls in fugitive emissions from extraction, refining and distribution of fossil fuels, industrial process emissions and regulations reducing the solvent content of paints and other products have also contributed to reductions in NMVOC emissions.

Similar trends are evident in inventories for other countries in Europe. Inventories reported by each country can be extracted from the European Environment Agency's (EEA) Air Pollutant Emissions Data Viewer[7]. The combined emission totals for NO_x and NMVOC for 33 EEA countries[8] from inventories reported in 2020 are shown in Figure 38, compared alongside the inventories for the UK indexed to emission levels in 1990.

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[7] https://www.eea.europa.eu/data-and-maps/dashboards/air-pollutant-emissions-data-viewer-3

[8] EEA33 countries include Austria, Belgium, Bulgaria, Croatia, Cyprus, Czechia, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Liechtenstein, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey, UK

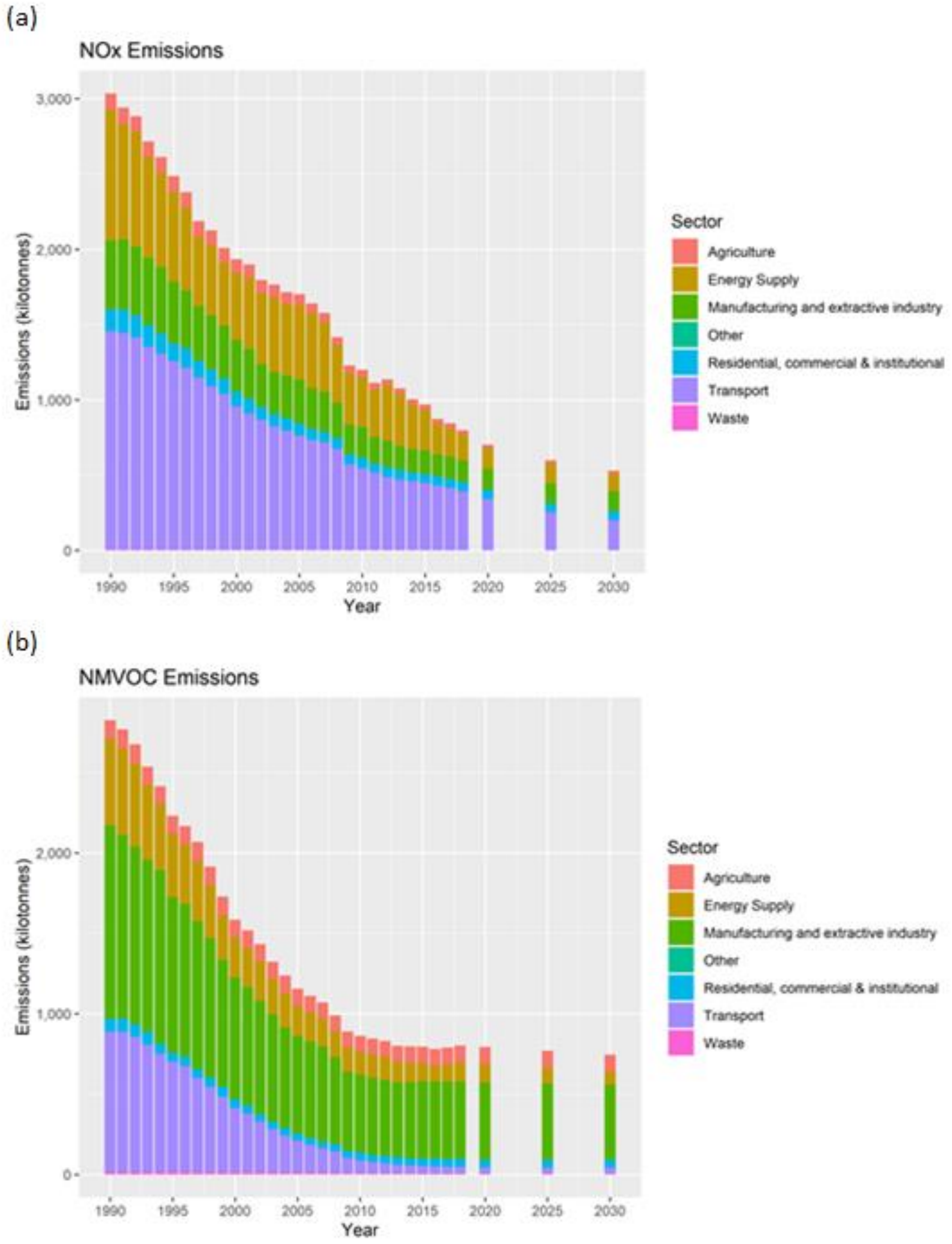

Figure 37: Emissions of (a) NO_x and (b) NMVOCs from sources in the UK from 1990-2018 and projected to 2030 according to the NAEI (2020).

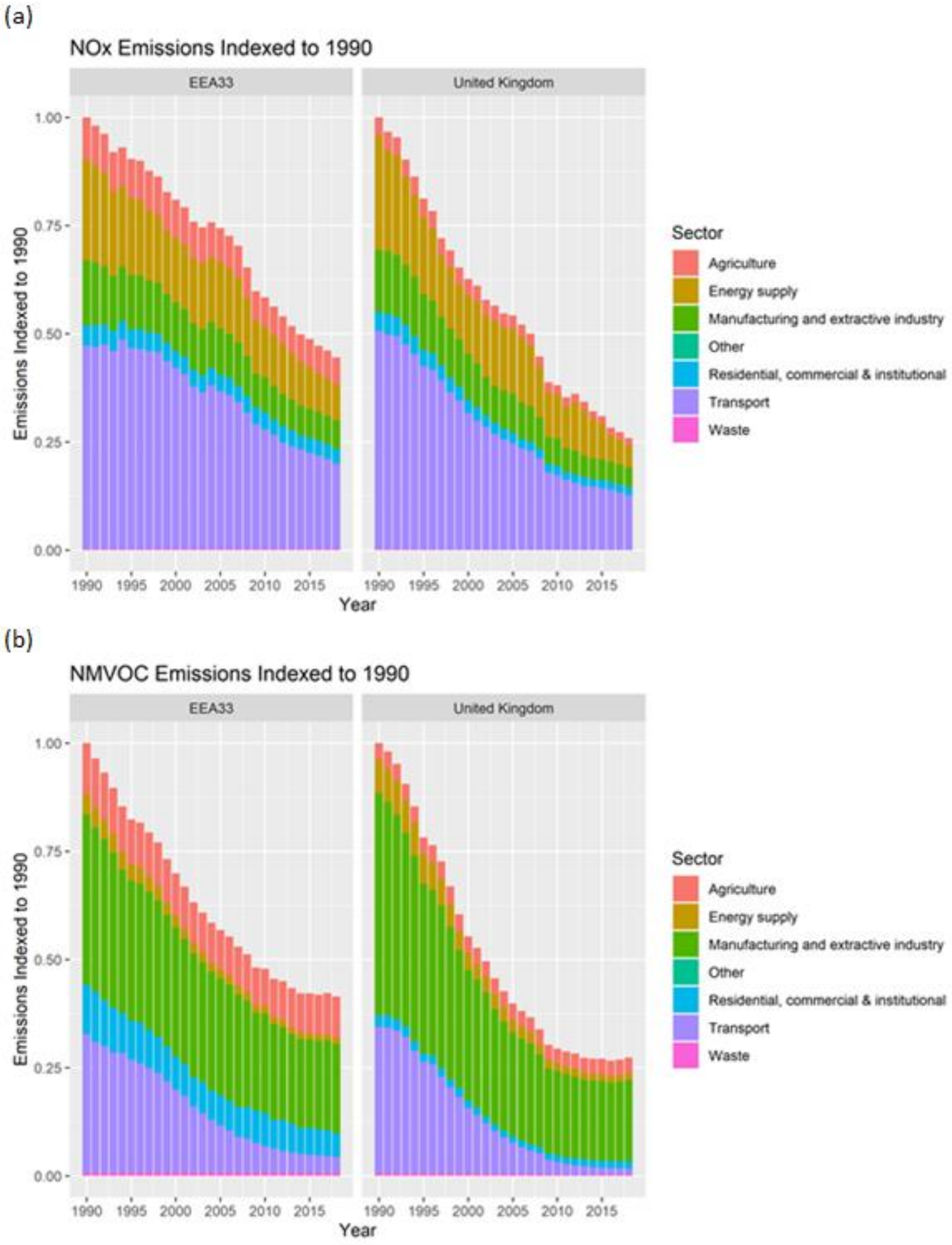

Figure 38: Trends in emissions of (a) NO_x and (b) NMVOC from sources in the EEA33 countries and the UK from 1990-2018 relative to emissions in 1990. Data for the UK taken from the NAEI (2020). Data for the EEA33 countries taken from EEA's Air Pollutant Emissions Data Viewer.

For NO_x, there are some differences in the contributions made by the various source sectors to emissions in different countries, but overall across all 33 countries the contributions are similar to those shown in the UK. For example, road transport contributed 31% to emissions in 2018 in the UK compared with 36% in EEA33. For the energy sector, the contributions to emissions in the UK and in EEA33 are 20% and 19% respectively. The rate of reduction in NO_x emissions from 1990 to 2018 has been somewhat slower for the EEA33 countries (55%) compared with the UK (73%). This appears to be largely due to the rate of reduction from transport emissions in the UK.

For NMVOCs, there are also differences in the contributions made by the various source sectors to emissions in different countries, but again, overall across all 33 countries the contributions are similar to those shown in the UK. Significant reductions in NMVOC emissions from road transport are evident in the EEA33 countries and the UK such that by 2018, the contributions of this sector are 8% and 4% respectively. The manufacturing and extractive industries (which includes fugitive and solvent emissions) are dominant sources across Europe and the UK (50% and 69% respectively in 2018), but agriculture and residential and commercial combustion sources make larger contributions in the EEA33 than in the UK (36% and 19% respectively). Again, the rate of reduction in NMVOC emissions from 1990 to 2018 has been somewhat slower for the EEA33 countries (59%) compared with the UK (73%).

The long-term trends in Figure 38 show that emissions of NO_x are still on a downward trajectory, but emissions of NMVOCs are tending to level off. For the UK, this pattern is predicted to continue to 2030.

From the point of view of the role of these precursors in ozone formation, it is worth considering how the ratio of NO_x to NMVOC emissions has been changing over the years. For the UK, total NO_x emissions have always exceeded NMVOC emissions by a modest amount, with the ratio of NO_x/NMVOC emissions increasing from 1.1 in 1990 to around 1.5 in the mid-2000s; but it has since declined to 1.1 again in 2018 as further reductions in NMVOC emissions have stalled. The current NAEI predictions are that the ratio will decrease to 0.75 by 2030 as further reductions in NMVOC emissions are expected to be limited.

For the EEA33 countries, the NO_x/NMVOC emission ratios are somewhat lower than the UK, but follow a similar pattern in that the ratios increased from 0.9 in 1990 to 1.2 in the mid-2000s, declining to 1.0 in 2018, again due to reductions in NMVOC emissions having stalled.

These trends, which are based on national inventories, hide local and regional differences in ratios of NO_x to NMVOC emissions. From the NAEI, it has been possible to estimate trends in road transport emissions of NO_x and NMVOCs in just urban areas. The changes in the ratios of NO_x/NMVOC emissions for the road transport sector have been much more significant ranging from 0.6 in 1990 to 2.7 in 2010 and 4.4 in 2018 for urban areas as a whole. This has been due to the limited success in reducing NO_x emissions from road transport in the 2000s, but current NAEI predictions are that this ratio will start to turn around and reduce to 1.7 by 2030. Such analysis, considering emission trends only in urban areas of the UK, is not so straightforward for other source sectors. However, given the likely prevalence of solvent emissions of NMVOCs from small industrial processes and household products in urban areas, and the lack of any significant reductions in these solvent emissions in recent years, it is likely that the ratio in overall urban NO_x/NMVOC emission has not increased by as much as the NO_x/NMVOC ratio for road transport emissions alone. If these solvent NMVOC emissions continue to show little change then the overall urban NO_x/NMVOC ratios in emissions will start to decrease more significantly in future years.

4.1.1 Precursor speciation

To understand the full impact of precursor emission on ozone formation, it is also necessary to consider the speciation of the NMVOC and NO_x emissions into their chemical component parts. Inventories tend to just deliver estimates of total NMVOC and NO_x mass emissions as defined under international reporting guidelines. These are predominantly used for tracking progress towards emission reduction targets. Given the different reactivities of individual NMVOCs, speciation is essential for modelling atmospheric ozone. The speciation of NO_x into NO and NO_2 is also important to understand as the direct emissions of primary NO_2, mainly from road vehicle exhausts, are a source of oxidant and hence ozone in urban areas.

The NAEI provides source-specific chemical speciation factors to enable the reported NMVOC and NO_x emissions to be divided into their component parts. The chemical speciation of the NMVOC inventory was discussed in some detail in the AQEG report on NMVOCs in the UK (AQEG, 2020b). The NAEI's NMVOC inventory is broken down into 664 chemical species or groups of species using profiles for each detailed emission source sector. Much of the data used to develop the speciation profiles were gathered during a short period in the late 1990s and early 2000s, and since more recent data are not available, it is still assumed that the species emitted by a particular source are the same in all years. This may not be the case for certain chemical processes and use of solvents and consumer products. In addition, as the contribution of different sources to overall NMVOC emissions has changed over the years, then a change in the contribution of different types of NMVOCs is to be expected. The AQEG (2020b) report particularly emphasised the increased dominance of alcohols from sectors such as food and drink production and domestic use of solvents. The implications of this to ozone formation is discussed in the next section.

Most NO_x occurring from combustion sources is emitted as NO, but an appreciable amount of NO_x from diesel vehicles is emitted as NO_2 (Carslaw et al., 2016), particularly those vehicle equipped with catalyst-based exhaust after treatment devices such as diesel particulate filters, oxidation catalysts and selective catalytic reduction (SCR). The proportion of NO_x emitted as NO_2 is highly variable and dependent on type and design of the technology but levels as high as 50% (by volume) have been reported.[9] Using information on the current and projected fleet composition, NO_x emissions and primary NO_2 factors (f-NO_2) for the different vehicle categories, the NAEI has developed weighted factors representing the average f-NO_2 factors for traffic on urban roads in the UK in years out to 2035 shown in Table 5[10]. Based on current estimates of f-NO_2 factors for individual vehicle types, the trend overall shows a small reduction in the fleet average value over time, although NO_x emissions themselves, and hence direct NO_2 emissions will be decreasing more significantly as lower NO_x emitting vehicles enter the fleet.

Table 5: Fraction of NO_x emitted as primary NO_2 from urban UK road transport weighted by the relative amounts of NO_x emissions occurring from the mix of vehicle types on urban roads.

	2015	2020	2025	2030	2035
f-NO_2	0.268	0.277	0.258	0.225	0.225

4.2 Implications of recent trends in VOC emissions on UK ozone generation

Anticipated future reductions in NO_x in the UK will require that VOCs are also reduced in concert if optimal ozone controls are to be achieved, but individual VOC species vary in their capacity to generate ozone. This is encapsulated in their Photochemical Ozone Creation Potential (POCP) which provides a relative weighting for ozone formation from a given VOC as it passes along a specified atmospheric trajectory and chemical field (Derwent and Jenkin, 1991; Derwent et al., 1998). In general terms alkenes, aromatics and aldehydes have higher POCPs than alkanes, alkynes, alcohols and chlorinated compounds.

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[9] Values recommended for a Euro 3 diesel car with a diesel particulate filter in the EMEP/EEA Emissions Inventory Guidebook 2019, https://www.eea.europa.eu/publications/emep-eea-guidebook-2019/part-b-sectoral-guidance-chapters/1-energy/1-a-combustion/1-a-3-b-i/view

[10] Further data on f-NO_2 factors are provided each year on the NAEI website at https://naei.beis.gov.uk/data/ef-transport

UK emissions of non-methane VOCs have reduced substantially over the last 30 years (AQEG, 2020b), as a consequence of multiple source-sector regulatory interventions including Euro vehicle standards, the Solvents Directive and the Paints Directive. Ambient measurements and the national atmospheric emissions inventory have shown particularly steep reductions in emissions of hydrocarbons associated with road transport and combustion, for example short-chain alkenes and mono-aromatics. The shift towards relatively greater contribution from solvent-related emissions means that short-chain aldehydes and alcohols, particularly ethanol and methanol, are now the most abundant VOCs. Longer-chain VOCs from diesel vehicles are also a component of urban VOC emissions.

AQEG (2020b) showed that the total POCP of the changing mixture of UK VOC emissions reduced slightly more over the period 1990-2017 than the reduction in total mass of VOC emissions. The former reduced by about 75% (as quantified by the POCPs of the top 40 emitted species each year), whilst total mass emissions reductions were about 72%, i.e. the average POCP of the emitted VOC mixture over this period declined by around 4%. The change in average POCP is the net effect of contrasting underlying trends in individual VOC species. The largest emissions decline has been in ethane (a low POCP compound) but there has been increases in emissions of ethanol (an intermediate reactivity species). However, declines in a range of different alkenes and aromatic compounds have more than offset the growth in ethanol. In terms of contributions from different functional groups, alcohols are now the largest single POCP-contributing class of VOC.

More comprehensive POCP weightings of the full NAEI speciation inventory have been carried out by Derwent et al. (2007). This study developed POCPs for each of the ~250 emission source categories included in the NAEI using an explicit chemical mechanism and considered the consequences for VOC emission control strategies based on the reactivities of the VOCs emitted from the different sources. It would be beneficial to repeat this type of analysis with more recent versions of the NAEI as well as using re-estimated POCP values for some VOC species based on an optimised approach developed in a more recent study by Jenkin et al. (2017).

Since VOC emissions are now increasingly de-coupled from energy and gasoline processes, transformation in the UK towards Net Zero Carbon in 2050 will not necessarily lead to further reductions in VOCs. Further reductions in VOC emissions will therefore need further VOC-specific reduction strategies that target solvent-based sources such as coatings, adhesives, and consumer products (Lewis, 2018).

The impact of hemispheric-wide trends in methane emissions on ozone is discussed in Section 5.1.

4.3 Trend away from NO_x saturation in ozone generation

Jin et al. (2017) used the Geos-Chem atmospheric chemistry transport model to link the tropospheric column formaldehyde (HCHO) to NO_2 ratio (FNR), derived from the Ozone Monitoring Instrument (OMI) on the Aura satellite, to the ground-level HCHO/NO_2 ratio, as an indicator for NO_x-limited versus NO_x-saturated ozone-formation regimes. Examining historic satellite data, they report that ozone production over much of the UK in 2015 was NO_x-limited rather than being NO_x-saturated as it was over central and eastern England in 2005 (Figure 39). They also report an increasingly longer period of NO_x-limited ozone chemistry in the warm season.

The decreasing areas of NO_x saturation reflects the NO_x emissions reductions over the period and implies that further NO_x emissions reductions in these areas will reduce ozone production more now than a decade ago. For the UK as a whole, the implication of this study is that ozone generation is generally now more sensitive to NO_x than to VOC.

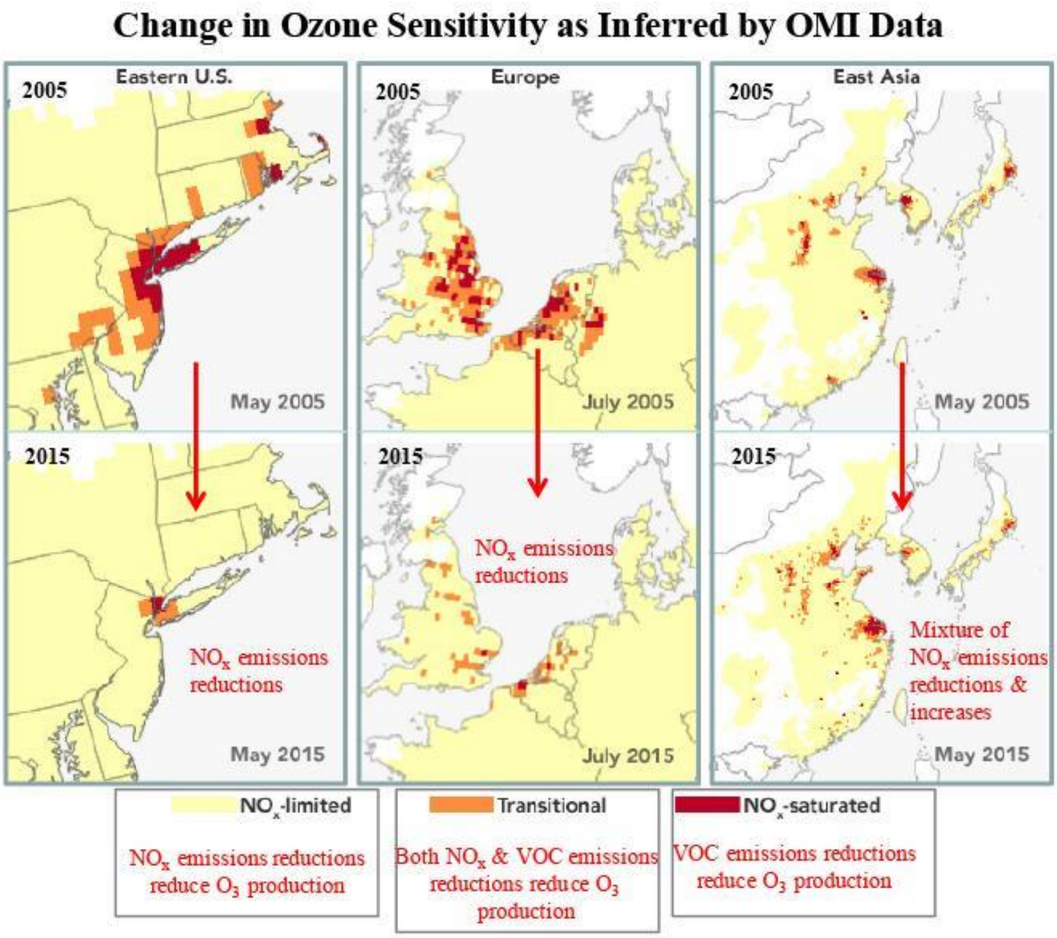

Figure 39: Ozone production regimes derived from OMI satellite column HCHO/NO_2 ratios for three world regions in 2005 and in 2015. In the US and Europe, major decreases in NO_x emissions in high NO_x emission areas have caused this ratio to increase, indicating that ozone production is more sensitive now to further reductions in NO_x emissions than it was a decade ago. The changes in the ratios over East Asia indicate a patchwork of emission changes and concomitant changes in ozone production sensitivities. Image from https://aura.gsfc.nasa.gov/science/feature-20171228b.html, derived from methodology and figures in Jin et al. (2017).

4.4 Current status of knowledge on ozone deposition to vegetation

Ozone is highly reactive and readily deposited to terrestrial surfaces, the process being termed dry deposition to distinguish it from removal by precipitation which is rather inefficient for ozone due to its insolubility. The rate of removal at the surface relative to its downward supply to the surface by turbulent mixing is the cause of much of the short-term variability in mixing ratios in surface air (Coyle et al., 2002). Air chemistry is also important in contributing to short term variability, removing ozone where nitric oxide is present and is an important contributor to depletion of ozone from urban air as described in Section 2.

Measurements of ozone deposition have been made since the early 1970s, primarily using flux/gradient micrometeorological methods (e.g. Galbally, 1971). Rates of dry deposition are commonly expressed as a deposition velocity (v_d) defined as follows.

Deposition velocity (v_d) = flux ($\mu g\ m^{-2}\ s^{-1}$) / concentration at reference height ($\mu g\ m^{-3}$)

The measurements by Galbally (1971) showed deposition velocities of approximately 10 mm s^{-1}, but did not reveal the processes at the surface controlling rates of deposition. Interestingly, his paper stated that the chemistry of ozone destruction at terrestrial surfaces was unknown; and some 50 years later the statement remains largely correct despite several hundred papers on the subject and many thousands of flux measurements over a wide range of vegetation, soil, snow and water surfaces (Clifton et al., 2020).

Reported deposition velocities for terrestrial surfaces lie in the range 1 mm s^{-1} to 20 mm s^{-1}, with typical values in the daytime of 10 mm s^{-1} and nocturnal values of 3 mm s^{-1}. These values for deposition velocity limit boundary layer ozone lifetime to about a day and are an indicator of the importance of removal at the surface in regulating ozone concentrations in surface air.

Late in the day, terrestrial surfaces gradually cool due as outgoing long-wave radiation fluxes dominate the surface energy budget. The coolest air close to the surface rapidly becomes ozone depleted and gradually deepens with time through the night in calm conditions. The resulting diurnal cycle of ozone has been used to estimate ozone dry deposition rates (Garland and Derwent, 1979).

Large numbers of ozone dry deposition fluxes have been measured, as reviewed by Fowler et al. (2009) and more recently by Clifton et al. (2020), although the number of UK observations is more limited (see Section 6.5). These reviews show the state of understanding of the deposition processes and summarise the variability in deposition rates for a wide range of terrestrial surfaces.

The deposition process

Ozone in the boundary layer is transported to within a few hundred µm of the surface by turbulence; from there to the surface turbulence is suppressed by the viscosity of the air and molecular diffusion transports ozone to the sites of deposition. The variability of sites for reaction and their spatial complexity introduces important uncertainties in understanding at this point. The large number of primary measured fluxes only report the overall flux to the surface. In the case of vegetation, the sites of reaction at the surface include the external structure of vegetation comprising a wide array of organic compounds as well as surface water films and contaminating inorganic compounds from soil. The stomatal apertures of vegetation present additional sites for uptake/reaction and, importantly, access to the intercellular fluid and cell contents.

Measurements of ozone fluxes to vegetation in laboratory conditions show uptake by stomata to exhibit negligible internal resistance, so that for a given stomatal resistance (or conductance), ozone fluxes through stomata may be readily quantified. Field measurements over a range of crops show diurnal cycles of ozone deposition corresponding to the opening and closing of stomata, with daytime maximum deposition velocities in the range 10 to 20 mm s^{-1} and minimum values at night in the range 3 to 5 mm s^{-1} (Figure 40).

Deposition rates at night with closed stomata reveal rates of ozone deposition to the external surface of vegetation (non-stomatal uptake) with deposition velocities in the range 1 to 3 mm s^{-1}. Non-stomatal deposition of ozone represents a substantial fraction (between 30% and 60%) of the annual deposition as the process is continuous and at some locations it is the dominant component of annual deposition flux (Coyle, 2005). The processes regulating non-stomatal ozone deposition are not known in detail, but surface temperature and the presence of water on foliage are important. Rates of ozone non-stomatal deposition increase with temperature and also with surface wetness (Coyle, 2005; Clifton et al., 2020).

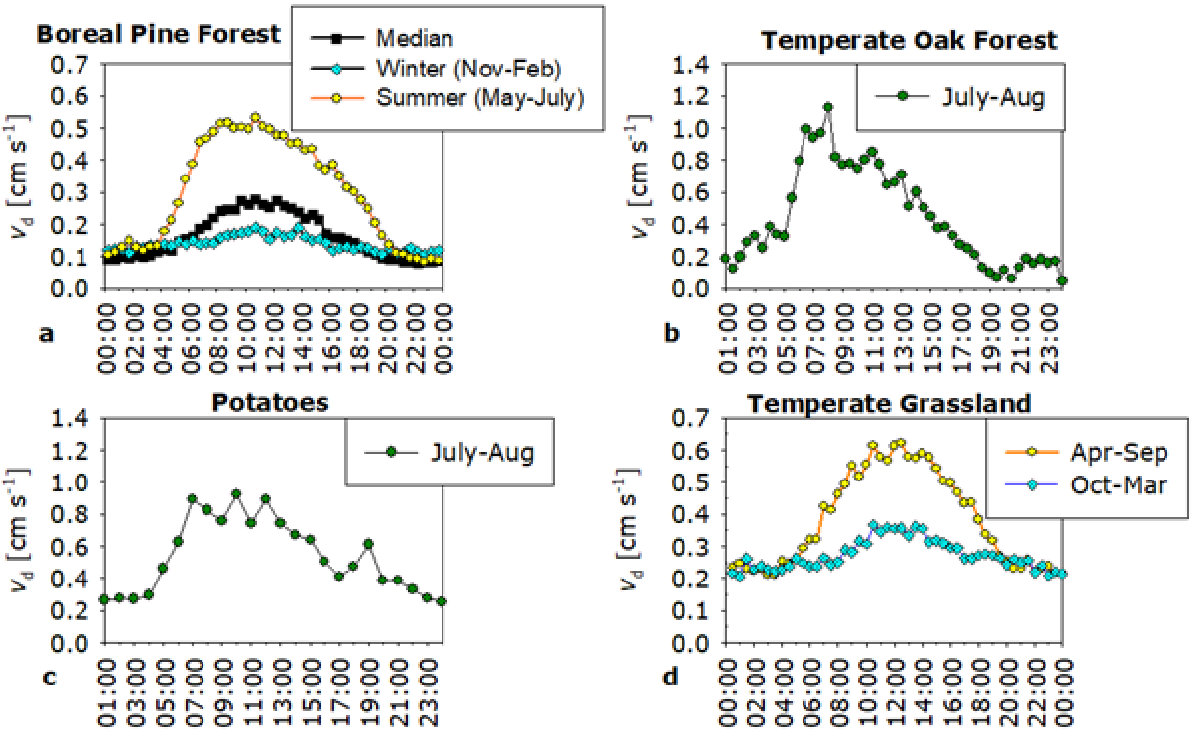

Figure 40: Median diurnal cycles in deposition velocity for (a) boreal forest in Finland, (b) temperate oak forest in southern England, (c) a potato crop in southern Scotland and (d) temperate grassland in southern Scotland (Fowler et al., 2009).

The sensitivity of dry deposition to climate change

The stomatal sink for ozone in vegetation is sensitive to all the environmental factors which influence stomatal conductance, which especially includes water vapour pressure deficit and soil water status (Clifton et al., 2020). As crop canopies become water limited, stomatal conductance declines, reducing ozone dry deposition. Summer conditions and heat waves are the conditions leading to most of the extreme ozone episodes in the UK and are the conditions in which the dry deposition sink may be substantially reduced. The heat wave in the summer of 2003 in Europe was notable for both temperature and ozone episodes. Vieno et al. (2010) show that reduced dry deposition contributed to the elevated ozone concentrations observed. This link between vegetation water limitation and reduced dry deposition has been reported as a contributing factor to the lack of significant downward trend over recent years in high percentile concentrations of ozone over Europe, including the UK (Section 2.3.2) (Lin et al., 2020).

An increased frequency of summer droughts and elevated temperatures as the UK climate gradually changes is very likely to be associated with reduced dry deposition of ozone during these conditions and hence to higher surface ozone concentrations than would otherwise have been the case. The degree to which modellers are able to simulate the removal of ozone at the surface by dry deposition in these conditions would be improved by establishing long-term ozone flux measurements in the UK (see Section 6.5).

4.5 Source attribution of surface ozone in Europe and the UK

4.5.1 Origins of surface ozone in Europe

Figure 41 shows the attribution of annual-mean surface ozone (in 2010) in the European HTAP Tier 1 region derived from tagging different sources in a global chemical transport model (CAM4-Chem) (Butler et al., 2020). Attributions are apportioned to anthropogenic emissions of NO_x and VOC in other Tier 1 regions and from shipping (the 'ocean' source), biogenic and biomass burning emissions, methane, lightning NO_x and downward transport of ozone from the stratosphere. Figure 42 shows monthly ozone attribution for the HTAP 2 receptor region of 'north west Europe' (UK, Scandinavia, and continental Europe north of ~47° N and west of ~15° E).

Anthropogenic terrestrial NO_x emissions in Europe are responsible for ~30% of the ozone in Europe (Figure 41). However, whilst European NO_x emissions are responsible for more ozone than is attributed to anthropogenic NO_x emissions in any other region, in total external anthropogenic NO_x emissions contribute more than the European sources, and are dominated by the NO_x emissions from shipping. Light ning NO_x contributes about 6%. The authors note that the coarse resolution of their model may exaggerate the effects of ship NO_x on ozone production due to rapid dilution of the emissions and exaggerate the transport of NO_x and ozone near coastlines due to unrealistically high diffusion between adjacent land and ocean grid cells.

Methane and BVOC emissions are the dominant sources of reactive carbon contributing to European ozone (~35% and ~25%, respectively). Anthropogenic emissions of NMVOC contribute to only about a quarter of European ozone, of which the anthropogenic NMVOC emissions from the Europe region contribute about a third.

Biomass burning is a negligible source of precursor emissions to surface ozone in Europe.

There is strong seasonality in some of the attributions. For example, whilst stratospheric ozone contributes ~8% as an annual mean (Figure 41), this occurs almost exclusively in the spring (Figure 42) contributing up to 20% of surface ozone in March. The springtime rise in ozone is also due to an increased contribution from transported ozone arising from precursor emissions outside the north-west Europe domain, shipping included.

The increased ozone in later summer months is related to increased contribution of local photochemical production from the combination of locally emitted anthropogenic NO_x and biogenic VOC (Figure 42). Biogenic emissions of NO_x (from soils) also contribute to this summertime maximum in the local photochemical ozone production. The contribution of methane to surface ozone is also slightly higher in summer. This is consistent with local photochemical ozone production from enhanced local methane oxidation.

These model simulations are for one model and averaged across a domain much larger than the UK. As there will be spatial variations in source attribution it cannot be directly assumed that these model results apply exactly to the attribution of ozone in the UK. There will also be variability in attribution when considering shorter duration 'episodic' periods of high ozone. Nevertheless these findings emphasise the important influences of methane, shipping and long-range transport (and in early spring, also of stratospheric ozone intrusions) on surface ozone in north-west Europe. The significance of intercontinental transport on UK ozone was highlighted in AQEG's previous report on ozone (AQEG, 2009).

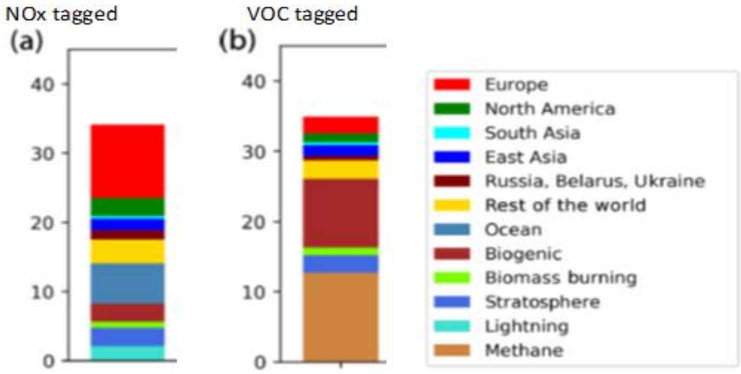

Figure 41: Source–receptor relationships for annual mean surface ozone (ppb) in the Europe HTAP Tier 1 region. The attribution relates the annual mean surface ozone modelled in each region to the emitted precursors of (a) NOx and (b) reactive carbon, from all HTAP Tier 1 regions and to other sources. Adapted from Butler et al. (2020).

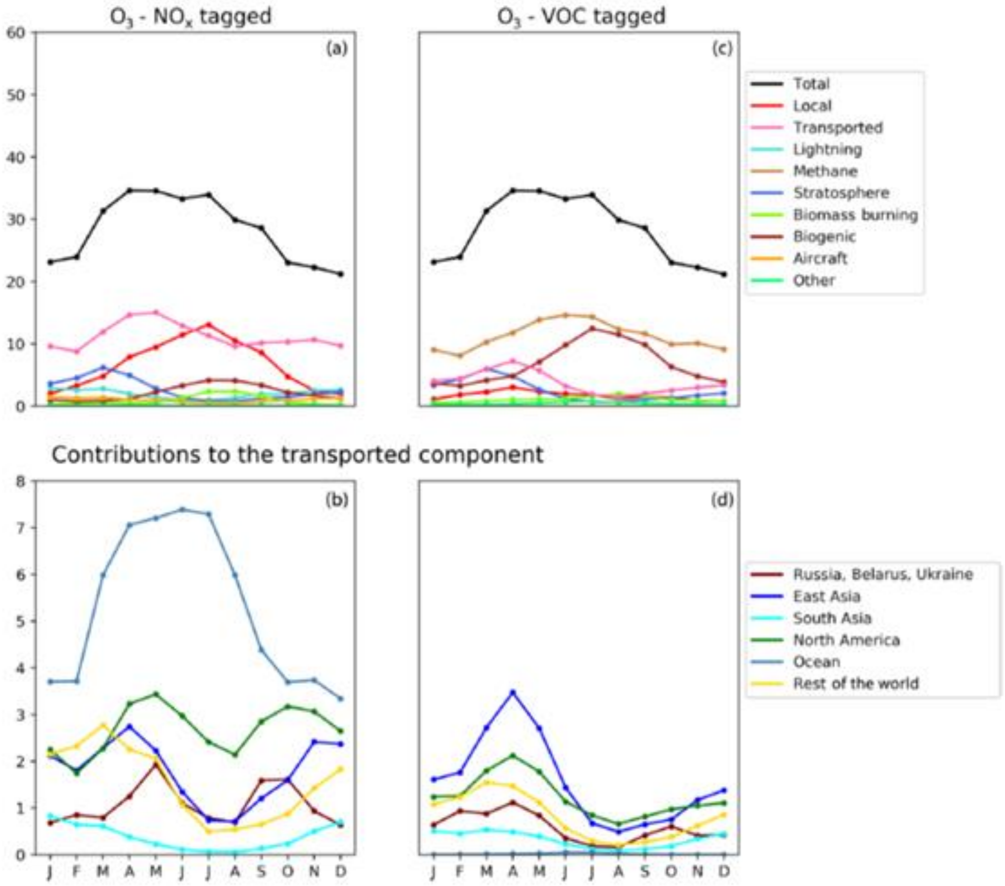

Figure 42: Seasonal cycle of surface ozone (ppb) in the HTAP Tier 2 receptor region 'North-west Europe'. NO_x tagging is shown in panels (a) and (b), and reactive carbon tagging is shown in panels (c) and (d). Panels (a) and (c) show the total monthly mean ozone (black line) as well as the local anthropogenic component, the long-range transported anthropogenic component, and the natural components. Panels (b) and (d) show the individual Tier 1 source regions responsible for the long-range transported component of ozone. From Butler et al. (2020).

4.5.2 Transboundary contributions to UK surface ozone

Which countries are the main contributors to photochemically generated ozone in the UK? Here the term 'photochemically generated ozone' is taken to mean the ozone formed from regional emissions of NO_x and VOC rather than the 'hemispheric baseline' concentrations. The former contribute to the elevated summer episode ozone concentrations above the baseline and operate largely on a regional scale. The country contributions to ozone in Europe, as well as to many other pollutants, are addressed by the EMEP 'source-receptor matrices' published annually by the Meteorological Synthesising Centre-West (https://emep.int/publ/reports/2019/EMEP_Status_Report_1_2019.pdf).

These matrices display the contribution of each emitting country in the EMEP domain to each receptor country. In the case of ozone, these matrices tabulate the response of SOMO35 in a receptor country (averaged over the whole country) to a 15% reduction in each of VOCs and NOx in each of the emitting countries in the EMEP domain. Figure 43 shows the effects on UK SOMO35 of the 15% reduction in VOCs for 2017 – the effects of NO_x reductions are much smaller.

The problem of which countries contribute most to UK ozone was addressed slightly differently by Stedman and Williams (1992). Using a simple Lagrangian trajectory model incorporating a very simple chemical scheme (Derwent and Hov, 1980), Stedman and Williams modelled daily maximum hourly ozone concentrations at four UK sites from 1 May to 31 August 1989. The simplicity of the model allowed concentrations arising from different countries to be calculated. The percentage contributions from neighbouring countries to the four UK sites were averaged and are also shown in Figure 43.

Figure 43 shows that ~55% of UK surface ozone was derived from precursor emissions in the UK and ~45% from emissions outside the UK. The calculations in the figure cover the whole year (EMEP data) and the whole of the summer period (Stedman & Williams data). An analysis focused only on the episodes of highest ozone concentration would reveal greater contribution from precursor emissions outside the UK.

Given the different approaches used, and time periods separated by almost 30 years, the agreement is surprisingly good. The reason is not that the earlier simple model of Stedman and Williams was particularly good, but the agreement between the two approaches is chiefly due to the fact that if an air mass trajectory picks up the necessary precursor emissions en route to UK locations then ozone will be formed given sufficient NO_x. Similar relative country contributions to secondary inorganic aerosol UK PM concentrations are also likely for the same reason.

The spatial and temporal averaging in the two models overemphasises the UK contribution in shorter high ozone episodes that tend to occur on winds from the easterly sector. During these periods the important countries will likely still be those highlighted in Figure 43 but with increased proportional contributions.

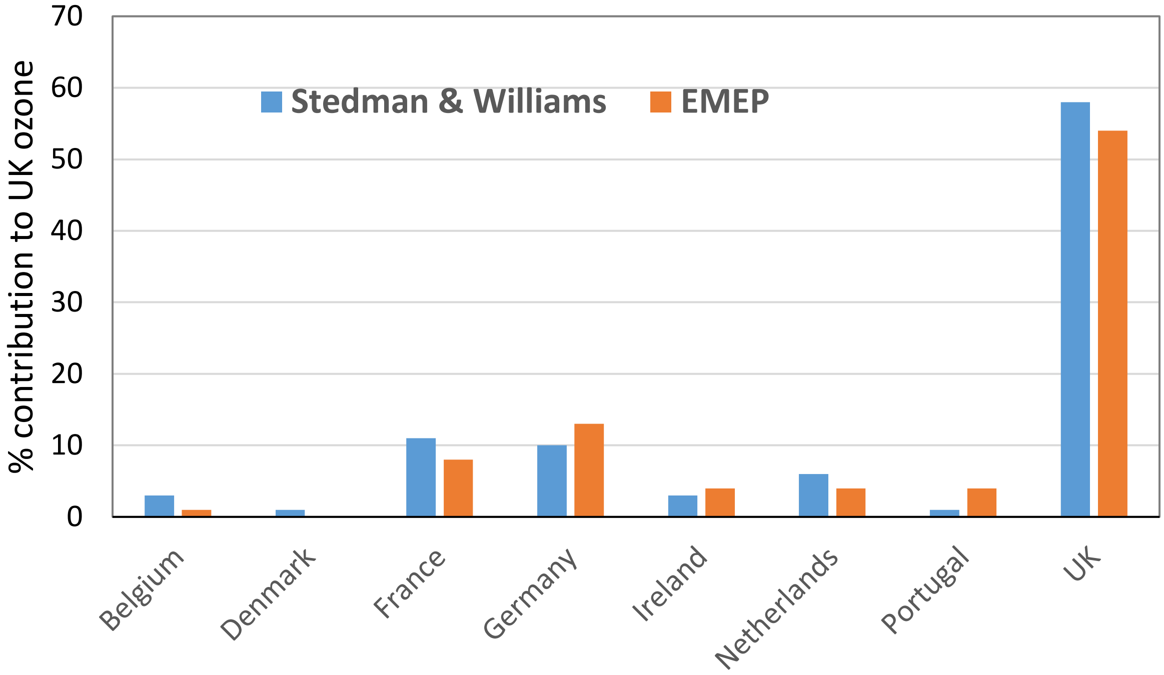

Figure 43: Modelled estimates of the % contributions to surface photochemical ozone in the UK from ozone precursor emissions in the UK and neighbouring countries. The EMEP data are for UK annual SOMO35 ozone in 2017 and derive from simulations with 15% reductions in VOC emissions in each country. The Stedman and Williams data are the contributions from each country derived from the average at four locations in the UK (Lullington Heath, Yarner Wood, High Muffles and Lough Navar) for daily maximum hourly ozone concentration in summer 1989.

Another approach to understanding the transboundary contributions to ozone in the UK is to use a tagging approach in which the nitrogen oxides (NO and NO_2) emissions at selected source regions are tagged and tracked through the chemistry enabling the direct attribution of ozone concentrations in receptor regions to specific sources (Butler et al., 2018). This was done in the Weather Research and Forecasting model coupled with chemistry (WRF Chem) for source regions across a European domain and for 12 receptor regions in the UK (Romero Alvarez, 2019). The model was run for May to August 2015, which included an episode of high ozone concentrations in the first two days of July when winds were from the east.

Figure 44 shows the contributions to the mean surface ozone mixing ratios in July 2015 and illustrates that the predominant source of ozone to the UK is the tropospheric hemispheric baseline (mean for the 12 regions of 73%). Of the anthropogenic emissions within the model domain those from the UK contributed an average of 47%, 10% was from shipping within the North Sea and English Channel and 44% was from the rest of the model domain, predominantly continental Europe. Of that 44%, on average France contributed 15%, Germany 6% and the Benelux countries 6%. These percentages are all remarkably similar to those from the other two studies shown in Figure 43, given the different methods used and periods examined.

Figure 44 also illustrates the differences in these contributions across the UK. Unsurprisingly, the hemispheric baseline made a greater contribution to ozone in the receptor regions in the west and north of the UK, whilst the UK, France, Germany and the Benelux countries made greater contributions to receptor regions in the east and south.

In summary, approximately three-quarters of ozone in the UK may be considered as deriving from the hemispheric baseline on average.

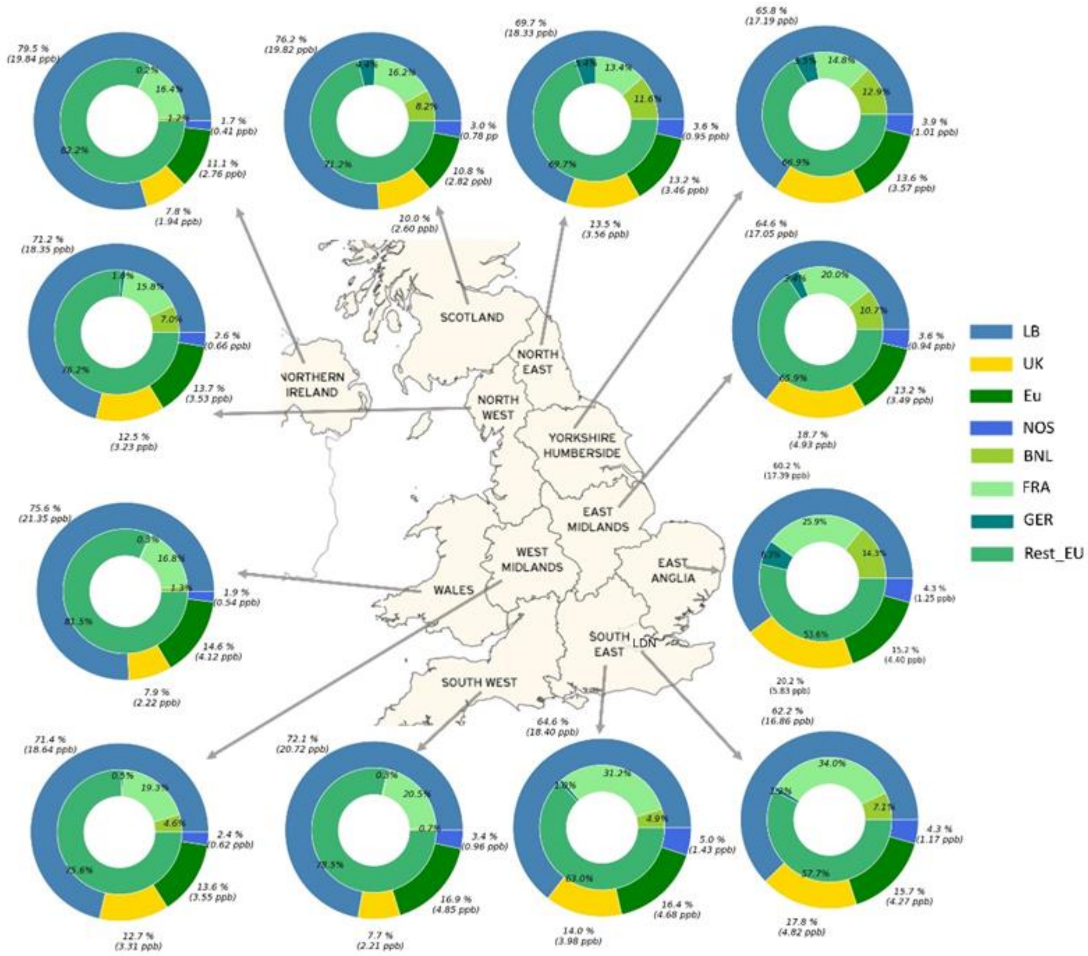

Figure 44: Contributions to the mean surface ozone mixing ratios in July 2015 for 12 receptors regions in the UK as simulated using the WRF Chem model set up for the European region. Outer circles depict the contributions from the UK, the North Sea and English Channel (NOS), the rest of the model domain (primarily continental Europe) (Eu) and transport from outside of the model domain (i.e. the lateral boundaries conditions (LB)). The inner circles apportion the contribution from the Eu region into four sub regions: the Benelux countries (BNL), France (FRA), Germany (GER), and the rest of Europe (Rest_Eu). Note that values correspond to contributions from anthropogenic sources only, except for the LBC which includes ‘hemispheric baseline’ ozone. From Romero Alvarez (2019).

Chapter 5 – Future projections

5.1 Global climate and emissions simulations of future ozone to 2050 and beyond

Archibald et al. (2020b) used the UKESM1 global climate and chemistry model to simulate surface ozone forward from 2015 to 2100 for seven shared socioeconomic pathway (SSP) scenarios. Figure 45 shows the simulations for ozone over Europe (the HTAP-2 domain). The scenarios span a range of combinations of low, medium and high climate change and air quality emission trajectories (Table 6).

The key observation from Figure 45 is that future ozone levels in Europe, including the UK, are critically dependent on the socioeconomic, climate and air quality emissions pathway that is followed in practice. Figure 45 shows surface ozone trajectories ranging from continued increases in ozone until the end of the century (for high climate change scenarios), to ozone levels peaking in the next few years followed by a decline in ozone to levels present in the early 1900s (for low climate change scenarios). The ensemble spread in projected ozone for a given scenario is substantially smaller than the differences between scenarios.

A very important driver for the different trajectories in ozone between these different SSP simulations is their very large differences in methane emissions (SSP3–70 has the highest methane trajectory of all the SSP scenarios), which in turn is driven by the underlying assumptions of air quality/climate control that underpin the scenarios (Table 6). The dominance of the influence of future (global) methane emissions on future surface ozone in Europe is shown in Figure 46 (Turnock et al., 2019), which provides more detailed breakdown of source/sectorial influences on ozone for four of the SSP scenarios. In general, if methane concentrations continue to rise, average ozone will increase. The major anthropogenic sources of methane in these scenarios are the energy, waste and agricultural sectors.

Figure 46 shows that the transport, residential and shipping sectors have the next strongest influence on future surface ozone in Europe. Strong emission controls (of NO_x and VOC) in these sectors should reduce surface ozone. However, it is clear from simulations of these SSPs that emission policies targeting local and regional energy and transport sectors will not be sufficient to achieve substantial ozone air quality benefits compared with the present day without also targeting methane sources.

These simulations are for the evolution of annual mean surface ozone, and with relatively coarse spatial resolution. They do not yield insight into accompanying changes in high percentile ozone concentrations. Climate change is likely to lead to periods of higher temperatures that are known to reduce the dry deposition of ozone and hence increase its surface concentrations (Section 4.4). This is reported to be a contributing factor to the lack of significant downward trend in high percentile concentrations of surface ozone over Europe in recent years (Lin et al., 2020) (Section 2.3.2). A continuation of this ecosystem-atmosphere climate penalty is expected with increasing frequency of hot and dry summers.

Uncertainty in ozone simulations in global models arises from the use of reduced chemical mechanisms. An important manifestation is uncertainty in the production of ozone as a function of temperature as mediated by the simulation of isoprene emissions and oxidation chemistry (Archibald et al., 2020b).

Another area of uncertainty in simulating future surface ozone is the role of transport of ozone from the stratosphere, which is covered in the next section.

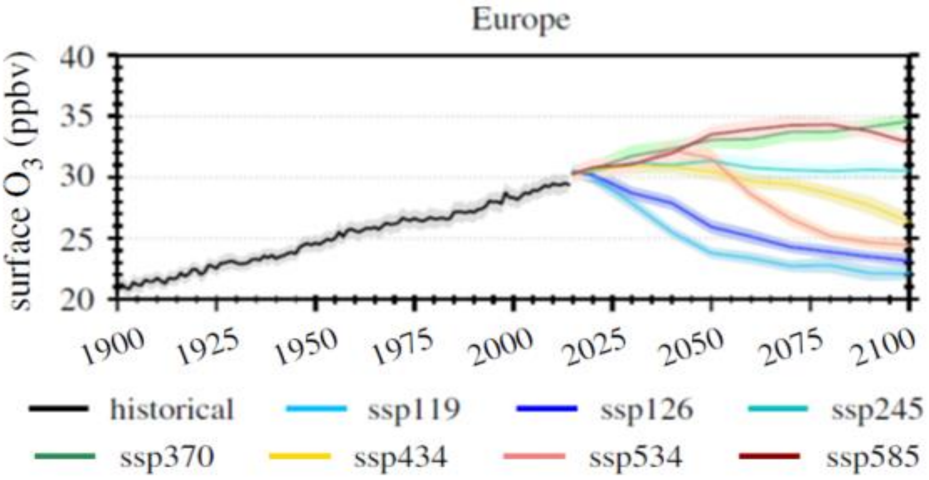

Figure 45: Evolution of surface ozone in Europe as modelled by the UKESM1 model from 1900 to 2100. The black line is the ensemble mean of CMIP6 Historical simulations, while the coloured lines are ensemble means for seven shared socioeconomic pathway (SSP) scenarios for future climate and air quality. A brief description of the scenarios is given in Table 6. Shading is ±1 sd of 9 ensemble members for the historic simulation and 5 ensemble members for the future simulations. Adapted from Archibald et al. (2020b).

Table 6: Qualitative descriptions of the ScenarioMIP scenarios used by Archibald et al. (2020b) in the UKESM1 simulations of future ozone shown in Figure 45. The acronym SSP stands for shared socioeconomic pathway. The first number indicates the global socioeconomic narrative (Riahi et al., 2017), whilst the latter two numbers indicate the projected radiative forcing in 2100 relative to pre-industrial, for example ‘26’ indicates a projected radiative forcing of 2.6 W m^{-2}.

Figure 45 label	**Scenario**	**SSP narrative**	**climate change scenario**	**air pollution trajectory**
historical	historical		historical changes	historical changes
ssp119	SSP1 1.9	sustainability	low	low
ssp126	SSP1 2.6	sustainability	low	low
ssp245	SSP2 4.5	middle of the road	medium	medium
ssp370	SSP3 7.0	regional rivalry	high	high
ssp434	SSP4 3.4	inequality	medium	high
ssp534	SSP5 3.4	fossil-fuelled development	medium	low
ssp585	SSP5 8.5	fossil-fuelled development	high	low

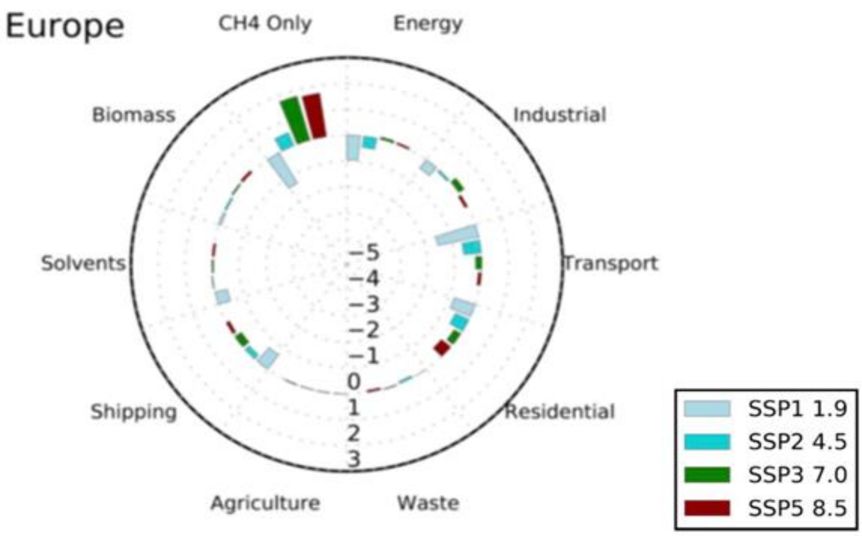

Figure 46: Attribution of changes in annual mean surface ozone (ppbv) over Europe between 2015 and 2050 due to individual emission sectors for four of the future climate/emissions scenarios described in Table 6. Adapted from Turnock et al. (2019).

5.1.1 Future contributions of stratospheric ozone to surface ozone

Source-tagging modelling studies have highlighted a small, but significant contribution to springtime surface ozone in north-west Europe from transport of ozone generated in the stratosphere (AQEG, 2009; Monks, 2000; Butler et al., 2020). Data from Butler et al. (2020) suggests up to 20% in March, although negligible at some times in the year (see Section 4.5.1).

Chemistry-climate model simulations of future scenarios predict increasing contribution of stratospheric ozone to tropospheric ozone abundance throughout this century (Meul et al., 2018; Abalos et al., 2020). For example, stratospheric ozone in the troposphere is projected to increase 10-16% by the end of the 21st century in the Representative Concentration Pathway (RCP)6.0 scenario (Abalos et al., 2020). This is mainly driven by changes in the stratospheric Brewer-Dobson circulation and in the tropospheric Hadley cell circulation caused by greenhouse gas increases, but also in part to the increasing abundance of stratospheric ozone as ozone-depleting substances continue to be phased out. The former is the dominant cause in the Northern Hemisphere mid-latitudes but the mid-to-high latitude regions are also the locations where the stratospheric ozone reservoir will increase the most.

These global studies report tropospheric ozone burdens and columns and it is not clear the extent to which surface ozone is impacted and in particular over small geographical areas such as the UK. The largest effects on tropospheric ozone are manifest with the more pessimistic greenhouse gas scenarios. Nevertheless, it must be assumed that any future climate change pathway that increases stratosphere-troposphere exchange will lead to enhanced surface ozone. More work in attribution of surface ozone to this source is required (Archibald et al., 2020b).

5.2 UK ozone in 2050 under pathways to achieve Climate Change Act target

Global simulations described in Section 5.1 show that the future trajectory of surface ozone in Europe (and elsewhere) is closely coupled to the level of ambition on climate change mitigation regionally and globally. This is because climate change mitigation actions usually directly affect the emissions of precursors central to ozone formation (and to its chemical and depositional removal).

The UK Climate Change Act sets a legally-binding commitment to achieve net zero greenhouse gas emissions by 2050. The Committee on Climate Change (CCC) has developed a range of scenarios for how the UK could achieve this. AQEG has made an initial assessment of the possible impacts on UK air quality for one of the scenarios supplied by the CCC (AQEG, 2020c). The scenario considered describes a large number (47) of greenhouse gas emission mitigation measures that can be applied across a very wide range of sectors (15: agriculture and land use; aviation; buildings; carbon capture and storage (CCS); electricity generation (wind and solar); electricity generation (other); F-gases; gas grid; GHG removal/CCS; hydrogen use; industry; industry with CCS; shipping; surface transportation; waste). In the absence of air quality simulations, AQEG's approach was to assign to each action a value ranging from −3 to +3 to reflect the anticipated scale of beneficial impact of that action on UK levels of each of five air quality pollutants (including ozone). The evaluation endeavoured to take into account the likely scale of implementation of the action being considered.

Any measure that reduces emissions of NO_x and/or NMVOC has benefit in reducing ozone formation. These measures include all reductions in combustion emissions from electricity and heating production and from industry, electrification of transport (road and rail), and reductions in coastal shipping emissions. They also include measures that reduce agricultural land NO_x emissions. Due to the non-linear chemistry on ozone formation, reductions in NO_x emissions may cause increases in ozone because of the reduced chemical removal of ozone by reaction with NO. This was seen in the UK following restrictions associated with the COVID-19 pandemic (see Section 2.7). However, sufficiently large-scale and wide-ranging reductions in NO_x and NMVOC will still result in net benefit on ozone.

These latter points are illustrated by Williams et al. (2018) who modelled the air quality impacts of pathway scenarios to meet an earlier Climate Change Act target of an 80% reduction in carbon dioxide equivalents by 2050 compared with a 1990 base. Figure 47 shows the time series of hourly ozone concentrations over the years 2011 and 2050 for Harwell and for London North Kensington for a pathway with a very large degree of electrification of the vehicle fleet. This scenario incorporated very large NO_x reductions in urban areas as well as large reductions in VOC emissions in the transport and other sectors. A qualitatively similar pattern is seen in both plots. The winter/autumn hourly values increase significantly as a result of the reduced reaction with NO. The model runs also suggest a reduction in peak concentrations in the summer months as the reduction in precursor emissions reduces the extent of the NO_x-VOC photochemical reactions.

Reductions in UK methane emissions under net zero actions (e.g. from natural gas production and leakage, landfill and agriculture) will have little immediate benefit on UK ozone but will contribute to the longer-term reduction in tropospheric hemispheric baseline ozone that is important for the UK.

The net zero mitigation measures identified by AQEG (2020c) as having potential disbenefit on ozone relate to increased planting of forests (for carbon sink) and crops for biofuels including for BECCS (bioenergy crops for carbon capture and storage). Vegetation varies widely in its emissions of isoprene and other BVOCs which, in the presence of NO_x, lead to ozone formation. Selection of low-emitting plant and tree species should be a key factor in the design of future land-use and bioenergy policies.

It must be remembered that the impacts on UK ozone of UK net-zero greenhouse gas mitigation actions and other direct air quality emissions actions in the next few decades will be superimposed on the levels of ozone that are consequent on all such actions elsewhere.

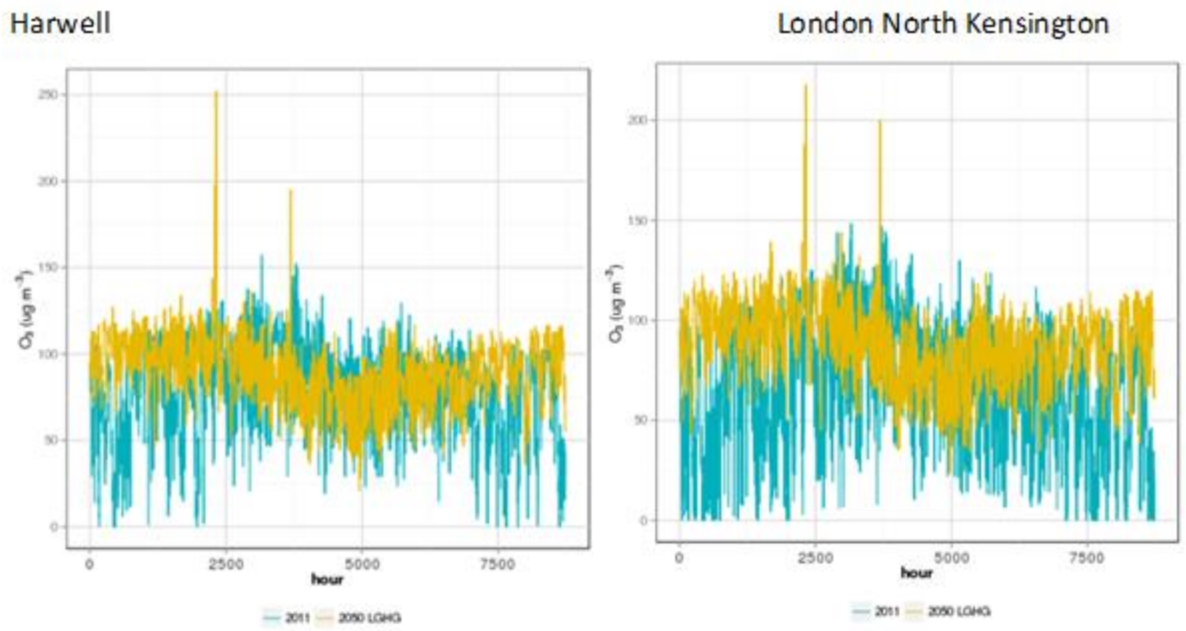

Figure 47: Modelled hourly ozone at Harwell (left plot) and London North Kensington (right plot) for 2011 (blue) and for 2050 under a Climate Change Act scenario incorporating a very large degree of electrification of the vehicle fleet (orange). Details in Williams et al. (2018).

5.3 Ozone changes in 2030 from changes in European anthropogenic emissions only

Figure 48 shows simulations of the potential changes in four measures of surface ozone and its impacts that result from application of one emissions scenario for UK and European emissions in 2030. The four measures are annual mean ozone, SOMO35, AOT40 for forests and POD_1 for deciduous forests. The simulations derive from the EMEP4UK model (rv4.17, WRF v3.7.1). In order to isolate the impacts of changes in European anthropogenic emissions of NO_x and NMVOC, the simulations use fixed 2015 meteorology, land cover, biomass burning emissions, volcanic emissions, and European domain boundary conditions. Shipping emissions (from the

Finnish Meteorological Institute (Jalkanen et al., 2016)) were fixed at 2011. The fixed domain boundary conditions mean that the methane concentration is effectively also fixed. The 2030 emissions scenario is NECD2030 for Europe and Central2030[11] for UK.

These simulations are for one ‘central’ scenario of anthropogenic emissions in Europe in 2030, and focus only on the effects of those European (inc. UK) emissions. Even if this scenario is correct, the maps in Figure 48 do not provide the anticipated ozone concentrations and health and vegetation impact metric values in 2030 because the effects of these emission changes will be superimposed on changes to UK ozone additionally caused by changes in other drivers not included in these simulations: for example changes in baseline ozone levels, long-range transported ozone, climate, land-use, and meteorology in a given year. Sections 5.1 and 5.2 describe that ozone over Europe in the next few decades is extremely sensitive to regional and global socioeconomic and climate-change mitigation trends and could increase or decrease. Nevertheless the present simulations provide insight into the changes in ozone that might be attributed solely to the European anthropogenic emission changes currently anticipated under 2030 NECD commitments.

Bearing in mind these caveats, Figure 48 shows a continuation to 2030 of the same trends between 2001 and 2015 that were shown in Figure 22 for annual mean ozone and in Figure 32 for SOM35, AOT40 and POD_1.

Continued decreases in local transport and other combustion-related NO emissions lead to further marked increases in urban ozone, and to ozone in the vicinity of major transport corridors (Figure 48a). The decline in NO emissions also leads to an increase in ozone more generally across the UK, England in particular.

The trend for SOMO35 is similar (Figure 48b), but more marked over some urban areas where the ozone decrement was formerly sufficiently large that the daily maximum 8-hour running mean ozone did not often exceed the 70 µg m^{-3} concentration for it to contribute to the SOMO35 value. The increase in SOMO35 values in populated areas substantially outweighs the further small decreases in SOMO35 over rural areas in the northern UK brought about by small, continued, decreases in photochemical episodes of ozone. Since population is associated with urban areas, the population health impact as quantified by SOMO35 is simulated to increase further in 2030. The UK population-weighted mean SOMO35 corresponding to the distributions shown in Figure 48b increases by ~20% between 2015 and 2030 on top of the ~25% increase between 2001 and 2015. However, again it is important

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[11] https://uk-air.defra.gov.uk/assets/documents/reports/cat08/1212100954_31772_MPMD_Draft_Final_Report_for_comment.pdf

to remember that actual SOMO35 values are dependent also on other changes to ozone not included in these simulations. It should also be noted that COMEAP (2015) recommend not to include any threshold concentration in the calculation of short-term health burden from ozone, in which case the straight concentration maps in Figure 48a may more closely represent the changes in health burden from European anthropogenic emissions changes than the maps in Figure 48b. In either case, both Figure 48a and Figure 48b demonstrate the current strong relationship in the UK between decreasing NO_x emissions and an increase in urban ozone concentrations.

The AOT40 metric is simulated to continue to decrease between 2015 and 2030 (Figure 48c) over all but the major urban areas (where it will increase). This broad trend is driven by the further decrease in NO and NMVOC emissions. Given that the bulk of forest cover is not in the areas shown in red in Figure 48c, the reductions in European anthropogenic emissions will have a positive benefit on ozone vegetation impacts as quantified by AOT40. In contrast, the POD_1 metric is simulated to change very little in rural areas between 2015 and 2030 (Figure 48d). The flux-based POD_1 metric is considered a more reliable quantification of impacts of ozone on vegetation than the AOT40 metric. It is emphasised again that the changes in the metrics simulated here would be superimposed on changes to ozone caused by other influences on ozone that were not held constant in these simulations.

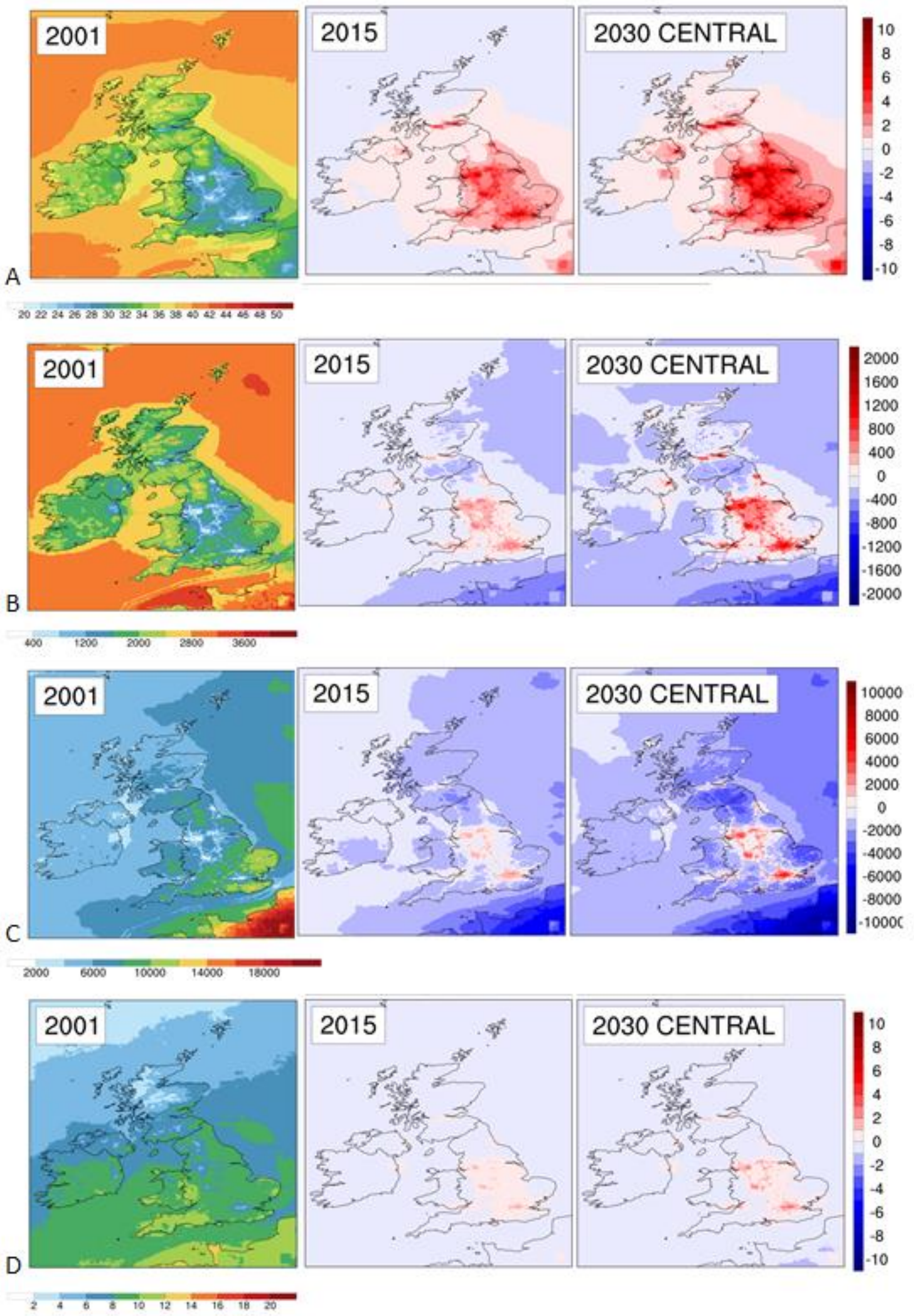

Figure 48: EMEP4UK-modelled changes in ozone metrics for 2015 and for 2030 compared with the value of the metric in 2001, removing the effect of meteorology. Row (A): annual mean surface ozone (ppb); row (B): SOMO35 human health metric (ppb days); row (C): AOT40 for forests (ppb h); row (D): POD_1 for deciduous forest (mmol m^{-2} y^{-1}). For ozone, 1 ppb = 2 µg m^{-3}. The 2030 emissions scenario is NECD2030 for Europe and Central2030 for UK. All years use 2015 meteorology, 2015 Europe-external boundary conditions and 2011 shipping emissions in order to isolate the impact of land-based emissions changes in the UK and the rest of Europe. (EMEP ver. rv4.17; WRF ver. 3.7.1)

Chapter 6 – Monitoring changes in ozone over the next 20 years

6.1 Real-time ground-level ozone measurements by UV absorption

Measurement of ground-level ozone is primarily undertaken in the UK with instruments using a light absorption method. The intensity of an ultraviolet light is measured after it passes through a chamber, called the sample cell, where it is absorbed in proportion to the amount of ozone present. A switching valve alternates measurement between a gas stream containing ozone and a stream that has been scrubbed of ozone. The analyser also records the ambient temperature and pressure of the gas being measured.

This approach adheres to the European Reference method for ozone monitoring (EN14625:2012) and the Environment Agency's Performance Standards for Continuous Ambient Air Quality Monitoring Systems[12]. The data quality objectives set down in the Ambient Air Quality Directive (2008/50/EC)[13] dictates that the following data quality objectives must be achieved in respect of ozone measurements[14]:

- 15% uncertainty for fixed measurements
- 90% data capture in summer and 75% data capture in winter

Location and number of sampling points

Many of the UK's rural background ozone monitoring sites were established as part of a long-running research monitoring programme going back to the mid-late 1980s. In the 1990s some of these sites were upgraded to include co-located measurements of NO_x and SO_2.

The rural ozone monitoring network was supplemented by urban background monitoring as part of the multi-pollutant Enhanced Urban monitoring Network programme in the early 1990s.

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[12] https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/532491/LIT_7050.pdf

[13] https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32008L0050&from=en

[14] Other criteria apply to indicative measurements of ozone and modelling of ozone, which are not considered here for the purposes of brevity and focus on existing fixed measurement infrastructure.

These early research measurements contributed greatly to the work of the Photochemical Oxidants Research Group in the 1990s (Photochemical Ozone Review Group PORG, 1997), and to the compilation of AQEG's earlier report on ozone (AQEG, 2009).

Since the late 1990s the number of locations for ozone monitoring in the UK has been largely driven by the needs of European Air Quality Directives, which require the division of the UK into zones and agglomerations for annual reporting purposes. A "Monitoring Regime Assessment[15]" is regularly carried out to determine that the UK continues to comply with the minimum requirements for numbers and locations of ozone monitoring sites. The long-term research monitoring locations have been preserved and incorporated into one single ongoing monitoring network referred to as the Automatic Urban and Rural Monitoring Network (AURN).

As of September 2020, ozone is measured at 75 sites in the AURN, including the Mace Head site on the west coast of Ireland (https://uk-air.defra.gov.uk/networks/network-info?view=aurn). Figure 49 illustrates the spatial distribution of the sites, whilst Table 7 summarises the number of locations by site classification. Annex A.1 provides further details of the individual AURN ozone monitoring locations including their start date. Other sites across the UK monitor ozone but may do so at lesser quality standards.

Three of the rural background sites, Mace Head, Auchencorth Moss and Chilbolton Observatory, are EMEP Level 2 supersites. Chilbolton Observatory replaced Harwell on 1st January 2016 as the southern UK EMEP supersite. Mace Head is also a Global Atmospheric Watch (GAW) global site. These supersites measure a very large range of chemical and meteorological variables.

Ozone is one of a large suite of atmospheric composition measurements now being made at three new NERC-funded urban background supersites instigated in 2018/2019, in London (Honor Oak Park sports ground, Lewisham), Birmingham (Elms Road Observatory Site (EROS), Edgbaston campus), and Manchester (Research Development Gardens, Fallowfield Campus, south Manchester). These supersites are urban background equivalents of the long-running EMEP rural background supersites and the London Marylebone Road urban traffic site.

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[15] https://uk-air.defra.gov.uk/assets/documents/reports/cat09/1312171445_UK_Air_Quality_Assessment_Regime_Review_for_AQD.pdf

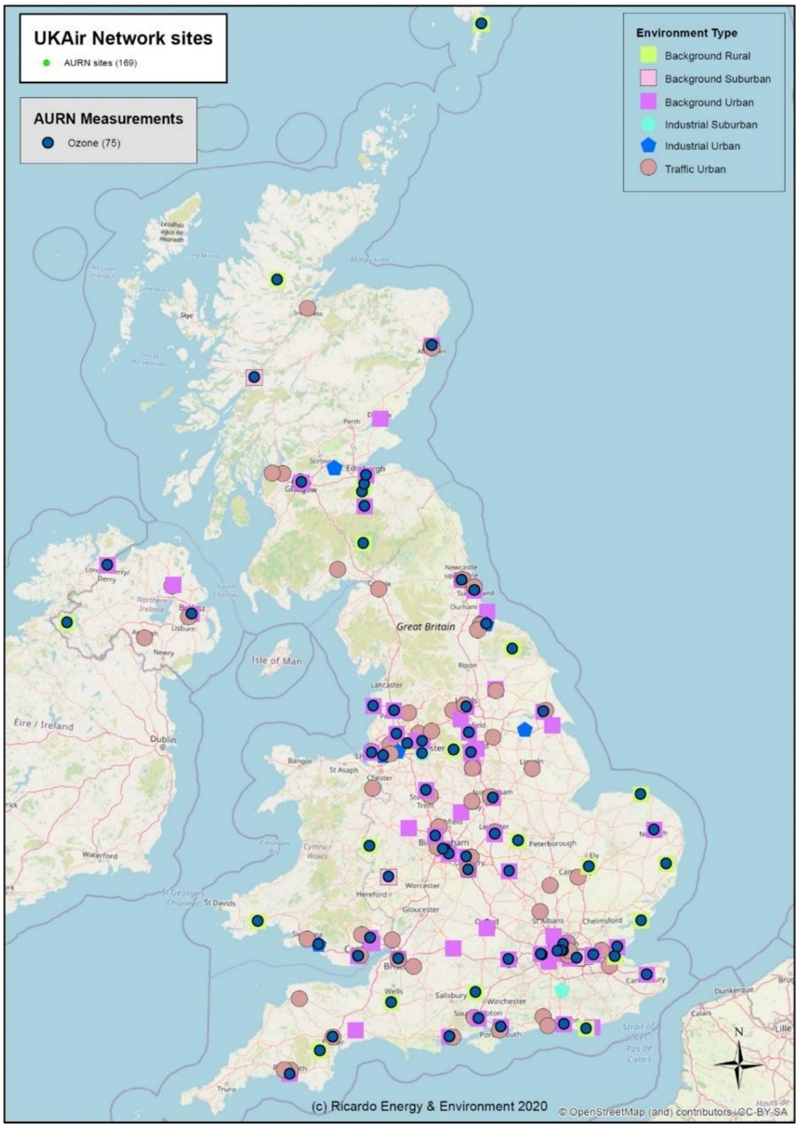

Figure 49: Location and classification of sites in the AURN with ozone measurement. Mace Head on the west coast of Ireland is also included in this network.

Table 7: Numbers and types of sites with continuous ozone measurement in the AURN.

Site classification	***No. of sites***	**Site classification**	***No. of sites***
Rural background	21[a]	Urban background	43
Suburban background	3	Urban industrial	4
Suburban industrial	1	Urban traffic	3

[a] Three of these sites (Auchencorth, Chilbolton, Mace Head) are also EMEP Level 2 sites.

Since ozone is not a regulated pollutant under the Local Air Quality Management regime only a relatively small number of measurements are undertaken using the reference method outside of the AURN national monitoring network. Ozone is currently measured at 25 sites in the London Air Quality Network (LAQN, www.londonair.org.uk), although 9 of these are also AURN sites. A few local authorities and other organisations outside of London operate additional sites that measure ozone using similar instrumentation and with similar data assurance protocols as the main AURN and LAQN networks, and whose data is available from regional UK websites: www.scottishairquality.scot, www.airqualityni.co.uk, www.airquality.gov.wales, www.airqualityengland.co.uk, https://sussex-air.net/, http://www.kentair.org.uk/.

Quality and traceability of AURN and equivalent ozone measurements

Ozone is a gas that is unstable due to its reactive nature. As such, unlike stable gases such as CO, NO, SO_2, etc., calibration of ozone instruments cannot be achieved through known concentrations in air (i.e. calibration cylinders). However, due to the principles of the measurement method being governed by the Beer-Lambert law a standard reference photometer provides for a calibration check: the international ozone standard is realised as an ozone standard reference photometer (SRP). The Bureau International des Poids et Measures (BIPM) currently maintains three US National Institute of Standards and Technology (NIST) Standard Reference Photometers as ozone reference standards to underpin its international comparison programme. The BIPM and NIST are cooperating to transfer the international responsibility for the comparison of national ozone standards to the BIPM. The BIPM organised inter-comparisons of ozone SRPs held by national metrological laboratories (the National Physical Laboratory (NPL) for the UK). Results for the UK typically show deviations less than 1% from the BIPM reference at 80 nmol mol^{-1}.

Transfer reference photometers are used for calibration of AURN ozone analysers. The AURN QA/QC Unit obtains calibration of their transfer reference photometers every 6-months against the NPL UK reference photometer. This calibration is undertaken by NPL who provide UKAS accredited calibrations in the range 0 to 1 ppm with a ±3.0% relative uncertainty (at the 95% confidence level). The transfer reference photometers are commercial photometers certified to the UK standard as described above. These photometers are taken to every site in the AURN every 3 months to calibrate ozone analysers on site. The uncertainty of the calibration of on-site analysers is typically 3-4%. Hence, as for the other gaseous pollutants, there is an unbroken chain of traceability from the analysers on site to national and international ozone standards.

As an independent check, the QA/QC Unit also participates in EU network inter-calibrations for ozone, organised by the JRC Ispra. Recent results for ozone inter-comparison show agreement of the transfer standard photometer with the JRC reference to within approximately 2%.

In addition, the QA/QC Unit also provides UKAS accredited calibrations of Equipment Support Unit (ESU) photometers, to enable them to provide a traceable ozone analyser calibration as part of their routine service and maintenance of the analysers on-site.

Where AURN ozone instruments are found to deviate by more than 5% from the transfer standard at a site audit then measurements will be corrected accordingly during the data ratification process. Ratification of AURN ozone data also considers consistency of regional concentrations, expected changes in ground-level ozone due to meteorology and air mass back-trajectories, observed interactions between pollutants, any changes in local emissions activity, and continued integrity of the sampling systems and monitoring site infrastructure.

Future network measurement requirements

The continuation of a centrally coordinated network of monitoring sites spanning the full range of site types (remote to kerbside) is essential for monitoring ozone changes in the future. As has been noted elsewhere in this report, long multi-year time series of measurements at the same locations are necessary to discern trends that may be obfuscated by inter-annual meteorological variation over the timescale of a few years.

Multispecies measurements at monitoring sites are also essential for interpreting the chemical climate and for evaluating atmospheric composition models. The UK is well covered by rural background measurement of ozone. However, continued changes in traffic and other urban emissions, for example in NO_x and in different volatility classes of VOC, may lead to important changes in chemical production and loss routes for urban ozone. This will require emphasis on multispecies urban background and roadside monitoring. The inclusion of photolytic flux measurements such as $j(NO_2)$ or total solar irradiance, and other meteorological data, would also be beneficial.

6.2 Ozone passive diffusion tubes

Ozone diffusion tubes are inexpensive Palmes-type diffusion tubes used for long-term monitoring over 2-4 weeks. Ozone can be detected in the low parts per billion to low parts per million ranges. The design is a fluorinated ethylene polymer tube fitted with thermoplastic rubber caps, one of which contains the absorbent. A 1 µm porosity filter is fitted to the “open end” of the tube to prevent the ingress of airborne particulate nitrate. The concentrations of nitrate ions chemically adsorbed are quantitatively determined by ion chromatography with reference to a calibration curve derived from the analysis of standard nitrate solutions.

Ozone diffusion tubes have been used for carrying out spatial or localized assessments for ozone in ambient air, workplace or industrial monitoring. Their application to ambient ozone monitoring is limited due to the long exposure period compared with the 1-hour and 8-hour mean air quality standards set by the WHO, EC and UK government for protection of human health.

6.3 Ozone sensor measurements

'Low-cost' sensors for ozone have been available for many years, based on both gas-sensitive semiconductor (metal oxide) and electrochemical methodologies.

In common with similar sensor technology for other pollutants, numerous co-location and inter-comparison evaluations have highlighted variable ozone sensor performance (for example, Borrego et al., 2016; Borrego et al., 2018; Castell et al., 2017; Jiao et al., 2016; Karagulian et al., 2019). As well as potential confounding from temperature, humidity and co-pollutant gases (particularly NO_2 for ozone sensors), the issue of drift in sensor sensitivity (i.e. calibration) over a few months currently limits their deployment for routine long-term ozone measurement (Feinberg et al., 2018; Mueller et al., 2017).

Many of the studies cited above and others suggest that at least some of the effects of confounding factors can be suppressed through multivariate post- (or quasi-real-time) processing of the data. Increasingly sophisticated approaches to calibration and data assurance of sensors within networks are being developed, including use of multiple replicate sensors per node. Short-term (up to a few months) deployment of networks of ozone sensors in, for example the Fraser Valley, British Columbia (Bart et al., 2014), Auckland (Weissert et al., 2017) and Los Angeles (Miskell et al., 2019) have revealed intra-urban spatial variations in ozone not captured by the many fewer fixed-site ozone analysers.

On the one hand, it may be anticipated that improvements in sensor head sensitivity and specificity, and in data processing algorithms, means that long-term intraurban networks of ozone sensors may become routine in the future. On the other hand there is potential concern that the extensive data processing that is likely to accompany deployment of such sensor networks both reduces the perceived cost-effectiveness of these measurements and obscures a traceable and intelligible link between the raw sensor signal at a given point and the final output pollutant concentration value.

The prospect for sufficient reliability of individual ozone sensors for mobile and personal exposure applications is less certain. However, it could be argued that if there was significant future expansion in the spatial density of monitoring networks, including indoor environments, there might then be less need for portable sensors to assess personal exposure (Morawska et al., 2018).

6.4 Open path and remote sensing measurements

Open path measurement techniques allow instruments to determine concentration of a specifically targeted pollutant over an extended measurement path. Some methods allow the concentration to be spatially resolved. Others give the average concentration over the whole path length, which typically finds application in assessing the transfer of pollutants across site boundaries and along roads and runways. Some commercially available differential optical absorption spectroscopy (DOAS) instruments can use a double-ended system to measure the average concentration between the instrument and a reflector up to hundreds of metres away. Such systems are able to measure many common pollutants including ozone, but the difficulty in calibrating the instrument and interpreting integrated-path data compared to fixed point monitors needs to be recognised.

Ground-based MAX-DOAS (multi-axis differential optical absorption spectroscopy) has been used to determine lower-atmosphere vertical profiles of ozone (e.g. Wang et al., 2018) but not for horizontal near-surface ozone distributions, for example over a city, as has been done for NO_2 in Leicester (Kramer et al., 2008) and Vienna (Schreier et al., 2020) using MAX-DOAS at very shallow elevation angles.

Vertical columns of ozone can be measured using ground-based UV/vis spectrometers that use scattered sunlight as a source. A long-standing instrumental variant of the absorption method is the Brewer Ozone Spectrophotometer. Within the British Isles, measurements of ozone column using the former instrument at Valencia, Ireland, and with the latter instrument at Aberystwyth, UK, currently contribute to the Network for the Detection of Atmospheric Composition Change, part of the WMO Global Atmosphere Watch programme (De Maziere et al., 2018). Spatially resolved vertical profiles of ozone are periodically measured using compact balloon-borne ozone electrochemical sensors (ozonesondes) (Thompson et al., 2011; Tarasick et al., 2019).

Surface ozone is not easily directly quantifiable from satellites because the large amount of ozone higher in the atmosphere obscures surface values. Instead, satellite-measured column densities of tropospheric NO_2 and HCHO, which are more sensitive to the lower troposphere, can be used. For example, Jin et al. (2017) used the Geos-Chem atmospheric chemistry transport model to link the tropospheric column ratio of formaldehyde to NO_2 (FNR), derived from the Ozone Monitoring Instrument on the Aura satellite, to the ground-level HCHO/NO_2 ratio, as an indicator to identify NOx-limited versus NOx-saturated ozone-formation regimes. OMI is a UV/vis spectrometer with spatial resolution up to 13 km x 24 km at nadir. They report that the FNR in the model surface layer is a robust predictor of the simulated near-surface ozone production regime.

According to Zhang et al. (2018), there is good prospect for deriving full spatial coverage (at a few km spatial resolution) of daily surface ozone and predictors for daily maximum 8-hour ozone from high-quality NO_2 and HCHO column densities derived from satellites. Cloud cover will, as for other atmospheric composition parameters, mean that coverage will be highly weather dependant and this often limits measurements in UK winter.

6.5 Measurement of ozone fluxes

As outlined in Section 4.4, the dry deposition flux of ozone can be measured using micro-meteorological flux measurement approaches. This requires a combination of turbulence measurements and measurement of either vertical gradients to apply flux/gradient approaches or fast ozone fluctuations (typically 10 measurements per second) to provide fluxes by eddy covariance methods (Muller et al., 2009). In either case the measurements need to be made over extensive, homogeneous vegetation. Overall, the measurement and data processing of deposition fluxes is a much more complex endeavour than the measurement of concentrations in air.

Fluxes are not currently measured in official networks or centrally supported research programs. A number of usually short-term ozone flux studies to UK vegetation were made during the period 1960-2010 (e.g. Colbeck and Harrison, 1985a; Fowler et al., 2001; Hargreaves et al., 1992; Coyle, 2005; Coyle et al., 2009; Muller et al., 2009). At present, longer-term flux measurements are ongoing only at Auchencorth Moss (Fowler et al., 2001), a moorland in central Scotland, as part of UKCEH’s NERC-funded National Capability function, and over coastal water at Penlee Point, Cornwall (Loades et al., 2020). There is therefore a lack of measurement evidence to validate and/or improve the parameterisations used in the atmospheric chemistry and transport models as well as fluxed-based ozone impact metrics such as POD_Y (Section 3.2.2).

It is the total dry deposition flux that controls the removal from the atmosphere and thus affects the atmospheric concentrations of ozone. However, the effects on the plants to which the ozone is deposited are most closely linked to the amount of ozone entering the plants through stomata and this is the basis for the flux-based effects metrics, including POD_1 (Emberson, 2020). The stomatal flux of ozone cannot be measured in isolation, but needs to be inferred from the total flux and a measure of the stomatal conductance, the efficiency by which the ozone can diffuse into the leaves. In field measurements, to partition the ozone flux between external surfaces (of vegetation and soil) and the stomata it is therefore necessary to measure both water vapour and ozone fluxes (e.g. Coyle et al., 2009).

There would be scope to develop an ozone deposition network as part of the UK's work under Article 9 of the European National Emissions Ceilings Directive (2016/2284), which requires member states "to improve information on the impacts of air pollution, including the extent of any impacts and the recovery time when the impacts are reduced, and to contribute to review of critical loads and levels"..."based on a network of monitoring sites that is representative of their freshwater, non-forest natural and semi-natural habitats and forest ecosystem types …". Such a measurement network for ozone flux would need to cover ozone concentration and flux, water flux, as well as a number of ancillary meteorological and plant physiological parameters, that would allow an improved model representation of the deposition process to be developed.

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Appendices

A.1 Sites in the AURN measuring ozone

The following table provides the location, classification and start date of the 75 AURN sites measuring ozone as at September 2020.

Site Name	Environment Type	Start Date	Latitude	Longitude
Aberdeen	Background Urban	18/09/1999	57.15736	-2.09428
Aston Hill	Background Rural	26/06/1986	52.50385	-3.03418
Auchencorth Moss	Background Rural	01/01/2003	55.79216	-3.2429
Barnsley Gawber	Background Urban	07/07/1997	53.56292	-1.51044
Belfast Centre	Background Urban	08/03/1992	54.59965	-5.92883
Birmingham A4540 Roadside	Traffic Urban	06/09/2016	52.47609	-1.87502
Birmingham Acocks Green	Background Urban	18/03/2011	52.43717	-1.830
Birmingham Ladywood	Background Urban	01/06/2018	52.48135	-1.91824
Blackpool Marton	Background Urban	14/06/2005	53.80489	-3.00718
Bournemouth	Background Urban	05/03/2001	50.73957	-1.82674
Brighton Preston Park	Background Urban	03/11/2004	50.84084	-0.14757
Bristol St Paul's	Background Urban	15/06/2006	51.46284	-2.58448
Bush Estate	Background Rural	01/04/1986	55.86228	-3.20578
Canterbury	Background Urban	02/01/2001	51.27399	1.098061
Cardiff Centre	Background Urban	12/05/1992	51.48178	-3.17625
Charlton Mackrell	Background Rural	03/09/2008	51.05625	-2.68345
Chilbolton Observatory	Background Rural	11/01/2016	51.14962	-1.43823
Coventry Allesley	Background Urban	11/06/2014	52.41156	-1.56023
Cwmbran	Background Urban	20/07/2001	51.6538	-3.00695
Derry Rosemount	Background Urban	21/03/2016	55.00282	-7.33118
Edinburgh St Leonards	Background Urban	01/01/2003	55.94559	-3.18219
Eskdalemuir	Background Rural	23/04/1986	55.31531	-3.20611
Exeter Roadside	Traffic Urban	02/07/1996	50.72508	-3.53247

Fort William	Background Suburban	22/06/2006	56.82266	-5.1011
Glasgow Townhead	Background Urban	07/10/2013	55.86578	-4.24363
Glazebury	Background Rural	01/04/1988	53.46008	-2.47206
High Muffles	Background Rural	16/07/1987	54.33494	-0.80855
Hull Freetown	Background Urban	06/11/2002	53.74878	-0.34122
Ladybower	Background Rural	15/07/1988	53.40337	-1.75201
Leamington Spa	Background Urban	26/07/1996	52.28881	-1.53312
Leeds Centre	Background Urban	04/01/1993	53.80378	-1.54647
Leicester University	Background Urban	01/10/2013	52.61982	-1.12731
Leominster	Background Suburban	18/07/2005	52.22174	-2.73667
Lerwick	Background Rural	16/01/1990	60.13922	-1.18532
Liverpool Speke	Industrial Urban	24/11/1995	53.34633	-2.84433
London Bloomsbury	Background Urban	23/01/1992	51.52229	-0.12589
London Eltham	Background Suburban	08/10/1993	51.45258	0.070766
London Haringey Priory Park South	Background Urban	26/10/2012	51.58413	-0.12525
London Harlington	Industrial Urban	01/01/2004	51.48879	-0.44161
London Hillingdon	Background Urban	02/08/1996	51.49633	-0.46086
London Marylebone Road	Traffic Urban	01/01/1997	51.52253	-0.15461
London N. Kensington	Background Urban	01/04/1996	51.52105	-0.21349
Lough Navar	Background Rural	02/04/1987	54.43951	-7.90033
Lullington Heath	Background Rural	04/10/1986	50.7937	0.18125
Mace Head	Background Rural	03/04/1987	53.32644	-9.90392
Manchester Piccadilly	Background Urban	18/12/1995	53.48152	-2.23788
Manchester Sharston	Industrial Suburban	27/01/2016	53.37131	-2.23922
Middlesbrough	Industrial Urban	01/01/1993	54.5693	-1.22087
Narberth	Background Rural	20/01/1997	51.78178	-4.69146
Newcastle Centre	Background Urban	08/03/1992	54.97825	-1.61053
Northampton Spring Park	Background Urban	01/04/2017	52.27226	-0.91661

Norwich Lakenfields	Background Urban	01/09/2009	52.61419	1.301976
Nottingham Centre	Background Urban	02/09/1996	52.95473	-1.14645
Peebles	Background Urban	06/11/2009	55.65747	-3.19653
Plymouth Centre	Background Urban	29/09/1997	50.37167	-4.14236
Port Talbot Margam	Industrial Urban	01/01/2007	51.58395	-3.77082
Portsmouth	Background Urban	01/01/2001	50.82881	-1.06858
Preston	Background Urban	06/06/2000	53.76559	-2.68035
Reading New Town	Background Urban	17/10/2003	51.45309	-0.94407
Rochester Stoke	Background Rural	26/01/1996	51.45617	0.634889
Sheffield Devonshire Green	Background Urban	31/10/2013	53.37862	-1.4781
Sibton	Background Rural	01/07/1973	52.2944	1.463497
Southampton Centre	Background Urban	04/01/1994	50.90814	-1.39578
Southend-on-Sea	Background Urban	24/07/2000	51.54421	0.678408
St Osyth	Background Rural	11/05/2002	51.77798	1.049031
Stoke-on-Trent Centre	Background Urban	11/03/1997	53.02821	-2.17513
Strathvaich	Background Rural	18/03/1987	57.73446	-4.77658
Sunderland Silksworth	Background Urban	09/12/2004	54.88361	-1.40688
Thurrock	Background Urban	01/09/1996	51.47707	0.317969
Walsall Woodlands	Background Urban	19/06/2012	52.60562	-2.03052
Weybourne	Background Rural	30/05/2001	52.95049	1.122017
Wicken Fen	Background Rural	15/10/1997	52.2985	0.290917
Wigan Centre	Background Urban	08/10/2004	53.54914	-2.63814
Wirral Tranmere	Background Urban	14/05/2000	53.37287	-3.02272
Yarner Wood	Background Rural	26/06/1987	50.5976	-3.71651

A.2 The upcoming change in the internationally agreed value for the ozone absorption cross-section at 253.65 nm and its effect on reported ambient ozone concentrations

Background

Most measured ozone concentrations are made using instruments that determine the absorption of ultraviolet light passing through the air sample. The narrow band of wavelengths used corresponds to a resonance of the ozone molecule. Converting the absorption coefficient to an ozone concentration involves a property of ozone called its absorption cross-section at that wavelength. The absorption coefficient, the reciprocal of the distance over which the intensity of the ultraviolet light drops by a factor e, is measured in units cm^{-1}, for example. This is divided by the cross-section, with unit cm^2 per molecule, to give the molecular concentration, with the unit molecules per cm^3. This can in turn be converted to a mass concentration in $\mu g\ m^{-3}$ using the mass of an ozone molecule, or a value in molar parts per billion (ppb) using the number of air molecules in a cubic centimetre.

The absorption cross-section must be determined experimentally. However, because the absorption cross-section is common to measurements using many different instruments of varying designs, an agreed value is generally used. This practice has the advantage that ozone measurements are more comparable, by avoiding differences due to the specific choice of cross-section value, but it runs the risk that all these measurements are slightly offset from the most accurate value, if, as experimental results improve, the agreed value is found to differ significantly from the best experimental value.

While the comparability of ozone measurements from absorption instruments is important, accuracy is necessary when comparing the concentrations of ozone obtained using different principles, and when comparing ozone concentrations to concentrations of nitrogen monoxide, for example, where the molecules react on a one-to-one basis.

Ultimately it is good measurement practice to present all measurement results as traceable to the definitions of the SI units used, rather than making them dependent on a conventional value that is known to be significantly different from the best SI-traceable value.

Current position

The current conventional value of ozone absorption cross-section at 253.65 nm is **1.147×10^{-17} cm^2 per molecule** (Hearn, 1961) being used with standard uncertainty of **0.024×10^{-17} cm^2 per molecule** (Hodges et al., 2019).

The recommendation from the global metrology committee covering these matters, the Consultative Committee for Amount of Substance – Metrology in Chemistry and Biology (CCQM), after a re-evaluation of all available experimental data, is that a value of **1.1329×10^{-17} cm^2 per molecule** (Hodges et al., 2019) and standard uncertainty **0.0035×10^{-17} cm^2 per molecule** (Hodges et al., 2019) be adopted for high accuracy work at national and international metrology institutes.

The variation of the absorption cross-section at this wavelength with temperature is very weak (fractional change of -5×10^{-5} K^{-1} at 295 K) (Barnes and Mauersberger, 1987; Malicet et al., 1989) so this value can be adopted for all measurements at ambient temperatures.

The date at which this change is to be made official will be decided after consultation with stakeholder communities, including a CCQM workshop in September 2020.

Consequences

Once field instruments have been calibrated using the established links to national metrology institutes, the change will mean that an ozone concentration previously reported as y µg m^{-3} or z ppb will in future be reported as $1.012y$ µg m^{-3} or $1.012z$ ppb respectively, a step change increase of 1.2% in reported concentrations. To put it another way, concentrations reported before the change will be seen to have underestimated the true concentration by 1.2%. An evaluation of the scale and impact of change in cross-section on air quality compliance were reported in Sofen *et al.* (2015).

This change is small compared to the measurement uncertainty of individual field ozone measurements, which is typically 15%. However, where small changes in long-term trends are being evaluated, the change may need to be taken into account, for example by retrospectively correcting the earlier data. Also, when mean concentrations are compared to target values, the proportions of data above and below the target value will be significantly affected if the concentrations are near that value.