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# Ozone – the persistent menace: interactions with the N cycle and climate change

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Tropospheric ozone is involved in a complex web of interactions with other atmospheric gases and particles, and through ecosystem interactions with the N-cycle and climate change. Ozone itself is a greenhouse gas, causing warming, and reductions in biomass and carbon sequestration caused by ozone provide a further indirect warming effect. Ozone also has cooling effects, however, for example, through impacts on aerosols and diffuse radiation. Ecosystems are both a source of ozone precursors (especially of hydrocarbons, but also nitrogen oxides), and a sink through deposition processes. The interactions with vegetation, atmospheric chemistry and aerosols are complex, and only partially understood. Levels and patterns of global exposure to ozone may change dramatically over the next 50 years, impacting global warming, air quality, global food production and ecosystem function.

## Addresses

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## Introduction

Tropospheric ozone (O<sub>3</sub>) is unique among the gases which contribute to global warming (GW), in that as well as being the third most important anthropogenic greenhouse gas [1], it causes major health problems (both

directly and through products of ozone-related reactions), and also has strong interactions with vegetation and hence the carbon and nitrogen cycles [2,3,4<sup>\*\*</sup>]. Measurements and models both suggest that ozone has been increasing as a result of anthropogenic emissions. Indeed, the title of this paper reflects the identification of long-range transported ozone as a ‘mounting menace’ in the early 1980s [5], which still persists. Future trends in ozone are highly uncertain. Levels and patterns of global exposure to ozone are likely to change dramatically over the next 50 years, impacting GW, air quality, global food production and ecosystem function [6<sup>\*\*</sup>].

The range of issues to be discussed in this paper is sketched out in [Figure 1](#). A complete picture would be far more complex, but below we refer to relevant review articles which cover each topic in more detail. The italic letters in the section headings below refer to the pathways indicated in [Figure 1](#).

## Atmospheric chemistry ([Figure 1a,b](#))

Although produced naturally in the stratosphere, O<sub>3</sub> in the troposphere is mainly produced from chemical reactions involving organic precursors (CH<sub>4</sub> and non-methane volatile organic carbon, NMVOC), CO and nitrogen oxides (NO<sub>x</sub>, =NO + NO<sub>2</sub>). The biggest source of NO<sub>x</sub> emissions is from fossil-fuel combustion, but emissions from lightning, biomass burning and soil-microbes are also significant [*but highly uncertain*; 7,8<sup>\*\*</sup>,9<sup>\*</sup>]. Emissions of biogenic NMVOC (BVOC) are significantly greater than anthropogenic NMVOC; this source is discussed below.

Chemical processes, frequently enhanced by anthropogenic emissions, account for over 90% of ozone production, and almost 80% of ozone loss ([Table 1](#)). [Figure 2](#) illustrates some of the main reactions in connection to reactive nitrogen (Nr) species, as well as noting the dry and wet depositing compounds. This chemistry is complex in that many Nr species act as both sources and sinks of O<sub>3</sub> and other oxidants (see e.g. [10], or more descriptive summaries in [3]). In particular, NO is a direct sink of O<sub>3</sub> close to sources, but with sufficiently high NO<sub>x</sub> levels, O<sub>3</sub> formation is enhanced downwind. Ozone is a product of photo-chemistry, but also the main source of the key OH radical which controls the lifetime of many traces gases, the most important among these for GW being methane. At high NO<sub>x</sub> levels ozone production is sensitive to NMVOC compounds emitted from



Paasonen *et al.* [16\*\*]. Further, although BSOA is mainly associated with ‘natural’ VOC precursors, BSOA loadings have likely changed over the last century time as a result of changes in ozone (see Ozone trends section) and other factors [18]. Such assessments are complicated, however, by the influence of CO<sub>2</sub> and even ozone itself on BVOC emission rates, see below.

Ozone also impacts black-carbon (BC) aerosol, another key air-quality and (warming) RF component [19]. Increases in O<sub>3</sub> increase the rate at which oxidised compounds coat (or ‘age’) BC. Such aged BC is much more readily wet-deposited than fresh hydrophobic BC; faster aging would give lower residence times in the atmosphere [20], hence reduced RF. Aerosols also impact ecosystems in a number of ways (*c*) that can affect growth and hence CO<sub>2</sub> uptake beyond, for example, direct N<sub>r</sub>-fertilisation. Aerosols reduce total radiation reaching the surface, but increase the fraction of diffuse radiation relative to direct. Mercado *et al.* [21] estimated that variations in the diffuse fraction, associated largely with ‘global dimming’ enhanced the land carbon sink by approximately one-quarter between 1960 and 1999 [see also 4\*\*,20].

### Ozone impacts on primary productivity (Figure 1e)

Ozone is considered to be more damaging to vegetation than any other air pollutant [6\*\*], with significant effects on the growth of trees, semi-natural vegetation, and several important crops, including wheat, soybean and rice [6\*\*,23\*\*,24]. Globally, ozone is estimated to account for yield losses of between 3% and 20% for crops [25], and to reduce biomass production of northern hemisphere forest trees by ca. 7% at current ozone levels [26].

Reduced photosynthesis implies reduced uptake of ozone and CO<sub>2</sub>; allowing more of both to remain in the atmosphere, enhancing RF. This indirect warming effect of ozone may contribute as much warming as the direct radiative effect of O<sub>3</sub> itself [2] and for NO<sub>x</sub> and VOC emissions, ozone impacts on the carbon cycle are the dominant contributor to changes in global surface temperature [22].

It should be noted though that all estimates of these indirect effects of O<sub>3</sub> are built upon a number of uncertain assumptions. For example, Kvalevag and Myhre [27] suggest that inclusion of N-limitation effects on plant growth would reduce the negative effect of O<sub>3</sub> on carbon uptake by a factor of four, and RF by a factor of six compared to earlier studies. This study may however have underestimated ozone effects as it did not account for the important effect of ozone on leaf-senescence/shedding.

### Phyto-toxic ozone metric, POD<sub>Y</sub>

Within the scope of the LRTAP Convention,<sup>1</sup> the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) has been instrumental in developing ozone risk methodology for Europe. In the last decade, a new metric for assessing cumulative ozone uptake through stomata, POD<sub>Y</sub>, (Phyto-toxic Ozone Dose over threshold Y nmole m<sup>-2</sup> s<sup>-1</sup>) has been developed by ICP Vegetation [28–30] (Figure 3). POD<sub>Y</sub> takes into account the instantaneous effects of climatic factors (temperature, humidity, light, soil moisture) and plant factors (growth stage) on the amount of ozone that is taken up by the plant. Unlike earlier metrics which were based upon O<sub>3</sub> concentration rather than uptake, POD<sub>Y</sub> typically has lower values in hot, dry conditions (reflecting stomatal closure) whilst often having relatively high values in central and northern climates that are highly conducive to stomatal uptake, leading to a more even map of ozone-risk across Europe than given by concentration-based approaches [31]. This is also more consistent with field evidence [23\*\*].

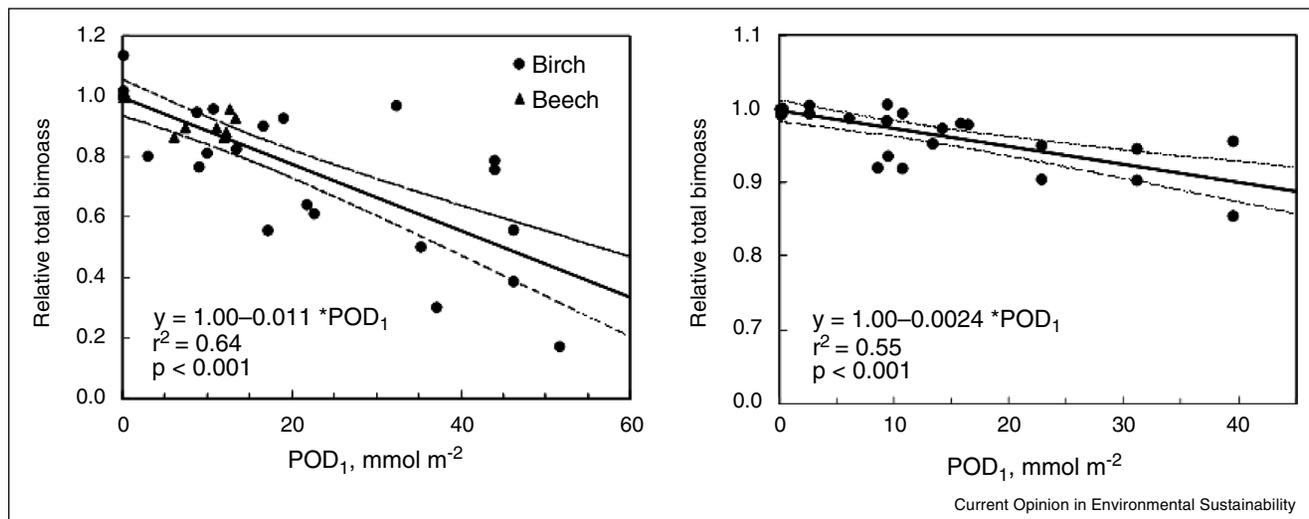
### Forests

Although peat-wetlands accumulate tremendous amounts of C over millenia [4\*\*], forest ecosystems have the greatest C sink capacity over time-scales of decades to centuries [32]. Therefore we here focus specifically on evidence of ozone effects on forest productivity.

Several methods have been used to determine effects of ozone on forests, with the most common being open-top chambers (OTCs, usually ca. 3 m diameter and ca. 2.5–3 m high) in which juvenile trees (≤10 years) are exposed to controlled concentrations of ozone, usually under ample water supply. Deciduous trees are found to be more responsive to ozone than conifers within these systems [e.g. 29] (Figure 3). The challenge has been to relate effects detected in juvenile trees growing in a non-competitive OTC environment to effects in real forest stands. Until now, there have been only two ecologically realistic free-air O<sub>3</sub> enrichment experiments in forests. In the largest of those, the so called Rhinelander Aspen FACE experiment in Wisconsin, stands with northern hardwood tree species were exposed to 50% elevated O<sub>3</sub> and/or CO<sub>2</sub> concentrations over 11 years [33\*\*]. At the end of the experiment, total tree biomass and ecosystem carbon content were reduced by 16% and 9%, respectively, in elevated O<sub>3</sub>. Negative effects on productivity diminished towards the end of the experiment, possibly because of altered tree community composition in favour of O<sub>3</sub> tolerant genotypes [34,33\*\*]. There was no evidence of elevated CO<sub>2</sub> modifying productivity responses to elevated O<sub>3</sub> [33\*\*]. Reductions in biomass production per unit POD<sub>Y</sub> were of similar magnitude in this free-air

<sup>1</sup> The Convention on Long-range Transboundary Air Pollution, www.unece.org/env/lrtap.

Figure 3



The relationship between the relative total biomass and  $POD_1$  for sunlit leaves of (a) birch (*Betula pendula*) and beech (*Fagus sylvatica*) based on data from Finland, Sweden and Switzerland, and (b) Norway spruce (*Picea abies*) based on data from France, Sweden and Switzerland. The dashed lines indicate the 95%-confidence intervals; note the different starting point of the Y-axis for Norway spruce. From the so-called 'Mapping Manual' ([http://www.icpvegetation.ceh.uk/manuals/mapping\\_manual.html](http://www.icpvegetation.ceh.uk/manuals/mapping_manual.html)); these data underlie the critical levels summarised in Mills *et al.* [30].

$O_3$  enrichment experiment (ca. 1% per mmole  $O_3 \text{ m}^{-2} \text{ year}^{-1} POD_{1,6}$ ; biomass data in [33<sup>\*\*</sup>],  $POD_{1,6}$  data in [35]) as in the juvenile beech and birch experiments of Karlsson *et al.* [29] (1.2% per mmole  $O_3 \text{ m}^{-2} \text{ year}^{-1}$ ).

In another free-air  $O_3$  experiment in a 50-year to 70-year old mixed beech and spruce forest in southern Germany, five trees of each species were exposed to experimentally doubled  $O_3$  concentrations during eight years. Accounting for a pretreatment difference in productivity between the elevated  $O_3$  plot and the neighbouring control plot, it was concluded that elevated  $O_3$  strongly decreased stem volume growth in beech (−44%) but not in spruce [36]. Expressed per unit  $POD_1$ , the negative  $O_3$  effect on mature beech stem volume increments were larger than biomass reductions found in the OTC experiments with juvenile beech and birch experiments as used in LRTAP [30].

Another, thus far poorly explored, approach to estimate  $O_3$  impacts on forest productivity is to apply multivariate statistical methods to disentangle the effects of  $O_3$  from those of other environmental variables [37]. Other studies have detected short-term effects of elevated  $O_3$  on ecosystem  $CO_2$  fluxes as measured with eddy covariance (EC) techniques [38<sup>\*</sup>]. Indeed, the large network of sites measuring fluxes by EC offers a great potential for stand scale  $O_3$  impact estimation using multi-variate analysis. However, careful consideration of exposure and response indices and their temporal integration is needed, given

the cumulative impacts of  $O_3$  exposure on photosynthesis and stomatal conductance [e.g. 39, 40].

#### Stomatal sensitivity

Rising  $CO_2$  concentrations are likely to reduce stomatal conductance ( $g_s$ ) and have been expected to reduce ozone impacts by restricting stomatal uptake of ozone [6<sup>\*\*</sup>]. However, there is a growing body of evidence that the picture is more complex in a future environment with multiple stress factors. Chronic ozone exposure has been found to reduce stomatal sensitivity to environmental stimuli [e.g. 41], leading to either slower responsiveness or enhanced opening in several species and lower drought resistance [42]. This phenomenon has been measured in the field too; elevated  $O_3$  caused progressive loss of stomatal control over summertime transpiration in the Aspen FACE experiment [40]. Further, Sun *et al.* [40] attributed a significant proportion of spatial and temporal variation in late-season streamflow across six forested watersheds to  $O_3$  effects on transpiration.

This evidence, together with new results showing that ozone exposure can uncouple the critically important leaf processes of stomatal conductance and photosynthesis in the field [e.g. 38<sup>\*</sup>], is leading to a re-think over how ozone effects in a future changing climate should be modelled.

Finally, one common fallacy in connection with  $g_s$  is worth a mention; namely that changes in  $g_s$  (at least weighted by leaf-area) give proportional changes in evapotranspiration or other fluxes. Generally, the relationship  $\text{Flux} = g_s \times D$

(where  $D$  is some driving force, e.g. humidity deficit or concentration difference) is only true if the driver  $D$  is not affected by the flux, for example when near-canopy humidity levels are not affected by the changes in  $g_s$  for the vegetation under consideration. This point, and indeed links between  $g_s$ , water-vapour, and large-scale meteorology, is discussed in detail in Jarvis and McNaughton [43]. For ozone, the near-canopy  $O_3$  concentration driving the flux (here,  $D$  is near-canopy minus intercellular  $O_3$ , the latter usually assumed to be zero) is itself a function of the ozone-uptake, with higher  $g_s$  leading to lower near-canopy  $O_3$ , a classical negative feedback. For ozone, accounting for non-stomatal conductances is also critical [44].

### Links to N sequestration

Ozone-induced reductions in C-sequestration imply changes in N-sequestration also. C/N ratios in vegetation are reasonably well known (ca. 25–50, [8<sup>\*\*</sup>]). However, ozone impacts on tree foliage alter many below-ground processes involved in N cycling, including fine root production, mycorrhizal formation, nutrient acquisition by roots and soil respiration. For example, in the Aspen FACE experiments described above, ozone treatment generally decreased the N mass ( $g(N) m^{-2}$ ) of leaf litter thereby reducing N availability for microbial decomposition and subsequently whole tree N uptake [e.g. 33<sup>\*\*</sup>,45, and refs therein]. Conversely, deposition of Nr (Figure 1f) impacts C-sequestration, although the relationship is more complex than a simple fertilisation effect [4<sup>\*\*</sup>,46].

Ozone also has more subtle effects such as changing species diversity.

### Biogenic emissions (Figure 1h–k)

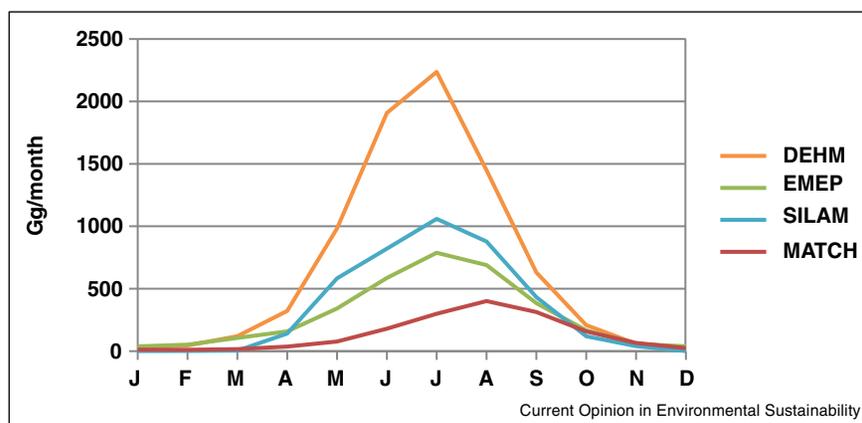
Globally, emissions of BVOC far exceed anthropogenic VOC emissions [47,48<sup>\*\*</sup>]. BVOC emissions play an

important role for ozone production [10] and for secondary organic aerosol [14,13<sup>\*\*</sup>,16<sup>\*\*</sup>,18]. Although there is some, possibly ‘illusory’, consensus on global emission rates of isoprene [47], emission estimates over smaller regions vary widely (Figure 4). The roles of BVOC and climate for future  $O_3$  and SOA formation are unclear. Climate change may well increase foliage in many areas, especially in the boreal and temperate regions [e.g. 49]. This, and direct temperature effects, might be expected to promote increases in BVOC emissions in future, and indeed many studies have thereby estimated notably increased emissions of BVOC, thus enhancing tropospheric  $O_3$  formation and SOA formation.

However, a number of studies have reported that higher  $CO_2$  levels will reduce BVOC emission rates [e.g. 48<sup>\*\*</sup>,50]. Arneth *et al.* [51,52] suggested that including the inhibition of  $CO_2$  on isoprene metabolism counteracts the warming/ $CO_2$  fertilisation effect and keeps BVOC emissions near current levels for long time scales into the future. Other studies have shown different overall effects, however; large uncertainties arise from both the ‘ $CO_2$ –BVOC’ algorithm that is used, and from assumptions about how changes in climate and  $CO_2$  concentration interact with vegetation growth [e.g. 53]. Calculations indicate a significant and regionally very heterogeneous effect on tropospheric ozone at the end of the 21st century [54]. The experimental basis for such predictions is at present too limited to draw firm conclusions; the sign of changes in BVOC and hence BSOA in future awaits new studies.

Other responses are also complex. For example, some BVOC species seem to play a role in reducing  $O_3$  concentrations in vegetation canopies [e.g. 55], thus protecting vegetation from the toxic effects of  $O_3$  [48<sup>\*\*</sup>]. It might therefore be speculated that BVOC emissions would

Figure 4



An uncertain input. Isoprene emission estimates ( $Gg C_5H_{10}/month$ ) from four chemical transport models. Data are for the European domain, using regional climate model meteorology for 2000–2009. From Langner *et al.* [71].

increase with increasing O<sub>3</sub>. However, both increases and decreases have been found [56]. Land use change, in particular in the tropics, can also significantly affect local and indeed global O<sub>3</sub> and SOA levels [52,57].

Loreto and Fares [48\*\*] have reviewed many other interactions (e.g. drought) of a wide range of BVOC; they state that ‘longer-term and field studies are still missing, and are deeply needed, to assess whether acclimation to higher temperatures will also affect future BVOC emissions’. This sentiment could be applied to many aspects of BVOC emission.

Finally, both Nr-deposition and ecosystem changes might affect soil NO (and C<sub>2</sub>O) emissions (*k*), with feedbacks to O<sub>3</sub> production [58]. An interesting new development is the recognition that GW might substantially enhance NH<sub>3</sub> emission rates, and hence Nr-deposition, above current forecasts [59,60]. The complexities of C–N interactions and soil–NO emissions are discussed elsewhere [4\*\*,61,8\*\*].

## Ozone trends

### ‘Baseline’ trends

Owing to its lifetime in the atmosphere (ca. 23 days, Table 1, [9\*]) the concentrations and long-term trends of ozone are the net result of a hemispheric ‘baseline’ level and more local/regional effects. Recent studies of baseline ozone [e.g. 62\*,63,64] paint a rather consistent picture of a rough doubling of O<sub>3</sub> from the 1950s in all sites in all seasons up to about the year 2000 followed by a decade with no growth or even reductions in O<sub>3</sub> at some sites in some seasons, particularly in summer. (Data before 1950 show much lower levels than in the 1950s, but these data are of uncertain quality and generality [7].)

Logan *et al.* [62\*] showed that at least some of the trends reported in the literature could be ascribed to problems with instrumentation, or were inconsistent in some way with other data. Data from three Alpine sites were determined to provide the most reliable trend data over Europe, with mean trends of 6.5–10 ppb for 1978–1989, 2.4–4.5 ppb in the 1990s. From 2000 onwards, ozone decreased by 4 ppb during the summer months, but with no significant trends in other seasons. The German mountain station Hohenpeisenberg [63] shows similar features. Recent studies also indicate a change in the mean seasonal cycle of the baseline O<sub>3</sub> with the seasonal maximum being shifted from summer to spring in recent years [65,64]. This could have important consequences for the ozone/vegetation interactions discussed above.

### European trends

In contrast to the consistent picture for the baseline studies, the results are more mixed for surface monitoring stations in Europe. Owing to the substantial reduction in European emissions during the last two decades (31% for

NO<sub>x</sub>, 46% for NMVOC [66\*]), a decline in O<sub>3</sub> levels is expected, but for many parts of the continent this is not seen. Colette *et al.* [67] found very good agreement between observed (Airbase data) and modelled monthly NO<sub>x</sub> levels for the period 1998–2007, but no systematic trends in O<sub>3</sub>. Wilson *et al.* [68] found significant increases in O<sub>3</sub> measurements (158 sites, 1996–2005) for the 5th-percentiles and 95th-percentiles (*p*<sub>5</sub>, *p*<sub>95</sub>) of hourly data for around half the sites, but the results were substantially influenced by individual years like the heat wave anomaly in summer 2003. Sicard *et al.* [69] found significant reductions in various O<sub>3</sub> parameters at Mediterranean sites for 2000–2010 for most analysed regions, particularly when looking at rural sites. Using rural background EMEP data over 1990–2010, Tørseth *et al.* [66\*] found a decrease in the highest levels (and a corresponding increase in the low percentiles) in the UK, Netherlands and some other sites, but no trends in Switzerland or Austria. For discussion of other studies, see [66\*].

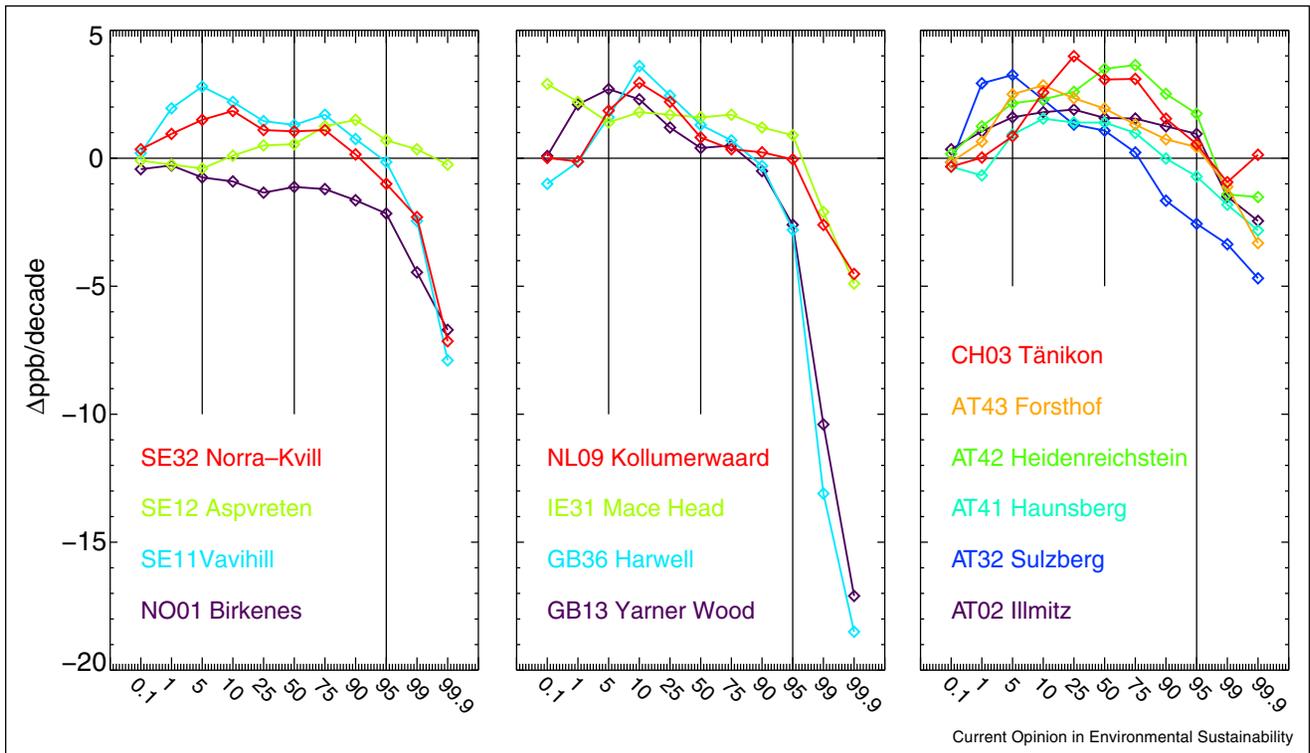
It is unclear whether the lack of trends can be explained by other physical processes counteracting the influence of the precursor emissions or if it is simply a problem with the ‘signal:noise’ ratio. The latter would indicate that the effect of the reduced precursors is masked by the large inter-annual variations in O<sub>3</sub>, caused by, for example, meteorology, or biomass burning events. One likely reason for the differences between studies is that the selection of time period is decisive for the trend estimates [70,62\*]. Thus, trend assessments become uncertain for networks with significant differences in the monitoring history for the various subregions. In addition, the trend estimates are determined by the choice of O<sub>3</sub> parameter (percentiles, mean values, etc.) and the methods applied (e.g. linear or quadratic). A key message seems to be that the time series need to be much longer than 10 years in order to distinguish a significant long term trend from inter-annual variability. Secondly, significant trends are mostly seen in the highest (*p* > 95) and lowest (*p* < 5) percentiles of the O<sub>3</sub> concentration distribution and not in mean values.

In order to illustrate the relationship between trends in different percentiles, Figure 5 shows the changes in the mean annual percentiles of O<sub>3</sub> from the decade 1990–1999 to 2000–2009 for EMEP sites. Results are shown for some Nordic, north-west Europe (Great Britain, Ireland, Netherlands), and central European sites separately. The results indicate significant regional differences within Europe with strong reductions in the highest percentiles (*p* ≥ 95) for the north-west Europe sites, variable results for the Nordic sites and very small changes for the central European sites.

### Future ozone

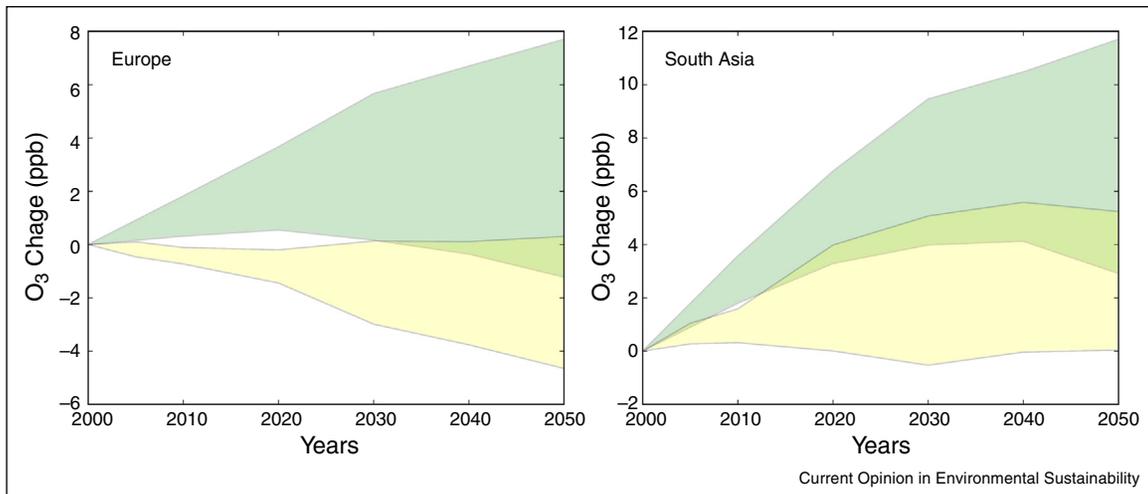
Although ozone may have important effects on climate change as discussed above, recent model studies suggest

Figure 5



The change in mean annual percentiles (of hourly ozone data) from the decade 1990–1999 to the decade 2000–2009, that is,  $P_x(2000s) - P_x(1990s)$ , where  $x$  ranges from 0.1 to 99.9, for selected European sites. Data and sites from [66\*], with a data-capture requirement of 75% completeness of hourly data in each year.

Figure 6



An uncertain future for ozone. Plots show estimates of future surface ozone in Europe and South Asia. The green area shows the range of  $O_3$  predicted from the IPCC 4th Assessment Report (SRES scenarios A2, A1B, B2, B1), and the yellow area gives the updated range using the IPCC 5th AR (RCP8.5, 6.0, 4.5, 2.6). Figure redrawn from Wild *et al.* [75].

low or modest impact of climate change on future ozone and/or N<sub>r</sub>-deposition [71,72,60]. The possibility remains however that future climate may be more extreme than used in these studies, which could change O<sub>3</sub> dramatically. The year 2003 provides a clear example, with severe ozone episodes and widespread drought in Central Europe [73]. Using regional climate simulations, Beniston [74] concluded that for ‘many purposes the 2003 event can be used as an analogue of future summers in coming decades in climate impacts and policy studies’.

Regardless of climate, the development of ozone in future is critically dependent upon emission changes. Figure 6 illustrates this with estimates presented by Wild *et al.* [75], in which the results of 14 global chemical transport models were parameterised so that surface ozone could be estimated from emissions of NO<sub>x</sub>, CH<sub>4</sub> and other precursors. The newer and more stringent ‘RCP’ emissions scenarios produce much smaller increases in O<sub>3</sub> than the older ‘SRES’ estimates. About 75% of the 5 ppb difference between the outlying RCP 2.6 and RCP 8.5 scenarios could be attributed to differences in methane abundance. There is clearly plenty of scope for emission control to change future ozone.

## Discussion and conclusions

Ozone is clearly involved with the N-cycles and C-cycles in a complex, and only partially understood way. Gas-phase atmospheric chemistry is reasonably well understood in principal, but emissions of especially natural VOC and NO precursors are very uncertain. The response of such emissions to climate change is unclear even with regard to the sign of the change. Changes in stratospheric–tropospheric exchange of O<sub>3</sub> may also affect future ozone, but uncertainties are again large [e.g. 9\*].

Ozone impacts on vegetation and hence N and C sequestration are also difficult to quantify, especially for forest ecosystems which are not amenable to small-scale and short-term experiments. There is a clear need to understand how ozone acts within the mix of climate, other pollutant, and biotic stresses (e.g. insect pests, fungal diseases) that occur now and are more likely in the future within natural or man-managed ecosystems. Many of the issues addressed above point to the need for better long-term monitoring data (e.g. of fluxes) in order to help untangle the complex web of interactions.

Modelling of the effects of O<sub>3</sub> on vegetation is dependent on improvements in the dose–response algorithms. A major challenge now is to take the POD<sub>Y</sub> approach to the next stage, incorporating effects of multiple stresses and climate change as well as the growing evidence of effects of ozone on stomatal functioning and the coupling with photosynthesis [see 6\*\*, and refs. therein].

The importance of ozone as a short-lived climate gas is receiving increasing attention, and mitigation of ozone through precursor control is seen as a promising strategy to help mitigate climate warming [3,19]. Some measures are complex however, with for example emission control of NO<sub>x</sub> likely to lead to warming in the short term (ca. 20 years) but cooling in the longer term [22]. Many studies stress the benefits of CH<sub>4</sub> control on a global scale, since emissions reductions are beneficial for most environmental issues.

## Acknowledgements

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Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest

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