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Surface ozone concentrations and ecosystem health: past trends and a guide to future projections

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Abstract

This paper reviews current understanding of the sources and sinks of ozone in the troposphere, recent studies of long-term trends, and the factors which have to be taken into consideration when constructing and interpreting future models of ozone concentration. The factors controlling surface O₃ concentrations are discussed initially to provide a basis for the ensuing discussion, followed by a summary of the evidence for recent trends in ground-level ozone concentrations, i.e. over the past 3 decades, which have shown a significant increase in the annual average in 'background' air typical of the unpolluted northern hemisphere. Closer to precursor sources, although urban winter concentrations have increased, rural peak spring and summer concentrations during ozone 'episodes' have decreased markedly in response to emissions reductions. In order to determine whether such trends are meaningful, the statistical techniques for determining temporal trends are reviewed. The possible causes of long-term trends in ozone are then discussed, with particular reference to the use of chemistry-transport models to interpret past trends. Such models are also used to make predictions of future trends in surface ozone concentrations, but few are comprehensive in integrating future climate changes with changes in land use and in emissions of ozone precursors. Guidance is given on the likely effects of climate/precursor/chemistry interactions so that model predictions can be judged.

Keywords

Ozone, photo-oxidants, climate change, plant health, global emissions

Introduction

Photochemical oxidants, and ozone (O₃) in particular, are recognised as posing a threat to human health and the health of vegetation across much of the industrialised world (Karnosky et al., 2007), and an increasing threat in areas with rapidly increasing industrialisation e.g. (Ashmore and Marshall, 1999; Emberson et al., 2001). Consequently, controls on emissions of the O₃ precursor pollutants, nitrogen oxides (NO_x) and volatile organic compounds (VOCs), have been introduced in order to reduce the prevalence of high concentrations of O₃, and the associated health risks. This has proved more complex than the regulation of emissions of sulphur dioxide (SO₂), because the sources are more varied; for NO_x, all combustion sources must be considered – large stationary sources such as power stations, vehicles and biomass burning – while for VOCs, sources include industrial emissions, vehicle usage and biogenic emissions. Moreover, the interplay between sources and sinks of O₃ and climate is complex, with non-linear behaviour, so that the overall effects of emission controls on O₃ production cannot be simply predicted. Nevertheless, emission controls have been implemented in Europe and elsewhere, and the effects on subsequent O₃ production have been investigated e.g. (Monks, 2005).

In terms of vegetation health, considerable evidence has been accumulated on the relationship between plant exposure to O₃ and either growth/yield reductions or visible injury e.g. (Ashmore, 2005). A commonly-used threshold for calculating effective dose is 40 ppb (nL L⁻¹), as the AOT40 (Fuhrer et al., 1997; Mauzerall and Wang, 2001) or D40 (Ollinger et al., 1997), defined as the accumulated ‘excess’ O₃ concentration above 40 ppb during daylight hours through the growing season. Even at ‘background’ measurement sites, remote from sources of O₃ precursors, peak hourly concentrations sometimes exceed 60 ppb and may exceed 100 ppb if polluted air masses are transported to the site (Vingarzan, 2004). Closer to sources of precursors, such concentrations are the norm during the spring and summer and have the potential to cause significant effects on plant growth and crop yield. The apparent threshold for O₃ effects reflects the capacity of plants to counteract the formation of reactive oxygen species (ROS) when O₃ is absorbed through stomata. Measures of exposure (such as the AOT40) do not include the rate at which O₃ enters leaves, and flux-based approaches to dose:effect relationships are being developed (Tuovinen et al., 2007). However, it is still not clear to what extent the observed damage to vegetation is the result of periodic exposure to high concentrations (well above any supposed threshold) or to chronic exposure to concentrations near the threshold. Part of the uncertainty is caused by a lack of understanding of the capacity of individual plant species to ‘detoxify’ the ROS formed when O₃ enters a leaf, and the ways in which factors such as nutrition, drought stress, genotype and phenology influence a plant’s ability to tolerate exposure to high O₃ concentrations (Tausz et al., 2007). The distinction between ‘acute’ and ‘chronic’ exposure becomes important when considering the pattern of O₃ exposure that has developed, at least in western Europe and North America, over the past decades, with a trend towards lower peak concentrations during spring and summer O₃ ‘episodes’, but higher average O₃ concentrations throughout the year (see below).

The purpose of this paper is to summarise recent research on trends in concentration of O₃ at the earth’s surface, and the causes of such trends, and to set in context the predictions of models that incorporate different future scenarios of precursor

emissions, the role of climate change, and the interactions between changes in climate and predicted O₃ formation.

Factors controlling surface O₃ concentrations

The main pathways of O₃ formation and loss in the troposphere are shown in Figure 1. Ozone is transported downwards from the stratosphere by stratosphere-troposphere exchange (STE), a process that is coupled to global weather patterns and sea surface temperatures, and therefore linked to long-term changes in climate (Olsen et al., 2007). Within the troposphere, O₃ is formed as a result of a cycle of photochemical reactions involving nitrogen dioxide (NO₂) and volatile organic compounds (VOCs) (Atkinson, 2000). The main reaction in the troposphere that forms O₃ is the photolysis of NO₂ to give NO and O, with the O atom reacting with O₂ to form O₃, which can then react with NO to regenerate NO₂. In the absence of other reactions, NO, NO₂ and O₃ coexist in an equilibrium (the NO_x photostationary state, Figure 1) determined by the rate of NO₂ photolysis (sunlight intensity). Photolysis of O₃ by short-wave ultraviolet light yields a reactive O atom, which may lose energy by collision with O₂ and N₂ molecules in air and then react with O₂ to re-form O₃, or may react with water vapour (H₂O) to generate hydroxyl radicals (OH). OH radicals react with VOCs (R-H), usually by abstracting a H atom to form H₂O; the remaining organic radical R· adds O₂ to form a peroxy radical, RO₂. Peroxy radicals can then react with NO to form NO₂ and other organic radicals or molecules; this reaction shifts the equilibrium between NO and NO₂ towards NO₂ leading to greater rates of net O₃ formation. The cycle can be closed by reaction of OH with NO₂ to form nitric acid (HNO₃) or by self-reaction of peroxy radicals at low NO_x concentrations (NO_x = NO + NO₂). The net photochemical formation of O₃ can therefore be limited by the availability of either NO_x or VOCs; over most of the continents net O₃ production is NO_x limited (i.e. reductions in NO_x emissions will lead to a reduction in average O₃ concentrations), but peak concentrations in summer may be VOC limited (Derwent et al., 2003). Over the oceans, where NO_x concentrations are small (<0.05 ppb) net O₃ destruction may occur (the Low NO_x pathway in Figure 1). The net global production of tropospheric O₃ represents a small difference between large production and destruction through chemical reactions in the troposphere, which is therefore sensitive to changes in emissions of precursors and destruction pathways, e.g. the reaction of O from O₃ photolysis with water vapour (H₂O).

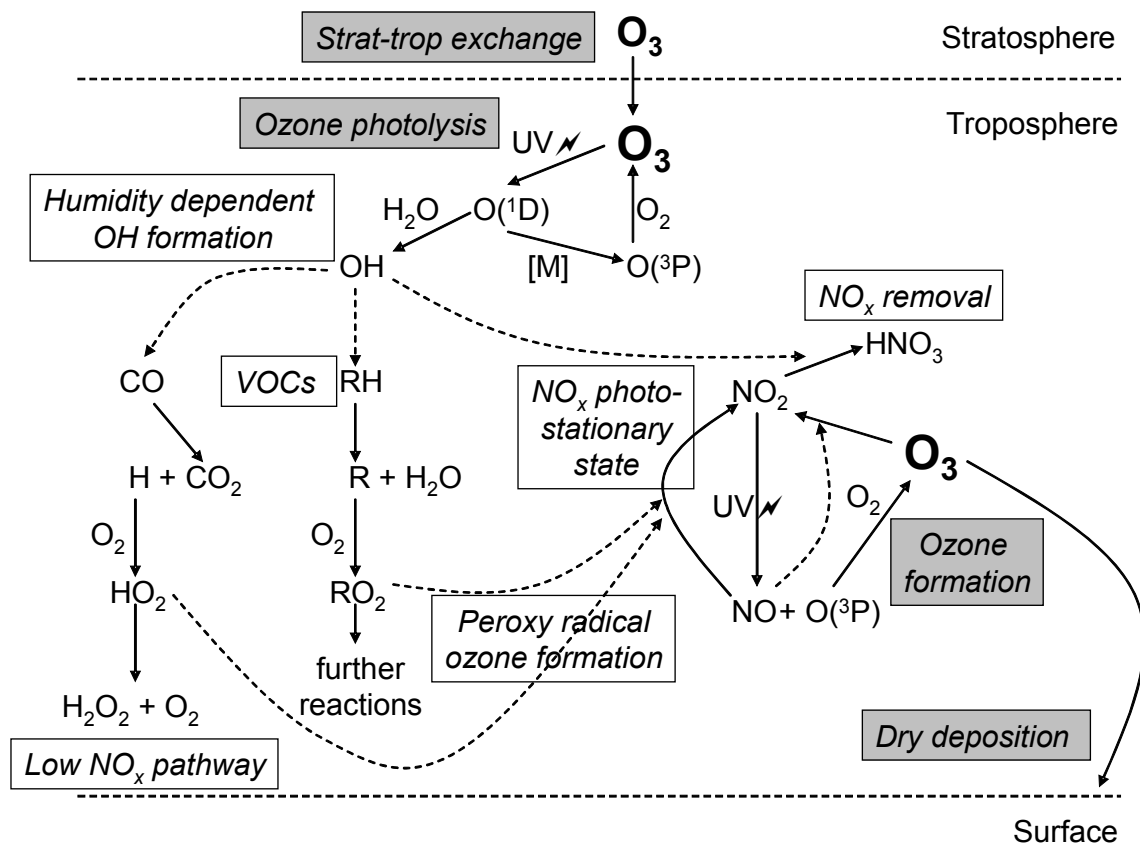


Figure 1: Schematic diagram of the major sources and sinks of ozone in the troposphere, showing the key chemical reactions involved.

The third contributory factor to tropospheric O_3 concentrations is removal at the earth's surface by reaction of O_3 in or on the surfaces of plants and soil, a process known as 'dry deposition'. Uptake into leaves is determined by stomatal conductance, which varies with water and CO_2 availability, and growth-stage of the vegetation. Bare soil and external leaf surfaces also act as efficient sinks for O_3 . The overall loss at the earth's surface approximately balances the transfer into the troposphere from the stratosphere.

Evidence for recent trends in ground-level ozone concentrations

A comprehensive review of surface O_3 background levels and trends was published in 2004 (Vingarzan, 2004), and while including measurements from the late 19th and mid 20th century, the review focused on data since the 1970s at 'background' stations. In this context, a 'background' station is one that is remote from sources of precursor pollutants. A more recent review of 'background' sites included both surface measurements and ozonesonde data from higher in the troposphere (Oltmans et al., 2006). However, because O_3 is a secondary pollutant (i.e. not emitted directly, but formed from precursors through photochemical processes in the atmosphere) remote sites can be influenced by air masses that have been transported many hundreds or even thousands of km. Consequently, a 'background' site may not always record 'background' O_3 concentrations, in the sense of O_3 concentrations in air masses that have not been exposed to emissions of man-made precursors. This point was made explicitly in studies of long-term O_3 trends from Mace Head, on the west coast of Ireland, where detailed analysis of other constituents of the sampled air and air-mass

back trajectory calculations were used to identify ‘true’ background air unaffected by regionally transported pollution (Derwent et al., 2007). Confusion in the use of the term ‘background’ may lead to confusion in describing the difference between trends from sites in remote regions, and trends in unpolluted air. Vingarzan’s (2004) review lists 22 ‘surface’ or ‘near surface’ background sites at which increasing O₃ trends have been reported, and 8 sites at which decreasing O₃ trends have been reported. There are no clear geographical patterns to these trends, and the picture is complicated further by the lack of long-term data sets. In some studies a pattern of decreasing concentrations during one decade may be followed by increasing concentrations in the subsequent decade, so the period over which the trend is assessed may determine the apparent direction. The review concluded somewhat cautiously that ‘background’ O₃ levels in the Northern Hemisphere mid-latitudes have increased over the past 30 years, with the greatest rate of increase in the earlier part of that period, and that the more recent slowdown in O₃ increases is attributable in part to emission controls on precursors. Attention was drawn, however, to the importance of intercontinental transport of O₃ and its precursors in contributing to ‘background’ concentrations of O₃ at remote sites, particularly in the northern hemisphere. The more recent review (Oltmans et al., 2006) confirmed these observations for mid-latitude sites in the Northern Hemisphere, including Japan – a result that is somewhat surprising given the recent large increases in O₃ precursor emissions in China and India (Streets and Waldhoff, 2000). Data from vertical profiles, however, indicate a recent increase in O₃ concentrations at higher altitudes in the troposphere which may be related to changes in transport patterns. Trends in the Arctic were small, but in the Southern Hemisphere, surface and mid-troposphere concentrations at mid-latitudes have been increasing, especially in spring (Oltmans et al., 2006).

Trends from ship-borne O₃ measurements in the North and South Atlantic from 1977 to 2002 show in more detail the latitudinal variation in O₃ behaviour (Lelieveld et al., 2004) under maritime ‘background’ conditions. For the North Atlantic between 40° and 60° N the trend was not significant, but to both north and south of these latitudes the trends were significantly upward, and ranged from +0.12 to +0.68 ppb y⁻¹. Analysis of the frequency distributions of the measurements showed an overall upward shift in the median concentrations rather than simply a shift in the frequency of high concentrations, which would be the case if samples represented increases in the frequency of sampling locally polluted air. Moreover, the loss of low concentrations from the frequency distributions suggested an overall increase in true background concentrations. Continental emissions of anthropogenic (fossil-fuel derived) NO_x in Africa, rather than changes in biomass burning, were suggested as the cause of the largest increases, which effectively doubled ‘background’ surface O₃ concentrations during the study period over the south-eastern subtropical Atlantic Ocean.

Recent site-specific studies of changes in ‘background’ O₃ concentrations in Europe have been concentrated around the margins of the continent. Measurements in Finland from 1989 to 2001 show non-significant increases in average O₃ concentrations in daytime hours between May and July, but (non-significant) decreases in the 99th percentile (peak) concentrations (Laurila et al., 2004). However, there were highly significant increases in O₃ concentrations in unpolluted air masses at several sites, of around 0.5 ppb y⁻¹. A broader study of measurement data, including sites in Finland, Norway and Sweden, was combined with a modelling exercise in an attempt to

interpret the measurement data (Solberg et al., 2005). Again, the data considered were from the summer months, and the daily maxima (hourly average) were used, being thought to be more representative of the well-mixed boundary layer than longer-term averages. Significant downward trends in the 99th percentile daily maxima were noted for southern Norway and southern Sweden, but not for southern Finland, from 1990 to 2000. These confirm earlier data for the United Kingdom (NEG-TAP, 2001), which showed a significant downward trend in peak concentrations from the 1970s to the 1990s.

A major study in Europe was published as a report in 2005 (Monks, 2005), pulling together data and modelling studies from across the whole of Europe. The report showed that European emissions of O₃ precursors had decreased over the past 3 decades (by between 20 and 40% for NO_x, with even larger reductions in Russia), and that peak O₃ concentrations had also decreased, but not in a linear fashion compared with emissions reductions; although peak concentrations at some sites had decreased by between 1 and 1.5% per year during the 1990s, average wintertime low concentrations had systematically increased, particularly in central Europe, attributed to the reduction of the titration of O₃ by nitric oxide (NO) caused by reduced NO emissions. The average O₃ concentration in unpolluted 'background' air had also increased, particularly in northern and western Europe, and in winter. However, the variability in weather patterns from year to year leads to a varying contribution of urban plumes at remote sites which can confound long-term trends, especially as it has been shown that the springtime maximum in average O₃ concentrations across Europe has a large contribution from O₃ formation in polluted European air (Monks, 2000). However, the report concluded that direct and measurable changes in mean O₃ concentrations that are attributable to emissions reductions are small, especially in the context of high year-to-year variability.

Some of the most detailed recent studies come from the western fringes of Europe, looking at the trends in O₃ concentrations in both polluted and unpolluted air masses at a coastal site on the west coast of Ireland, at Mace Head (Derwent et al., 2007; Simmonds et al., 2004). A significant increase in O₃ concentrations in background (unpolluted) air was seen from 1987 to 2007, of 0.31 ± 0.12 ppb y⁻¹, with a larger average increase from 1987 to 1999 followed by a period with little overall trend. The increase in background air varied seasonally, with largest changes in spring and smallest in summer. Anomalously large concentrations in some years (1998-99) were attributed to large-scale emissions of O₃ precursors from boreal forest fires. In regionally polluted air masses from Europe, smaller increases were seen, with no increase in the summertime production of O₃. These data confirm earlier reports of stable or decreasing O₃ concentrations in summertime O₃ peak concentrations, e.g. (Bronnimann et al., 2002; Derwent et al., 2003; NEG-TAP, 2001). An independent statistical analysis of the Mace Head data, separating long-term trends from seasonal variations, showed different behaviour depending on the air mass origin (Carslaw, 2005). In unpolluted background air the seasonal amplitude has increased, between the springtime maximum and the summer minimum, largely driven by a decrease in the summer minimum. Seasonal patterns of O₃ concentration in polluted air masses suggest a steadily decreasing influence of polluted air from Europe at this site. The source of air mass dictates the seasonal variation in O₃ – this may have implications for the future, as changes in emission patterns, and changes in weather patterns as a result of climate change, may influence the seasonal patterns. A similar type of study

in Switzerland (Pochanart et al., 2001) used the residence time of air masses over polluted regions of Europe to categorise surface O₃ concentrations measured at Arosa in 1996-1997, and showed very different seasonal cycles for polluted and unpolluted air. The 'background' seasonal cycle at Arosa was very similar to that at Mace Head, suggesting a regional scale pattern of concentration in unpolluted air.

Similar trends to those reported for western Europe are seen at the west coast of North America, where 7 out of 9 sites showed an average O₃ increase between 1987 and 2004 of 0.26 ppb y⁻¹ (Jaffe et al., 2003; Jaffe and Ray, 2007). No trends could be seen in vertical profiles from ozonesonde measurements, but this was attributed to the variability in the data set caused by irregular sampling intervals.

Statistical techniques for determining temporal trends

Although many analyses have used simple linear regression on maximum or average values to establish temporal trends, perhaps separated by season, more rigorous statistical techniques have also been applied, taking into account factors that might influence O₃ concentrations on similar timescales. Such approaches have been developed because of the large year-to-year variability in patterns of O₃ concentration. For example, the frequency distribution of the whole dataset has been used to characterise temporal changes (Lin et al., 2000); these results suggested an increase in the O₃ transported from outside the United States as a contributory factor to increasing rural background concentrations in the United States. In an alternative approach, the systematic seasonal variation of O₃ concentrations within a year may be removed prior to trend analysis (Jaffe and Ray, 2007). When considering periods as short as a decade, systematic variations in climate may be responsible for changes in O₃ concentration that might otherwise be ascribed to changes in precursor emissions, so care must be taken when using statistical analysis alone when ascribing potential causal factors. For example, at a global scale, analysis of satellite records of tropospheric O₃ shows inter-annual variability that is correlated with the El Niño – Southern Oscillation (ENSO) in some parts of the tropics such as northern India (Fishman et al., 2005).

The dependence of average O₃ concentrations on meteorological conditions is already well established. For example, a multi-layer perceptron (MLP) neural network approach to separating the effects of meteorological variability on O₃ data showed short-term downward trends in summer daily maximum O₃ concentration at sites in the UK (Gardner and Dorling, 2000). A more conventional time-series analysis of data from Switzerland, taking account of meteorological variability, which varied from site to site, suggested an increasing trend of around 1 ppb y⁻¹ in summer afternoon peak concentrations, which was attributed to an increase in background O₃ concentrations (Bronnimann et al., 2002). A subsequent study of Swiss O₃ data used an analysis of covariance to establish the influence of meteorological variability on daily maximum O₃ concentrations at 12 sites between 1992 and 2002 (Ordonez et al., 2005). In spring and summer, the most important meteorological variables were afternoon temperature and morning global radiation, whereas in winter, factors that affected vertical mixing (e.g. afternoon global radiation, wind speed, stability) were more important. The number of days after a frontal passage (i.e. after air has been well mixed) was important to account for O₃ production in summer and loss in winter. Application of the meteorological model greatly reduced the inter-annual variability in meteorologically adjusted daily maxima, and showed that there was no significant

decrease in summer maxima, despite reductions in emissions of European precursors. In autumn and winter, a small positive increase in O₃ concentrations could be the result of reduced NO emissions (and removal of O₃ by 'titration' – see Figure 1), but there was an increase in the sum of O₃ and NO₂ (collectively known as 'Ox') suggesting that this trend was not simply the result of reduced titration, but demonstrated a real increase in winter background O₃ concentrations across Europe. The strength of the statistical model was demonstrated by good predictions of the extreme O₃ concentrations observed in 2003, which was the warmest summer in Switzerland for over a century.

A study of datasets from 7 sites in Paris, France, involving extreme value statistics highlighted the importance of non-linearities in such data (Bellanger and Tomassone, 2004). The authors looked at the frequency of exceedance of a threshold O₃ concentration of 130 µg m⁻³ (ca. 65 ppbV) between 1988 and 2001, and concluded that there was an important increasing trend for exceedance time, although the size of the exceedance showed a small decrease. This type of analysis provides useful information for assessing the potential effects of O₃ 'episodes' on plants, as not only the degree of exposure, but also the duration is described, giving a better estimate of the likely uptake of O₃ by leaves.

A stratified approach to the detection of long-term O₃ trends has been applied to data from the city of Bologna, Italy, between 1994 and 2002, utilising climatic data to estimate standardised trends (Cocchi et al., 2005). The analysis showed the necessity of applying such techniques in order to remove the year-to-year variability in daily O₃ concentration maxima caused by variations in climate. No clear long-term trends in the data were identified for the relatively short period examined.

Complex statistical analyses have also been applied recently to O₃ data from North America, incorporating both spatial and temporal information. One study (Lehman et al., 2004) used principal components analysis to group observations across the eastern United States, showing that different regions have different characteristic seasonal cycles in O₃ concentration, and different characteristic persistence of O₃ concentrations. The authors suggest the use of statistical techniques to identify regions showing similar characteristics, rather than geographical or political boundaries, when assessing long-term trends or the influence of climate on O₃ concentrations. The interaction between meteorology and O₃ has recently been examined for the south-eastern United States (O'Connor et al., 2005), based on the average daily maximum concentration in each month between April and October from 1980 to 1994. This showed that maximum O₃ concentrations were positively correlated with temperature and inversely correlated with relative humidity in July and August. High O₃ concentrations were also associated with the number of days with high pressure stagnation. Using a similar approach, urban O₃ trends across the United States were shown to be closely related to meteorological conditions, but in a manner which varied across the country (Camalier et al., 2007). In the north and east, increasing O₃ concentrations were associated with increasing temperatures, particularly over 20 °C, whereas in the south, increasing O₃ concentrations were more closely correlated with decreasing humidity.

Causes of long-term trends in ozone

Several factors have been suggested as responsible for the observed trends. The possibilities include:

- Changes in anthropogenic emissions of precursors (both regional and global)
- Effects of biomass burning (both regional and global)
- Changes in stratosphere-troposphere exchange
- Changes in geographical emission patterns
- Changes in air-mass transport patterns

In practice, it is very difficult to be categorical about the causes of long-term trends at a particular site. For example, at Mace Head the long-term trends have been attributed to hemispheric changes in methane, changes in patterns of transport of polluted air from continental Europe, and large biomass burning emissions from Siberia and North America (Derwent et al., 2007). The most likely causes of the trends in O₃ concentrations in western North America were identified as regional biomass burning and long-range transport from Asia (Jaffe and Ray, 2007). The increasing trends in O₃ concentrations over Taiwan were attributed to decreasing 'titration' by emissions of NO (Chou et al., 2006), with important implications for urban emission control policies.

On a broader spatial scale, changes in the transport of O₃ from the stratosphere to the troposphere may also be important; there is some evidence from measurements and models that increasing O₃ concentrations in the lower stratosphere (particularly in the Northern Hemisphere) may have led to increasing transport to the troposphere (Fusco and Logan, 2003; Ordonez et al., 2007; Tarasick et al., 2005).

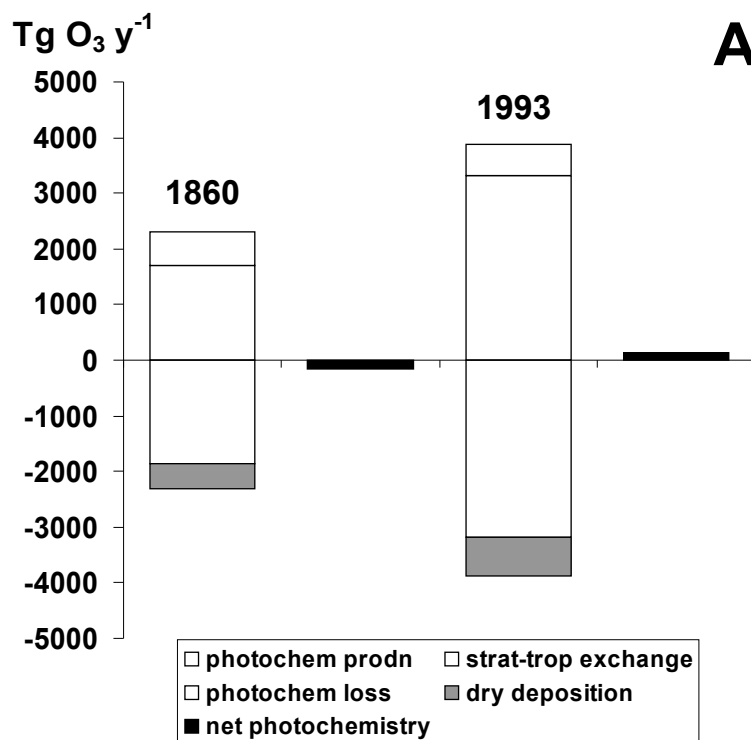
Detecting trends in O₃ concentrations is only the first step in attributing causes, and although techniques such as separating 'polluted' and 'unpolluted' air masses may help in interpreting the observations, research has turned to chemistry/transport models of the atmosphere to try to understand past and current trends, and to provide projections into the future. Vingarzan (2004) cites several studies of the historical changes in O₃ concentrations based on computer models of emissions, reactions and transport of precursor molecules and photo-oxidation products in the atmosphere. The conclusion from these global models was that the largest single cause of increased O₃ concentrations from the 1970s on a global scale is the anthropogenic emission of nitrogen oxides (NO_x) from the combustion of fossil fuels. Global increases in methane concentrations may also have played a role.

The use of chemistry-transport models to interpret past trends

There have been several modelling studies designed specifically to investigate the reasons for the observed trends in O₃ concentrations. Changes in NO_x and VOC emissions in a detailed chemical trajectory model (Derwent et al., 2003) predicted the downward trend in peak European O₃ concentrations and attributed this to reductions in European emissions of VOCs rather than NO_x. A different type of model, based on calculating the chemical transformations of emitted pollutants on a regional scale using a 44 km x 44 km horizontal grid and 16 vertical layers, examined the likely effects of European emission reductions during the 1990s on surface O₃ episodes in Nordic countries (Solberg et al., 2005). Although modelled data were scattered compared with measurements, a reduction in the 99th percentile (highest) O₃ concentrations of around 7.5 ppb was estimated for southern Norway and southern Sweden during the 1990s. A modelling study of the spatial variability in O₃

concentrations across the continental United States demonstrated some of the problems of reconciling model data with measurements, noting the importance of averaging times in assessing how well a model describes reality (Tong and Mauzerall, 2006).

Long-term trends (going back to the 19th century) have been simulated in global chemistry and transport models, and show how the budgets and fluxes of O₃ have changed in response to emission changes (Lamarque et al., 2005; Lelieveld and Dentener, 2000), with a net increase in the tropospheric O₃ burden of around 30%. The results (Figure 2) illustrate the general principles that are shown by most models: stratosphere-troposphere exchange (a source of O₃) is similar in magnitude to dry deposition (loss of O₃) at the earth's surface, with photochemical production and destruction within the atmosphere accounting for most of the O₃ turnover, but being almost in balance. The absolute production and destruction rates both increased greatly over the century, and the net O₃ production term shows the largest differences between the two models cited. This shows why relatively small changes in atmospheric chemical conditions can lead to much larger changes in O₃ budgets, and the overall O₃ concentration in the troposphere.



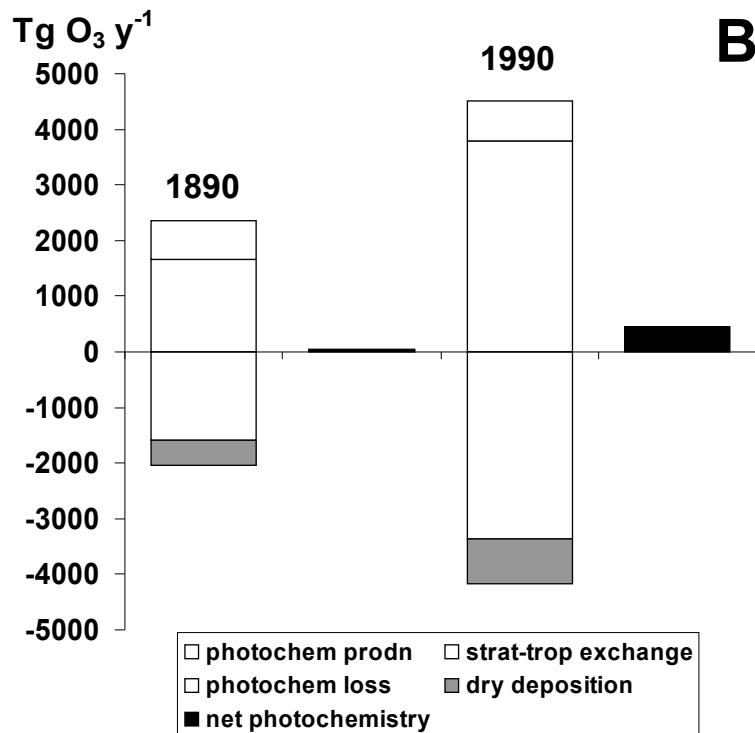


Figure 2: Calculated global ozone fluxes (Tg y⁻¹) in 19th and 20th centuries. Comparison of model outputs showing long-term historical changes in ozone production and loss. In both cases the chemical ‘turnover’ of ozone in the troposphere has greatly increased since the 19th century. Small differences in the models lead to a difference in the sign of current net ozone production globally, illustrating model sensitivity to details of the chemistry schemes used. A: 1863-1993 (Lelieveld & Dentener, 2000). B: 1890-1990 (Lamarque et al., 2005)

Models have proved very useful in understanding the influence of inter-continental transport, particularly the dynamics of the different levels in the atmosphere at which pollutants are transported. This is well illustrated in a recent model (Wild and Akimoto, 2001), in which the authors noted the distinction between local tropospheric production of O₃ followed by transport, as opposed to the vertical transport of precursors (e.g. through deep convection) followed by O₃ production in the upper troposphere and subsequent transport of O₃ to the surface. The latter route is more important for emissions from east Asia, and was shown to have the potential to affect surface O₃ concentrations significantly in both North America and Europe. Conversely, the greatest contribution of U.S. emissions to Europe appears to be from low-level transport of O₃ directly.

Of the more recent models, a Lagrangian model (Derwent et al., 2004) used a labelling technique to mark the origins of O₃ formed within the troposphere over Europe. The model showed a seasonal summer maximum over the Mediterranean, with a spring maximum in the north and west of Europe. The contribution to annual average O₃ concentrations from different sources were: stratosphere-troposphere exchange, 7 ppb (18%); European sources, 20 ppb (50%); N. American sources, 8 ppb (20%) and Asia, 5 ppb (11%). Intercontinental transport from North America and Asia contributed more to O₃ concentrations over Europe than did stratosphere-troposphere exchange in all months except December and February. Increases in NO_x

emissions in North America and Asia increased O₃ concentrations on the western edge of Europe but had little effect in central Europe. An Eulerian model (Auvray and Bey, 2005) quantified the contribution of long-range transport to Europe for 1997. Trans-Atlantic transport was dominated by mid-latitude cyclones transporting material to Europe in the upper troposphere. There was a strong seasonal pattern, with highest transport in spring in northern latitudes and in summer further south, matching the observed pattern of surface O₃ at remote sites in the north and west of Europe. The effects of Asian emissions were observed throughout the year, with a summer maximum at 8-12 km correlated with the monsoon season and increases in lightning-derived NO_x. Budget calculations in the troposphere over Europe showed an 11% contribution of North American sources, and an 8% contribution of Asian sources, with only a 9% contribution from European sources for this particular year (1997). This budget conceals vertical differences; surface O₃ concentrations have a much stronger dependence on local emissions, and are predicted to have declined in response to decreases in precursor emissions. However, mid- and upper troposphere concentrations are predicted to have increased, influenced by increased intercontinental fluxes of O₃.

The trends in European O₃ levels have been studied more explicitly using the EMEP regional photochemistry model (Jonson et al., 2006), run for the years 1990 and 1995-2002. Possible causes for the observed trends were investigated using different emission scenarios and boundary conditions in the model. The possible explanations for changes in surface O₃ over the decade were described and evaluated, drawing attention to differences between summer and winter, and between high and low altitude sites. Reference was made to the results of similar modelling studies as part of the TROTREP project (Monks, 2005). A positive trend in winter O₃ was observed, in response to decreased NO_x emissions and increasing 'background' contributions, but with no clear picture at other times of year. However, the increase in 'background' O₃ is not well explained by the model in terms of long-range transport. International shipping emissions were suggested as a possible contributory factor, along with large-scale boreal fires in Siberia and North America. The authors concluded that hemispheric circulation patterns may also be changing on similar timescales, so that "the magnitude and origin of O₃ trends in Europe are not completely understood."

A similar global study (Sudo and Akimoto, 2007) used tracers in a model to show that O₃ formed in the Asian free troposphere contributed to the overall concentrations in the northern hemisphere, and globally, and that there was free tropospheric transport of O₃ from the southern to the northern hemisphere. Ozone formation in the southern hemisphere is dominated by emissions from biomass burning. Of the global burden of tropospheric O₃ of 344 Tg, 48% came from chemical reactions in source regions, 29% from formation over remote regions, and 23% from stratosphere-troposphere exchange. Regional budgets calculated from a global model showed a similar pattern, with precursors in the outflow from continents leading to net O₃ production in remote regions (O'Connor et al., 2004). Recent models have looked at the specific regional and global impact of emissions from a particular area; for example, the O₃ produced from African emissions contributes significantly to tropospheric O₃ across the whole tropics (Aghedo et al., 2007).

The different types of model and differing results have prompted detailed comparisons and discussions of why differences arise in models, in particular why

more recent models consistently show a higher tropospheric burden of O₃ (ca. 340 Tg) than earlier models (ca. 300 Tg). (Wild, 2007; Wu et al., 2007). Although some of the differences can be attributed to changes in the emissions of precursors (especially biogenic VOCs) used in the models, as knowledge of emissions has improved, other factors such as the model definition of the tropopause height (which affects stratosphere-troposphere exchange), the formulation of wet and dry deposition processes, the role of clouds and the contribution of lightning are also important, as are scaling issues. In a sensitivity study in which some of these factors were varied systematically, keeping everything else constant, the effects on the tropospheric O₃ burden (Tg) were calculated as shown in Table 1 (Wild, 2007). These are global values – regional changes may be much greater, and not all sources of uncertainty were covered in this sensitivity study. Broad-scale spatial models (both in the horizontal and the vertical) were shown to overestimate stratosphere-troposphere exchange, underestimate dry deposition and underestimate net chemical production compared to models at finer spatial scales. Year-to-year variations in meteorology also can cause significant changes in ozone budgets and spatial distribution, so that comparisons of model outputs that use different model years may confound the differences in model structures and operation with differences in input data.

Table 1. Modelled estimates of ozone content in the troposphere in response to changes in model input parameters [Wild, 2007]

Process	Change in input parameter	% change in O ₃ burden
Stratosphere-troposphere exchange	± 50%	± 3%
Dry deposition	± 50%	± 4%
Wet deposition	± 50%	± 3%
Effects of temperature on chemistry	± 5°C	± 1%
Effects of humidity on chemistry	± 20%	± 7%
Convection	± 50%	± 2%
Lightning NO _x	-100% to +50%	- 10% to + 4%

Predictions of future trends in surface ozone concentrations

The dependence of current O₃ concentrations on climatic conditions begs the question of the effects of climate change on the long-term future trends in surface O₃ concentrations across the globe. Model predictions of future scenarios have taken several different approaches, but there are few studies that have fully integrated all the potential interactions. Some models use current climate along with projected emission increases to predict future ozone concentrations; others look at the effects of projected climate change on ozone formation under current emission patterns; one or two studies look at the combined effects of changing emissions and changing climate together, but few, if any, studies have incorporated all the feedbacks between predicted ozone (and other photochemical products such as aerosols) and climate in a combined model of chemistry, transport, emissions and climate.

Although it is tempting to use models to investigate the effects of changes in one or more model inputs in isolation (e.g. modelling the effects of different future emission scenarios using ‘fixed’ climatic conditions), the complexities and feedbacks between chemical processes, radiative forcing and climatic patterns mean that such studies can be misleading. As a simple example – changing emissions while keeping constant

climatic conditions suggests very large increases in global tropospheric O₃, depending on the particular emissions scenario chosen (Prather et al., 2003). However, changing climate conditions to a warmer and wetter world in future decades, while keeping emissions of O₃ precursors at present-day levels, leads to a decrease in global tropospheric O₃ (Stevenson et al., 2005). Similar patterns were seen in a comparison of an ensemble of models of current and future climates (Stevenson et al., 2006). The overall effect of increased emissions and increased temperatures approximately cancelled out on a global scale, but there were large regional differences, with some areas experiencing increased concentrations, and some decreased. The authors also highlight the difficulty with such large-scale models in accurately predicting surface concentrations. The vertical (and horizontal) mixing of precursors within grid cells, which is ‘instantaneous’ in the models, leads to greater homogeneity than is experienced in the real world, and consequently leads to an upwards bias in modelled surface O₃ concentrations. This criticism can be applied to all grid-based models, especially those on a global scale with large grid cells. Other potential sources of error were highlighted, including large differences among models in deposition rates over different terrains, and inadequate handling of convection, which would particularly affect the distribution and fate of highly water-soluble species such as nitric acid (HNO₃) and hydrogen peroxide (H₂O₂) (Figure 1). Convection also determines the occurrence of lightning and consequent NO_x generation, which is poorly defined. Seasonal patterns in the model output are driven by climate, rather than seasonal changes in emissions. For the whole troposphere, changes in O₃ burden were broadly proportional to changes in NO_x emissions, although this was not expected. Surface O₃ concentrations decreased in response to changing climate, particularly over the tropical oceans, with an overall decrease in average ‘lifetime’ of an O₃ molecule in the troposphere. The most important climate-chemistry feedbacks concern water vapour and stratosphere-troposphere exchange, although these have different sensitivities in the different models used in the comparison. It must also be recognised that current models do not always represent accurately present-day conditions, especially in the tropics; a recent set of measurements found much smaller concentrations above a rainforest than predicted by the model used, suggesting not all of the chemical reactions were correctly included in the model (Kuhn et al., 2007).

New model studies and predictions of future ozone concentrations in the troposphere are appearing every year. Table 2 lists some recent examples. Rather than attempt to describe each in detail, the key variables that can be manipulated in a modelling exercise are given below, with reference to Figure 3, which shows the more important interactions and feedbacks which ought to be considered in such models.

Table 2. Some recent modelling studies of future O₃ concentrations in the troposphere

Factors included in the model	
Changes in emissions, constant climate	[<i>Dentener et al., 2005; Jacob et al., 1999; Johnson et al., 2001; Laurila et al., 2004; Lelieveld and Dentener, 2000; Prather et al., 2003</i>]
Changes in climate, constant emissions	[<i>Johnson et al., 2001; Murazaki and Hess, 2006</i>]
Changes in climate, only BVOC emission changes	[<i>Langner et al., 2005; Laurila et al., 2004; Meleux et al., 2007; Stevenson et al., 2005</i>]
Changes in climate and emissions	[<i>Derwent et al., 2006; Gauss et al., 2006; Liao et al., 2006; Stevenson et al., 2005; Stevenson et al., 2006; Unger et al., 2006a; Wu et al., 2008</i>]
Radiative forcing by future ozone concentrations	[<i>Gauss et al., 2003; Horowitz, 2006; Naik et al., 2005; Unger et al., 2006b</i>]

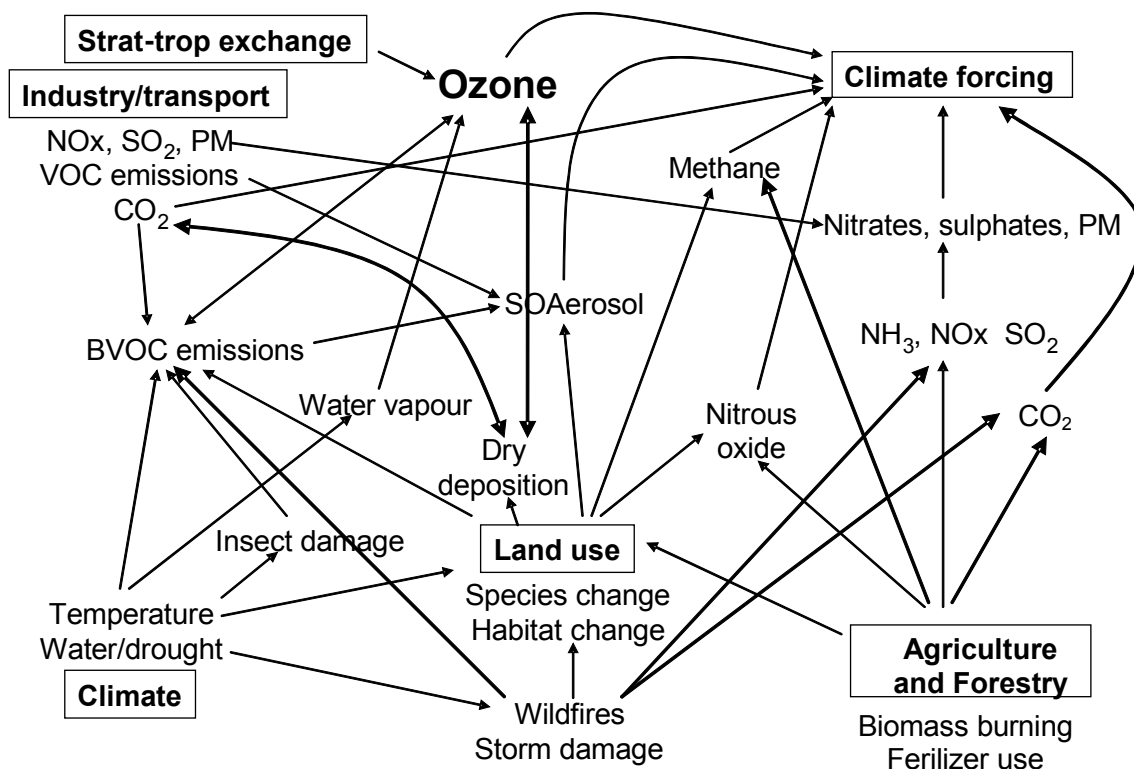


Figure 3: Schematic diagram showing the interactions between future changes in land use, climate and chemistry in influencing ozone concentrations. Increases in CO₂ concentrations affect climate, but also directly affect plants and therefore biogenic VOC emissions and O₃ deposition. Changes in land use play a large role in determining the pattern of future emissions and deposition, and future ozone concentrations. Regional effects are likely to be larger than overall global effects, but are not yet well represented by global models, which consider some, but not all, of the possible interactions.

Factors affecting future ozone scenarios

Anthropogenic emissions:

The IPCC Third Assessment report (IPCC, 2001) used a range of emission scenarios for anthropogenic emissions of O₃ precursors (NO_x and VOCs) depending on a variety of predictions of economic growth. Assumptions were made as to which emissions reductions strategies might be effective, and of the overall global rates of economic growth and development of new technologies. The range of scenarios encompassed the expected range of future anthropogenic emissions and were retained for the more recent report (IPCC, 2007).

Biogenic emissions:

Increased temperatures are predicted to increase emissions of biogenic VOCs, based on measurements of the response of vegetation to short-term temperature changes under controlled laboratory or field conditions (Guenther et al., 1995; Guenther et al., 2006). However, the predicted effects of gradual temperature changes over decades, and the possibility of vegetation adapting to higher temperatures, is still uncertain, especially if higher temperatures are associated with increased drought conditions, or insect damage, both of which can also increase BVOC emissions (Pare and Tumlinson, 1999; Pegoraro et al., 2005). Recent studies have also suggested that increased CO₂ concentrations may inhibit emissions of isoprene (one of the more important BVOCs for O₃ formation) (Monson et al., 2007), but again, these predictions are based on relatively short-term experiments and it is not clear to what extent such responses are general to different plant species, or sustainable over decades. Perhaps more importantly, future BVOC emissions are usually based on the combination of increased emissions caused by increased temperatures and increased above-ground biomass in response to increased CO₂ concentrations. Increased deposition of fixed nitrogen from the atmosphere, and applied as fertilizer, may also play a role. However, most models assume that the pattern of vegetation types will remain approximately constant, or if changes are modelled, they are based on predictions of potential land uses under future climate regimes. The biggest changes in land use today are caused by shifts in agricultural patterns, for example, the move towards biofuels, which occur rapidly (less than a decade) and may have a much greater effect on BVOC emissions through species changes (e.g. conversion of rainforest to oil palms) than any changes predicted from increased temperatures alone (Wiedinmyer et al., 2006). Changing agricultural patterns are also likely to produce changes in climate forcing through increased fertilizer use and soil emissions of the radiatively active gas nitrous oxide (N₂O), although quantitative predictions remain uncertain (Crutzen et al., 2008).

Global climate:

The increases in concentrations of greenhouse gases, primarily CO₂, CH₄ and N₂O, are used to model the radiative forcing of the atmosphere, and consequential changes in temperatures and humidity. Changes in temperature affect the rates of tropospheric reactions, so changing the rates at which O₃ is formed and destroyed. Higher water vapour concentrations at higher temperatures lead to greater loss rates of O₃ from photolysis and OH formation, and consequently higher OH concentrations, which in turn leads to faster turnover of VOCs. However, O₃ itself is also a radiatively active gas, so changes in O₃ concentrations feed back into climate forcing patterns (Gauss et al., 2003). Changes in the oxidising capacity of the troposphere, intimately related to

O₃ concentrations, also change rates of formation of airborne particles from both anthropogenic and biogenic emissions. The combined effects of increased particle concentrations and increased humidity on cloud formation, and the resultant direct and indirect effects on climate forcing are still very uncertain.

Stratosphere-troposphere exchange:

Difficulties in modelling the tropopause have already been mentioned (Wild, 2007). Recent studies suggest that sea-surface temperatures affect the rate of stratosphere-troposphere exchange (Olsen et al., 2007), thereby affecting O₃ transport from above into the troposphere. However, other studies show that the rate of exchange, and the amounts of O₃ entering the troposphere from the stratosphere, are highly variable and depend on climatic circulation patterns (Collins et al., 2003; Ordonez et al., 2007).

Dry and wet deposition:

Increased tropospheric humidity implies, if not greater overall wet deposition, then changes in patterns of precipitation, leading to changes in wet removal of material (including oxidants) from the atmosphere. Although this may not be particularly important for O₃, dry deposition of the gas at the earth's surface is affected by surface wetness (Altimir et al., 2006; Grantz et al., 1995; Lamaud et al., 2002), and by the state of vegetation, in particular its uptake through stomata. Increased CO₂ concentrations may inhibit O₃ uptake directly, by reducing stomatal conductance (Harmens et al., 2007; Sanderson et al., 2007; Tausz et al., 2007). Conversely, increased O₃ concentrations may damage vegetation and inhibit CO₂ uptake, leading to feedback effects on tropospheric CO₂ concentrations (Felzer et al., 2005; Sitch et al., 2007). Dry deposition of O₃ to external plant surfaces is still not well understood, but the process is known to be at least as important as stomatal uptake, at least for mid-latitudes, and has been shown to increase with increasing temperatures (Altimir et al., 2004; Gerosa et al., 2005; Hogg et al., 2007; Mikkelsen et al., 2004). These surface effects have not yet been included in global models.

Implications for plant exposures to ozone

In addition to the implications for plant health of changes in O₃ concentrations and changes in climate, the implications of the climate/ozone interactions need to be considered (Ashmore, 2005; Bytnerowicz et al., 2007; Karnosky et al., 2005). One of the most important is the interaction with plant development, i.e. the relationship between the occurrence of peak O₃ concentrations and phenology. In general, it may be supposed that an overall increasing global mean temperature would advance the onset of budburst and flowering of many temperate plant species, as appears to be the case (Badeck et al., 2004). This has implications for O₃ effects if the timing of peak O₃ exposure is likely to change in future. In Northern Hemisphere mid-latitudes the peak in O₃ concentrations in unpolluted air is in spring, whereas the peak O₃ concentrations in polluted air are in summer. There will therefore be a shift in the coincidence between a particular developmental stage and maximum O₃ exposure which depends on the relative influence of polluted and unpolluted air at a site. If circulation patterns change, as predicted (Murazaki and Hess, 2006), then the seasonal patterns of O₃ concentration for a given site may in future be rather different from those observed over the past decade or so. So little is known at present about the relative sensitivities of the different stages of plant growth and development across different species that it is not possible to predict whether changes in patterns of O₃ exposure will be positive or negative (Emberson et al., 2000).

Apart from alterations in timing, the potential effects of other aspects of a changing climate on O₃ effects can be predicted with slightly more certainty. Increased temperatures are likely to affect plant development (Pleijel et al., 2000), changing the period over which current indices of exposure are calculated. Drier conditions will decrease stomatal uptake of O₃ – a factor that is already apparent as important in interpreting different responses to exposure across Europe (from north to south), as measured by an index like the AOT40 rather than one based on O₃ uptake rate. Increased CO₂ concentrations will tend to decrease stomatal conductance, and reduce O₃ uptake rates for similar exposures (Tausz et al., 2007). Increased CO₂ uptake may provide additional photosynthate for damage repair, thereby increasing the apparent threshold uptake rate of O₃ which can be tolerated, but no general relationship between CO₂ uptake rate and O₃ resistance has been demonstrated. Although there are some experimental indications that such an interaction operates in the field (Karnosky et al., 2003), too little is known yet to make generalisations across all vegetation types, even for Northern Hemisphere mid-latitude species and ecosystems. Perhaps the most important factor to draw from the modelling of ozone-climate interactions is the regional differences in O₃ and climate that are predicted. For example, increased humidity over the central U.S. may have a strong effect on stomatal conductance and uptake of O₃, even though predicted O₃ concentrations and exposure in that region may not increase very greatly (Murazaki and Hess, 2006).

One of the interactions that has received very little attention is the predicted large rise in concentrations in the atmosphere of photo-oxidants other than O₃. Although generally higher temperatures are likely to reduce concentrations of peroxyacetyl nitrate (PAN) (Stevenson et al., 2005), large increases are predicted in concentrations of the hydroxyl (OH) and hydroperoxyl (HO₂) radicals, and hydrogen peroxide (H₂O₂) (Murazaki and Hess, 2006; Stevenson et al., 2005). Although these highly reactive chemical species have not been demonstrated to cause deleterious effects under present-day conditions, the potential for future impacts is not known (Cape, 1997).

Conclusions

Increased emissions of O₃ precursors globally, and in particular in the rapidly developing region of south and east Asia, have raised concerns over regional O₃ production, and long-range transport throughout the Northern Hemisphere. These concerns have been fuelled by observations of increasing concentrations of O₃ at remote sites in the U.S. and Europe, particularly in winter. Regional controls on precursor emissions of NO_x, and particularly of VOCs, have produced little measurable effect on average O₃ concentrations, but have reduced the magnitude of peak O₃ concentrations during photochemical ‘episodes’. However, these changes are small relative to the inter-annual variability, which is strongly driven by climate, making the identification of consistent trends difficult.

Application of multivariate statistics to separate the effects of climate from a time trend have successfully accounted for much of the inter-annual variability, on the basis of temperature, humidity and a number of other site-dependent parameters. Removing these sources of variation has made it easier to detect the long-term underlying trends at sites influenced by polluted and unpolluted air. The results from these adjusted data are similar to those detected at remote sites – increases in low O₃

concentrations in winter, and a slowing down of the summer day-time increases that had been observed since the 1970s.

The use of chemistry-transport numerical models, on regional and global scales, has shown the extent to which inter-continental transport of O₃ and its precursors can occur. Ozone may be exported from polluted regions within the boundary layer, or precursors may be entrained into the free troposphere through deep convection, especially over continents, and transported around the globe, before eventually being brought back to the earth's surface. During transport, precursors react to form elevated O₃ concentrations.

Predicted (modelled) changes in emissions of precursors over the next 20-50 years imply serious increases in O₃ concentrations across the whole Northern Hemisphere, to levels that would significantly affect both natural vegetation and crop yields. However, on these time-scales it is also predicted (modelled) that there will be subtle but important changes in climate that will act to mitigate the effects of increased precursor emissions on O₃ formation. In particular, although increased temperatures are likely to increase emissions of biogenic VOCs (an important O₃ precursor), most O₃ production is limited by the availability of NO_x. Increased temperatures also increase the water vapour concentrations in the atmosphere, leading to faster O₃ destruction, greater production of OH radicals, and consequent faster oxidation of ozone precursors (VOCs and NO_x). However, O₃ concentrations are predicted to increase significantly in future, even taking into account climatic changes, in regions where NO_x concentrations are high, but may decrease where NO_x emissions are low.

The strong dependence of surface O₃ concentrations on weather patterns and year-to-year changes in climate means that inter-annual variability will continue to be a feature of O₃ exposure, making the detection of long-term trends difficult from measurements alone. Models have helped to separate the different confounding factors involved in linking emissions to O₃ production, and show the importance of regional climate and global circulation on the end result. However, the spatial scale of global models, particularly the vertical resolution, is still sufficiently coarse that accurate predictions of O₃ exposure cannot yet be made, even for present-day conditions, at spatial scales relevant to predicting effects at a specific site.

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