## Review

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# Effects of ozone on agriculture, forests and grasslands

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The damage and injury that ground level ozone ($O_3$) causes vegetation has become increasingly evident over the past half century with a large body of observational and experimental evidence demonstrating a variety of effects at ambient concentrations on crop, forest and grassland species and ecosystems. This paper explores the use of experimental data to develop exposure-response relationships for use in risk assessment studies. These studies have typically identified the USA mid-West, much of Europe, the Indo Gangetic Plain in South Asia and the Eastern coastal region of China as global regions where $O_3$ is likely to threaten food supply and other ecosystems. Global risk assessment modelling estimates yield losses of staple crops between 3 to 16% causing economic losses of between US$14 to 26 billion in the year 2000. Changes in anthropogenic emissions of $O_3$ precursors in recent decades have modified $O_3$ concentration profiles (peaks versus background $O_3$) and global distributions with the Northern Hemisphere seeing increases in $O_3$ levels of between 1 and 5 ppb/decade since the 1950s and the emergence of Asia as the region with the highest $O_3$ concentrations. In the future, $O_3$ mitigation could focus on methane ($CH_4$) and nitrogen oxide (NOx) emissions; these will differentially influence global and local/regional $O_3$ concentrations and influence daily and seasonal profiles. The consequent effects on vegetation will in part depend on how these changes in $O_3$ profile alter the exceedance of detoxification thresholds for plant damage. Adaptation options may play an important role in enhancing food supply while mitigation strategies are being implemented. An improved understanding of the mechanisms by which $O_3$ affects plants, and how this might influence detoxification thresholds and interactions with other environmental

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variables such as water stress and nutrients, would help develop $O_3$ deposition and impact models to support the development of crop, land-surface exchange and ultimately earth system models for holistic assessments of global change.

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## 1. Introduction

Tropospheric ozone ($O_3$) occurs naturally in the environment but industrialization has seen a steady increase in $O_3$ pollution as anthropogenic emissions of nitrogen oxides (NOx), carbon monoxide (CO), non-methane volatile organic compounds (NMVOCs) and methane ($CH_4$) have led to the formation of $O_3$ through photochemical reactions. This has caused $O_3$ levels to increase from concentrations of less than 20 ppb in pre-industrial times [1] to current levels that have increased Northern mid-latitude average $O_3$ concentrations to 30–50 ppb [2]. Since the 1950s mean $O_3$ concentrations have been growing at a rate of 1–5 ppb/decade in the Northern Hemisphere (NH) and by 2 ppb/decade in the Southern Hemisphere (SH) [2]. As these concentrations have risen, evidence of $O_3$ injury and damage to vegetation due to the phyto-toxic nature of $O_3$, has also increased substantially over the last half-century [1]. The fact that $O_3$ is a secondary pollutant leads to significant geospatial and temporal variability in $O_3$ concentrations caused by conditions such as downwind proximity to large-scale emission sources, meteorological patterns (such as seasonality, land-coastal processes and monsoon systems) and stratosphere–troposphere exchange. This means that $O_3$ concentrations tend to be highest in rural and semi-rural areas downwind of urban and industrial sources of pre-cursor emissions, i.e. in those locations important for agriculture, forestry and grasslands, along with the ecosystem services they provide [3]. $O_3$ and its precursors are also transported around the world in air masses; when $O_3$ degradation (by chemical transformation and deposition) is slower than $O_3$ generation, background $O_3$ concentrations will be enhanced. These global processes influence local-to-regional $O_3$ concentrations (including the duration, frequency and magnitude of $O_3$ levels), all of which are important in determining vegetation response.

The earliest records of $O_3$-induced injury to crops were in the 1950s as 'oxidant stipple' on grapevines near San Bernardino, California [4] and 'weather fleck' on tobacco plants in the eastern USA [5]. Injury was also observed on a mixed conifer forest in southern California [6]; these observed injuries coincided with rapid increases in population and industry in the Los Angeles basin post World War II [1]. Since these first recordings, a large body of observational and experimental evidence has been collected demonstrating a variety of $O_3$ impacts on ecosystems in North America, Europe and more recently Asia [2]. This wealth of data provides ever-greater opportunity to understand and predict the cascade of effects that occur when $O_3$ exposure damages vegetation over extended periods. This review sets out what we know of the impacts of $O_3$ to crops, forests and grasslands including physiological, individual and ecosystem level responses. The review describes the evolution of metrics to identify target levels of atmospheric $O_3$ exposure, which has resulted in the development of new, more biologically relevant, flux-based methods to assess $O_3$ risk and damage to vegetation to inform emission reduction policy. The knowledge obtained from conducting these assessments is considered in relation to opportunities for mitigation and adaptation, providing insight on future research priorities to develop an improved understanding of those plant processes (from physiology to ecosystem level) that are influenced by $O_3$ and may have wider ecosystem-level implications. This will support the development of future risk assessment methods to determine the scale and magnitude of $O_3$ effects on a variety of ecosystems services that include crop yield, carbon sequestration, water provision and biodiversity. It will also inform the development of crop, land-surface exchange and earth system models that can assess the effects of stresses such as $O_3$ in the context of broader, global environmental change.

## 2. O₃ effects on agriculture, forests and grasslands

### (a) Agriculture

Arable agriculture, particularly the staple crops, is the most studied vegetation type for $O_3$ impacts. This is in part due to crops having been the focus of two coordinated regional efforts: the North America Crop Loss Assessment Network (NCLAN) [7] and the European Open Top Chamber programme [8]. These programmes used open-top chambers with standardized experimental protocols to assess the effects of a targeted range of pre-industrial, ambient and elevated $O_3$ exposures on crop growth, development and yield. The results from these programmes, coupled with additional studies that have been conducted since the 2000s in Asia, describe crop responses to $O_3$ which have been widely analysed and reviewed, e.g. [9–11]. These reviews show that $O_3$ causes a variety of responses including visible injury, reductions in Rubisco activity, chlorophyll content and photosynthesis and alterations in stomatal conductance ($g_{sto}$), alterations to carbon (C) allocation including decreased root:shoot ratios, and reductions in biomass and yield quantity and quality. A meta-analysis of studies on the effects of ambient versus pre-industrial $O_3$ levels found wheat yield losses of 8.4% demonstrating a significant and consistent crop response to current ambient $O_3$ concentrations [12]. In recent years, $O_3$ effects on crop quality have received more attention; the importance of these effects for global protein production were highlighted through estimates that current day $O_3$ levels could be reducing soya bean seed protein yield by 200 kg protein per hectare compared with pre-industrial levels [13].

Epidemiological studies detected the influence of $O_3$ in national level agricultural production statistics [14,15]. These studies use statistical multiple linear regression models to analyse 5–30-year time series of historical data to explore the relationship between past crop yield outcomes and trends or inter-annual variations in weather variables (e.g. monthly temperature and precipitation) and $O_3$ pollution (described by a particular vegetation $O_3$ metric, see §3a). A study on soya bean growing across the mid-west USA over a 5-year period was able to detect a 10% reduction in yield [14]. By contrast, only a 0.54% decrease in yield with a 10% increase in $O_3$ concentrations (characterized using the AOT40 metric (see §3a)) was found at wheat trial sites across the UK over a 13-year period, lower than would be expected according to experimental data [15]. Understanding such discrepancies is important and may be due to the influence of confounding factors (e.g. high temperatures and reduced soil water that tend to co-occur with $O_3$ and themselves cause yield losses), the inadvertent selection of resistant crop cultivars, and the use of $O_3$ metrics that may not estimate damage accurately.

Finally, studies have not only been confined to arable agriculture, $O_3$ effects on the yield and quality of component species of productive grasslands used for animal grazing have also been identified (e.g. [16]). Impacts on grasslands arise both from an $O_3$-induced reduction in the legume fraction [17] as well as from alterations in the feed quality of pasture, often measured as 'Relative Feed Value' [18].

However, even for agriculture there are substantial gaps in our knowledge with many species, especially those more commonly grown in tropical countries, having been less widely studied, even though evidence suggests growing conditions in these global regions may enhance $O_3$ sensitivity [19]. There is also substantial variability in the response to $O_3$ between cultivars of the same species, the reasons for which are not fully understood [20,21]. Studies have also suggested that $O_3$ can reduce the grain yield return from nitrogen (N) fertilizer applications which may increase the risk of N loss to the environment [22]. Finally, there is uncertainty as to how $O_3$ may influence crop response to abiotic (e.g. temperature, soil water, soil fertility [23], and biotic stresses (pests and disease [9])).

### (b) Forests

Our understanding of $O_3$ effects on temperate and boreal forests is also relatively strong, based primarily on studies conducted in North America and Europe [1,24]. Observational studies found

substantial $O_3$ impacts in the forest ecosystems of the San Bernardino Mountains and Sierra Nevada of southern California, the Appalachian mountains of the eastern USA and forests of Germany and eastern France [1,25]. This led to more focused and coordinated open-top chamber experimental studies on tree seedlings and saplings in the USA [26] and Europe [25] during the 1990s.

Together, observational and experimental studies have identified a substantial variety of $O_3$ impacts on forests, trees and ecosystems which have been extensively reviewed (e.g. [1,26,27]). These reviews show visible injury symptoms including chlorophyll degradation, chlorotic mottling and premature senescence. $O_3$ also affects physiology including reductions on photosynthesis and gsto, and can lead to accelerated leaf senescence and foliar loss of macro- and micro-nutrients and shifts in allocation to enhance above-ground biomass. These effects impact whole tree growth and productivity [28] and cause increased mortality. Wider ecological consequences include changes in forest stand composition and community structure (with $O_3$-tolerant species being favoured), alteration in forest successional pathways, and changes in species dominance of understory vegetation influencing drought and fire suppression. Ozone has also been found to increase forest susceptibility to drought, wind throw, as well as insect and pest attack (e.g. bark beetle, wood borer, fungal infection). Finally, $O_3$ was found to reduce late season stream-flow at six forested watersheds in the southeastern USA by as much as 23% based on analysis of 18–26-year data records [29]. The authors primarily attributed this reduced stream flow to increased transpiration through other factors such as reduced root biomass and subsequent soil water uptake may have contributed. Were such changes in transpiration to occur over sufficiently large areas, there may be implications for surface energy balance [30].

A meta-analysis of 263 peer-reviewed articles explored the effect of elevated $O_3$ (an average of 64 ppb) on northern temperate and boreal trees and found a decrease in tree biomass of 11% compared with trees grown at ambient $O_3$ [31]. In addition, significant reductions in root:shoot ratio, leaf area, Rubisco and chlorophyll content, transpiration rates, tree height and stem diameter were also found. Empirical evidence also suggests that deciduous tree species may be more sensitive to $O_3$ than evergreen coniferous species [32,33], which may be due to the higher rates of gas exchange [34] or reduced detoxification ability [35] of deciduous species. There is far less evidence to robustly quantify impacts of $O_3$ on forest types that fall outside the category of NH temperate and boreal forests, although recent studies have identified sensitive tree species of Mediterranean regions [33] and subtropical Chinese forests [36].

There have been two important long-term experimental studies on forest trees that have used free air concentration enrichment (FACE) systems. These systems allow studies on more mature trees, covering longer lifespans and on plant competition and multi-level trophic effects. Aspen FACE exposed hardwood tree species (trembling aspen, paper birch and sugar maple) of the northern USA to 50% elevated $O_3$ and/or $CO_2$ concentrations over 11 years [37]. This study found that $O_3$ exposure initially led to reductions in total tree biomass and ecosystem carbon content by 16% and 9%, respectively, under elevated $O_3$. The study also found that $O_3$ offset $CO_2$-stimulated growth of both trembling aspen [38] and paper birch [39]. However, after 12 years the long-term effect of elevated $O_3$ on net primary productivity (NPP) may be smaller than expected, possibly due to altered tree community composition in favour of $O_3$-tolerant genotypes [40]. The second major experimental study was 'Kranzberger FACE', a study in southern Germany which exposed trees in a mature stand (50–70 years old) of European beech and Norway spruce (five trees of each species) to twice ambient $O_3$ concentrations over 8 years [41]. Elevated $O_3$ was found to decrease stem volume growth in European beech by 44%, and to shift resource allocation from stem diameter to height growth in European beech and Norway spruce [42].

There remain substantial gaps in our knowledge of $O_3$ effects on forest trees. Many of the experimental studies have been conducted on young trees (seedlings or saplings) leading to large uncertainty on how $O_3$ effects on young trees might scale to mature trees [43]. These scaling issues further confound our understanding from empirical data on how $O_3$ affects C allocation and architectural structure of the roots, stem and canopy. Additionally, one of the key challenges to understanding forest ecosystem response is the lack of clarity on how $O_3$ affects competition

between species and how this might vary by life stage, species composition, tree density and leaf area distribution in space and time [44]. Finally, we are still unable to explain the mechanisms and processes behind the variability in the sensitivity of different forest tree genotypes, species and functional types to elevated $O_3$, although unifying concepts have been put forward suggesting the importance of gas exchange, leaf lifespan and leaf mass [34,43,45].

## (c) Ecosystems

The vast majority of research investigating grassland responses to $O_3$ comes from Europe, with little experimentation done in the USA, even less in Asia and none in the tropics [24]. Thus, compared to trees and arable crops, much less is known about how grasslands are impacted by current and future $O_3$ concentrations. Grasslands can be highly diverse, multi-species communities, with a wide range of productivities. Therefore, predicting a general response of grasslands to $O_3$ is complex, dependent upon the stress history of the community, the sensitivities of individual species, the mutualistic and/or competitive interactions between species and the specific microclimatic conditions to which individual species are exposed that will influence $O_3$ exposure and sensitivity. While experiments have shown decreases in productivity from elevated $O_3$ [46,47], other experiments on permanent temperate [48], calcareous [49] and alpine grasslands [50] have shown that NPP of these systems is relatively resilient to elevated $O_3$. For example, one of the longest running (7 years) experiments currently performed explored the combined effects of N deposition and $O_3$ free air concentration enrichment on the species composition of a subalpine Geo-Montani-Nardetum pasture at 2000 m a.s.l. in the Central Alps. This study found that elevated $O_3$ in the presence or absence of additional N exposure had no detectable effect on functional group composition and productivity [51,52]. Grassland species have also been shown to respond differently to $O_3$ depending on competition [53] and $O_3$ can have carry-over effects on growth and overwintering of species [54]. Ozone can also have more subtle changes on C assimilation, leaf longevity, the growth and flowering of plants, pollination efficiency, biomass partitioning of grassland species and species composition and richness [24]. Effects that influence at the ecosystem level include changes in water flux regulation and plant pathogen development. Recent research is leading to a better understanding of effects below ground, including changes in soil invertebrates, plant litter quantity and quality, decomposition, and nutrient cycling and C pools [55]. All of these changes are likely to be slow and may take decades to become detectable [24].

## 3. Methods to assess $O_3$ impacts

Regional controls on precursor emissions in Europe and North America have led to reductions in peak $O_3$ concentrations over recent decades; however, $O_3$ episodes can still occur under particular climatic and $O_3$ precursor emission conditions that are high enough to cause damage to vegetation. Since the 1990s, a large portion of the anthropogenic $O_3$ precursor emissions are now coming from Asia [2,56]. The influence of these changes in $O_3$ precursor emissions was apparent in the NH distribution of prevailing $O_3$ concentrations explored in a study of approximately 3300 $O_3$ monitoring sites [57]. This study found that between 2010 and 2014 the highest mean $O_3$ values were in the mid-latitudes of the NH, including southern USA, the Mediterranean basin, northern India, north, northwest and east China, the Republic of Korea and Japan. Furthermore, trend analyses conducted between 1995 and 2014 using various vegetation-relevant $O_3$ metrics found that the North America region was dominated by a significant decrease in $O_3$, while in Europe there was no change and in East Asia there was a significant increase in $O_3$ concentrations [57]. The findings from this study are consistent with other studies which show that vegetation exposure to $O_3$ in China in recent years is now greater than in any other region of the world [58].

Crucial to our ability to assess the injury, damage or risk caused by these ever-changing air pollution concentrations and regional distributions has been the development of robust $O_3$ vegetation damage metrics—essentially a means of characterizing those aspects of $O_3$ exposure

that are most important in determining $O_3$ damage. These metrics have been used to develop exposure-response relationships (ERRs) for different species, with regressions between the $O_3$ exposure metric and the response (most often defined as visible injury, yield or biomass), providing a useful statistical indication of which metrics most reliably capture $O_3$ injury and damage [59,60]. Experimental studies that control the $O_3$ concentration to which a receptor is exposed over a defined growth period have been widely used to define robust $O_3$ metrics and associated ERRs.

## (a) Ozone metrics and exposure-response relationships

Exposure-response relationship data from multiple experiments, locations and years can be pooled from studies that use a common approach to defining pollutant exposures and plant response allowing the development of robust ERRs. The experimental programmes that were conducted in North America and Europe during the 1980s and 1990s provided an excellent source of data for establishing ERRs [7,8] since they were conducted using standardized filtration and fumigation experiments at multiple locations and focused on key response parameters (i.e. yield and biomass). The development of these EERs over recent decades has seen metrics that describe daylight and growing season $O_3$ characteristics evolve from the use of concentration-based to flux-based approaches [61]. Some of the common $O_3$ concentration-based metrics include: (i) daylight hour (7 h (M7) or 12 h (M12)) growing season average ozone concentrations; (ii) accumulated daylight $O_3$ concentrations above thresholds (e.g. AOT40 and SUM06) or; (iii) continuously weighted growing season averages (W126) to emphasize the higher $O_3$ concentrations. Weibull (M7, M12, SUM06 and W126) or linear (AOT40) ERRs have commonly been used to relate the metrics to damage (for further details see [57]). It is important to understand the capabilities of different metrics in capturing the effects of different $O_3$ concentration profiles. The seasonal mean metrics such as M7 and M12 work well when there is not too much variation in $O_3$ concentration profile (i.e. when $O_3$ concentrations consistently fall close to a mean growing season value) and when other environmental conditions (e.g. water stress, heat stress) are not limiting $O_3$ uptake. However, these metrics will confer less emphasis to the damaging effect of elevated $O_3$ concentrations during pollution episodes. Here, metrics such as AOT40 and SUM06 that accumulate concentrations above a threshold will be more suitable, again so long as environmental conditions are optimum for $O_3$ uptake. For these reasons, the use of flux-based metrics is now encouraged since they capture concentrations that are likely to cause damage to vegetation (i.e. that occur when $O_3$ concentrations will lead to effective $O_3$ uptake) and consider both chronic and acute $O_3$ concentrations that contribute equally to $O_3$ damage.

The flux-based approach estimates a species-specific gsto and combines this with an estimate of the leaf/canopy $O_3$ concentration to estimate stomatal $O_3$ flux over the sensitive part of a species-growing season. Stomatal $O_3$ flux is considered to provide a more biologically meaningful characterization of $O_3$ exposure to vegetation as it describes the $O_3$ dose (uptake) experienced by the plant [62] but also requires more detailed datasets (describing hourly meteorology), which limit the number of empirical datasets that can be reanalysed to provide flux-response data. The phytotoxic ozone dose above a threshold 'y' (PODy) is the flux-based metric that accumulates stomatal $O_3$ flux, above a threshold that is considered to cause no plant damage.

The ICP Vegetation Task Force of the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) has established a number of PODy ERRs through (re-)analysis of empirical datasets [63]. The development of these ERRs requires the use of a gsto model. Currently, multiplicative models are used to estimate gtso (e.g. [61]) as a function of species, phenology and environmental conditions (i.e. irradiance, temperature, vapour pressure deficit and soil moisture). Importantly, these flux-based ERRs have been shown to have stronger statistical relationships between PODy and response than concentration-based metrics such as AOT40 [33,59,60]. There is also some evidence that presenting flux on a leaf mass, rather than a leaf area basis, may further improve the tightness of the relationship between uptake and damage and also help to identify variation in $O_3$ sensitivity between species and plant functional groups [45].

These flux metrics rely on being able to assess the time over the day and the growing season when $O_3$ uptake causes most plant damage. This is when stomatal $O_3$ flux exceeds the detoxification capacity of the plant [64,65]. Musselman *et al.* [66] hypothesised that $O_3$ detoxification capacity varies diurnally (and most likely seasonally) with photosynthesis, which fuels the metabolic synthesis of antioxidants [66]. The existence of this detoxification capacity is also crucially important in determining how plants respond to changing diurnal and seasonal $O_3$ profiles. The current flux-based ERRs [67] estimate this detoxification capacity ('y' threshold) *via* empirical analysis [33,60]. An alternative approach involves cellular level process-based modelling whereby detoxification is determined by apoplastic ascorbate, which is modelled as a function of gsto, mesophyll cell wall thickness and tortuosity, chloroplast volume, apoplast pH and ascorbate to $O_3$ reaction stoichiometry [68]. Neither of these modelling methods consider the 'costs' of maintaining such defence mechanisms, which might be expected to require increased respiration rates [23]. Understanding how these detoxification rates might vary diurnally, seasonally and by species and genotype is crucial to our ability to define damage thresholds by $O_3$ metric. The existence and value of such thresholds have a substantial bearing on the effectiveness of emission reduction policy, as discussed in §5a.

Empirical flux-based models have their shortcomings. Firstly, there are uncertainties in estimating gsto, largely due to challenges in the parameterization of gsto models for different species, cultivars and ecotypes. This is further complicated by the fact that $O_3$ can both positively and negatively affect gsto depending upon species and $O_3$ exposure profile [69] and that $O_3$ can modify the stomatal responses of plants to naturally occurring environmental stresses such as drought (e.g. [70–72]). There are only a limited number of flux-based ERRs for yield and biomass effects (table 1). ERRs exist for four crop species (wheat, potato, tomato and rice), five forest tree species/types (beech/birch, poplar, Norway spruce and Mediterranean deciduous oak and Mediterranean evergreen species) and one grassland species (perennial ryegrass) with only three ERRs for species/species types outside of Europe, all of which are Asian species. Interactive effects of co-occurring pollution and environmental stress are not included and hence only the relative risk, rather than absolute damage to $O_3$ under multiple stress conditions, can be assessed [23]. Finally, these models only assess impacts to individual species and therefore are unable to infer the level of $O_3$-induced competition effects on forest and grassland communities evident from experiments. In spite of these limitations, both concentration- and flux-based ERRs have played an important role in enabling national, regional and global assessments of $O_3$ damage.

## (b) Risk assessment methodologies

There are three main approaches to using ERRs in geospatial risk assessments to inform air quality management. These methods combine interpolated or modelled $O_3$ concentration fields (and associated meteorological data where additional plant-based modelling is required such as estimation of gsto) with data describing the distribution, both temporally and spatially, of the vegetation type being investigated.

The first approach requires the establishment of target levels for $O_3$ exposure to calculate exceedance and assess likely risk. This approach has been most widely developed and applied for vegetation in Europe largely thanks to the 'effects-based' approach coordinated within the UNECEs CLRTAP [67]. For gaseous pollutants such as $O_3$, targets were defined as 'Critical Levels' (CLs) - 'the concentration, cumulative exposure or cumulative stomatal flux of atmospheric pollutants above which direct adverse effects on sensitive vegetation may occur according to present knowledge' [67]. These CLs are identified through statistical analysis of ERRs that consider how best to combine experimental data from multiple experiments, years and locations and how to allow for the pre-industrial levels of $O_3$ concentration ([67]; table 1). Critical levels are defined for a species- or vegetation-specific percentage effect that is statistically significant (which will vary dependent upon the 95% confidence intervals of the ERR) and have used both AOT40 and flux-based metrics. These CLs have supported the development of EU 'target values' for the National Emissions Ceiling Directive (NEC) that represent the legally binding emission reduction

**Table 1.** Characteristics of current flux-based ERRs and associated target level (e.g. critical levels) for species and species groups. N.B. For Europe, only those ERRs that have been established under the CLRTAP are included. PODy is the phytotoxic ozone dose accumulated above a threshold 'y', CL is the critical level (see text for further definitions).

| species of vegetation type | global region covered | POD 'y' threshold (nmol $O_3$ m$^{-2}$ PLA s$^{-1}$) | potential maximum rate of reduction (%) per mmol m$^{-2}$ PLA of PODy | response variable | potential effect at CL (% reduction) | CL (mmol $O_3$ m$^{-1}$ PLA) | reference |
|---|---|---|---|---|---|---|---|
| **crops** | | | | | | | |
| wheat | boreal, temperate & Mediterranean Europe[a] | 6 | 3.85 | grain yield | 5% | 1.3 | [67] |
| | | 6 | 3.35 | 1000-grain weight | 5% | 1.5 | [67] |
| | | 6 | 2.54 | protein yield | 5% | 2 | [67] |
| | subtropical China | 12 | 0.082 | grain yield | — | — | [73] |
| | | 0–18[b] | 0.0214 | whole plant biomass | — | — | [74] |
| rice | Japan[d] | 10 | 0.487 | grain yield | — | — | [75] |
| potato | boreal, temperate & Mediterranean Europe[a] | 6 | 1.34 | tuber yield | 5% | 3.8 | [67] |
| tomato | boreal, temperate & Mediterranean Europe[a] | 6 | 2.53 | fruit yield | 5% | 2 | [67] |
| | | 6 | 1.3 | fruit quality | 5% | 3.8 | [67] |
| **forest trees** | | | | | | | |
| beech/birch | boreal & temperate Europe[a] | 1 | 0.93 | whole tree biomass | 4% | 5.2 | [67] |
| poplar[c] | temperate, semi-humid continental northern China | 7 | 1.2 | whole tree biomass | 5% | 3.8 | [76] |
| | continental monsoon China | 7 | 0.56 | whole tree biomass | 5% | 9.8 | [77] |

(*Continued.*)

**Table 1.** (*Continued.*)

| species of vegetation type | global region covered | POD 'y' threshold (nmol $O_3$ m$^{-2}$ PLA s$^{-1}$) | potential maximum rate of reduction (%) per mmol m$^{-2}$ PLA of PODy | response variable | potential effect at CL (% reduction) | CL (mmol $O_3$ m$^{-1}$ PLA) | reference |
|---|---|---|---|---|---|---|---|
| Norway spruce | boreal & temperate Europe[a] | 1 | 0.22 | whole tree biomass | 2% | 9.2 | [67] |
| Deciduous Oak species | Mediterranean Europe[a] | 1 | 0.32 | whole tree biomass | 4% | 14 | [67] |
| | | | 0.45 | root biomass | 4% | 10.3 | [67] |
| evergreen tree species | Mediterranean Europe[a] | 1 | 0.09 | above-ground biomass | 4% | 47.3 | [67] |
| semi-natural vegetation | | | | | | | |
| temperate perennial grasslands | boreal, temperate & Mediterranean Europe[a] | 1 | 0.99 | above-ground biomass | 10% | 10.2 | [67] |
| | | 1 | 0.62 | total biomass | 10% | 16.2 | [67] |
| | | 1 | 1.54 | flower number | 10% | 6.6 | [67] |
| Mediterranean annual pasture | boreal, temperate & Mediterranean Europe[a] | 1 | 0.85 | above-ground biomass | 10% | 16.9 | [67] |
| | | 1 | 1.61 | flower/seed biomass | 10% | 10.8 | [67] |

[a]Further detail on biogeographical zones is provided in [67].
[b]Variable threshold defined as a function of gross photosynthesis.
[c]Differences between CLs likely due to different number and $O_3$ sensitivity of poplar clones used by [76] (five clones) and [77] (two clones).
[d]Rice plants grown and fumigated in glasshouses.

targets for all EU member states adopted in 2001 [79]. Similar approaches in the USA are referred to as 'National Ambient Air Quality Standards' (NAAQS), but these currently only exist to protect human health although a vegetation standard has been proposed [80]. At the global level, the World Health Organisation (WHO) recommends vegetation target values for $O_3$ based on the UNECE CLRTAP CL approach; these are based on the AOT40 metric since the WHO guidelines were established back in 2000. There are currently no official target values for vegetation outside of Europe. Some protection to vegetation may be afforded *via* human health standards for $O_3$ where these exist (a notable exception is India) although these may be less stringent than the standards needed to protect vegetation.

The second type of assessment uses ERRs to estimate the spatial extent and magnitude of damage. In addition to the $O_3$ concentration fields and vegetation distribution, statistics describing the actual yield or biomass of crop and forest species are required to estimate damage in relative terms. As well as providing regional/global damage assessments (see §4) these risk assessments provide an opportunity to explore the ability of different metrics to estimate damage. For example, flux has been identified as a better predictor of the distribution and scale of damage for bio-monitoring and beech growth across Europe [62,81]. By contrast, neither flux-based nor AOT40 metrics could explain forest defoliation and declines in basal area increment in an Alpine region in northern Italy [82].

The third type of assessment incorporates ERRs into existing process-based modelling frameworks to allow the assessment of direct and indirect impacts of $O_3$ on growth, development and biomass/yield *via* changes in photosynthesis, C allocation and transpiration [23]. These models have $O_3$ directly or indirectly impacting on photosynthesis (and indirectly on gsto *via* coupling approaches) using a relationship between canopy conductance and gross primary productivity (GPP) so that GPP is ultimately limited by $O_3$ exposure according to an ERR (e.g. [83,84]). Often this approach uses land-ecosystem models and allows the interactive effects of $O_3$ with other environmental factors to be explored. There are some limitations with this type of modelling. Firstly, some use concentration-based threshold indices (e.g. AOT40) that ignore $O_3$ concentrations below thresholds which we know can contribute to damage. Secondly, the daily time step of some approaches precludes the capture of covarying factors that are known to determine actual levels of $O_3$ uptake. Thirdly, the use of season-long statistical relationships of $O_3$ response in combination with daily or monthly plant processes will miss interactions between $O_3$ uptake, detoxification and prevailing environmental conditions that will influence damage. Finally, these methods require robust and appropriate ERRs such as the response of photosynthesis to $O_3$ concentrations or PODy. This last aspect has been studied in relation to terrestrial ecosystem models for forest trees [85]. Substantial differences were found both in the ERRs used to describe leaf-level photosynthetic responses to $O_3$ and in the methods used to relate these ERRs to reductions in whole tree biomass. ERRs required re-parameterization before they were able to successfully simulate the whole tree biomass reductions found in $O_3$ fumigation field experiments.

## 4. Key findings from application of risk assessment methods

Even with the uncertainties in these concentration- and flux-based risk assessment methods they still provide useful information on risk and how this might change in light of emission reduction policies or climate change (the latter though only when using flux-based indices and only in relation to how climate variables would influence $O_3$ uptake).

### (a) Agriculture

A substantial number of modelling efforts have been conducted to assess the magnitude and extent of $O_3$ impacts on arable crops. The majority of these studies have used concentration-based $O_3$ metrics (M7 and AOT40) and hence should be treated with some caution since they are unable to allow for the modifying influence of environment on $O_3$ sensitivity; more recent studies
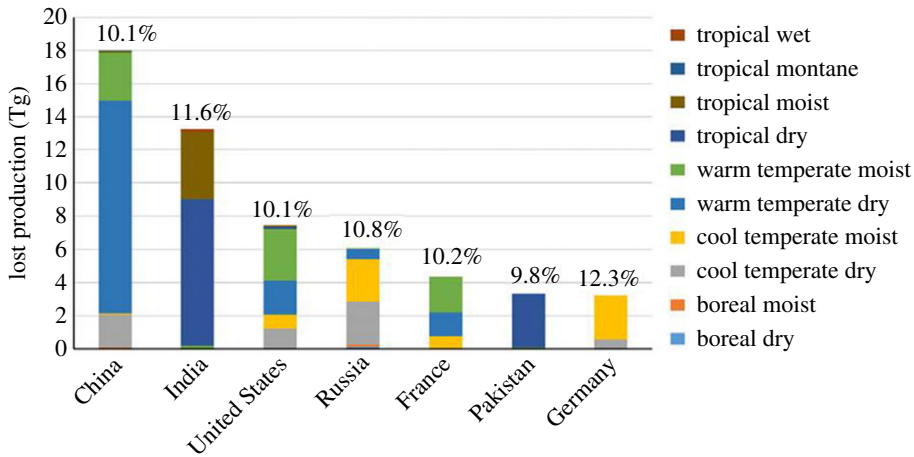
**Figure 1.** Production losses in wheat due to $O_3$ for the seven most affected countries allowing for irrigation. The mean percentage yield loss per country is provided above each bar. For further details see [93]. (Online version in colour.)

have used PODy. Studies assessing the exceedance of CLs have been largely limited to Europe and find exceedances of the AOT40 CL by a factor of three common in central and southern Europe; by contrast, the PODy exceedance tends to be more evenly distributed across Europe and only one to two times the CL [86]. A study that applied the AOT40 metric with CLs derived for rice and wheat from an OTC fumigation study conducted in the Yangtze River Delta [87] found exceedances of the CL by factors of approximately two and five across 75% and 83% of the rice and wheat growing areas, respectively [88].

Global-scale assessments of crop damage using ERRs suggest yield reductions for wheat, maize, soya bean and rice of between 3 and 16% which would translate into economic losses of $US 14–26 billion in the year 2000 [89,90]. These losses look set to worsen in the future with additional yield losses for wheat, soya bean and maize of between 0.1 and 11% globally by 2030 based on lower (B1) and upper (A1) IPCC SRES emission projections to 2030 [91]. More recent ERR damage studies for wheat using PODy have importantly allowed an analysis of the biophysical conditions associated with elevated $O_3$ concentrations that will most likely to lead to damage. Relative yield losses for wheat of approximately 6–15% for China and approximately 8–22% for India were found using the flux-based method with the warmer regions of India identified as having particularly high yield losses [92]. Global wheat yield and production losses for 2010–2012 were found to be particularly large in humid rain-fed and irrigated areas of major wheat-producing countries (e.g. USA, France, India, China and Russia) with reductions of approximately 10 and 6% in the NH and SH, respectively [93]. Highest yield losses were found under biophysical conditions that enhanced stomatal uptake of $O_3$, the warm-temperate-moist, tropical-moist and tropical-wet climates of the NH (estimated as having 12–17% mean yield losses) and the tropical-moist and -wet climates of the SH (with 9–11% mean yield losses). Figure 1 shows how these biophysical regions spilt out across the countries most affected by $O_3$-induced yield losses, clearly identifying China and India as having the majority of warm temperate dry and tropical dry conditions which suffer production losses [93]. Findings also showed that $O_3$ could reduce the potential yield benefits of increasing irrigation usage in response to climate change as added irrigation increases $O_3$ uptake and damage. This study clearly shows the opportunities afforded by the flux-based metric in identifying biophysical conditions that might enhance $O_3$ sensitivity.

Application of the ERRs within process-based models find that the effect of $O_3$ on productivity (often defined as GPP or NPP) is generally greater than that resulting from the change in climate when both are considered over time periods of a number of decades. For example, a larger effect of $O_3$ on NPP ($-2.6$ to $-6.8\%$) was found for the USA during the late 1980s and early 1990s than that caused by the long-term trends (1950–1995) in climate variability ($-1.6\%$) [95].

Environmental conditions that would support elevated $O_3$ levels are often likely to co-occur with high temperatures and soil water stress. A study of $O_3$-drought interactions in China found that climate variability and $O_3$ together led to an annual mean reduction of crop yield by 10% during 1981–2010 [96]. Crop response to air pollution and climate variables will likely occur under a variety of crop management practices and in combination with regional scale land-use change. Simulations were conducted to explore the interactive effects of elevated $CO_2$ concentration, climate variability, change in land use (with and without N fertilization), and $O_3$ (*via* direct effects on GPP based on the AOT40 index) on crop productivity across the USA for 1950–1995 [95]. This simulation study found that both $O_3$ and climate change effects were substantially less than the influence of agricultural management (+46.2%) and change in land use (−26.8%) on C sequestration. Similarly, a study of agricultural NPP found increases between 1980 and 2005 that were predominantly due to changes in management practice (application of fertilizer) but that these increases would have been greater in the absence of the combined effect of climate change and $O_3$ [97]. Since $O_3$ stress often coincides with other common stresses impacting agriculture (i.e. heat stress, pests and diseases, aridity and nutrient stress), especially in locations such as China, India and the USA, it is becoming ever more important that we improve our understanding of the impact of these stress combinations on productivity [94].

## (b) Forests and grasslands

The complex nature of forest systems with their multi-decadal life span, mix of species within a forest stand, variable age structure and community dynamics, coupled with the fact that ERRs are established for annual changes in whole tree biomass, mean that regional risk assessments using ERRs alone have to date been limited to estimating potential relative risk. A comparison of the spatial extent of risk inferred from application of different metrics found that flux-based metrics reduced both the spatial gradient and relative risk to forests across Europe when compared with concentration-based AOT40 metrics for the year 2000 [86]. Emission reductions according to a current legislation scenario dramatically reduced relative exceedances by 2020 although CLs for forests were still exceeded across most of Europe. A similar study in China found that AOT40 exceeded the CL on average by about five times with higher risks in northern compared with southern tropical and subtropical regions of China [98]. Feng *et al.* [88] assessed $O_3$ damage to annual forest tree biomass growth across China using an AOT40 metric ERR developed for broadleaf deciduous forests from analysis of fumigation experiments on young European forest trees [33]. The study estimated $O_3$-induced reductions in growth of annual biomass of 11–13% finding a similar $O_3$ risk to evergreen broadleaf forests of (sub-) tropical China and deciduous temperate forests of north–central China. This was due to the longer growing season of the evergreen trees compensating for their exposure to lower $O_3$ concentrations. However, this study assumed evergreen tree response could be simulated using a deciduous tree ERR which is likely to overestimate damage.

Studies using ERRs in combination with process-based models have also been reported for forest trees. The interactive effect of $O_3$, $CO_2$ and N deposition on hardwoods was simulated using the PnET-CN model [99] and found that $O_3$ counteracts the effect of increased $CO_2$ and N deposition on forest growth and C sequestration in the northeastern USA. Similar results were found by a study that explored the relative contributions of changes in temperature, precipitation, $CO_2$ concentration, N deposition and $O_3$ exposure (the latter using the PODy metric) on European forest growth between 1900 and 2050 [100]. Compared with 1990 levels, this study estimated an increase of 41% in average total C sequestration in forests and forest soils between 1950 and 2000, which was predominantly due to increases in $CO_2$ concentration and N deposition. These simulations compared favourably, although were slightly lower than those observed in net annual increment data. From 2000 to 2050, growth is expected to decline with $CO_2$ and temperature playing the greatest role in encouraging growth, helped somewhat by decreases in $O_3$ exposure; decrease in N deposition was the main factor decreasing growth rates. Ideally, forest community dynamics would also be included in simulations of the impacts of $O_3$. A recent study explored
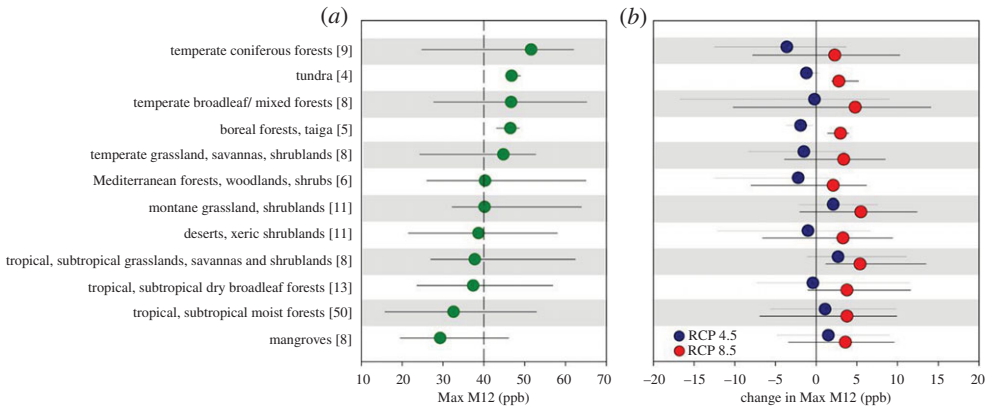
**Figure 2.** (a) Simulated $O_3$ exposure in 2000 in G200 terrestrial ecoregions (ERs). (b) Change in simulated $O_3$ exposure between 2000 and 2050 under RCP4.5 and RCP8.5. ERs are grouped by major biome, and the number of ERs in each biome is shown within brackets. For further details see [24]. (Online version in colour.)

the successional dynamics of species composition and structural change of a typical temperate deciduous forest in the southeastern USA [101]. The simulation was conducted for a 500-year period using an individual-based gap model that includes basic physiology as well as species-specific metabolic properties for 10 abundant species and 22 other species. The study found no reduction in forest productivity from elevated $O_3$ due to increases in the biomass of more tolerant species compensating for $O_3$-induced losses in sensitive species.

Due to the complexity of grassland ecosystems, studies have only assessed potential risk using concentration-based ERRs. An important global study explored the potential effects of current and future $O_3$ exposures (using the M12 metric) for Global 200 terrestrial ecoregions in 12 major biomes which included both forest and grassland biomes [24]. Figure 2a shows the range of mean M12 values within each major biome for the year 2000 based on the highest of four 3-month M12 means over the whole area of each ecoregion. Approximately 40% of the ecoregions had a mean M12 value above 40 ppb with the highest M12 values found in temperate forests and grasslands, boreal forests and tundra. Figure 2b shows the change in M12 from 2000 to 2050 for a range of emission scenarios (RCP4.5 and 8.5; IPCC [102]). For the more optimistic scenario (RCP4.5) the changes in biome mean M12 are relatively small (−3.6 to +2.7 ppb), and biome mean M12 values decline by 2050 in the temperate and boreal biomes, which had the highest M12 values in 2000, while mean M12 values for tropical, subtropical and montane biomes tend to increase. For the more pessimistic scenario (RCP8.5) increases of over 10 ppb in M12 were found in forests and grasslands, and in the region covering part of India, the Himalayas and western China. These are all regions identified as having high N deposition by 2030 [103], which highlights the need for improved understanding of $O_3$-N interactions in unmanaged systems [24].

Importantly, these risk assessments conducted for agriculture, forests and grasslands suggest that policies represented by the more optimistic scenarios do not always lead to a reduction in the spatial extent of $O_3$ risk. In fact, for some regions, particularly in Asia, the extent and magnitude of risks are likely to increase in the future [24,93]. Coupled with these increases in $O_3$ risk are changes in other stress factors such as enhanced N deposition [103], climate change and elevated $CO_2$ [102], which modelling suggests can have substantial impacts on modifying the sensitivity of vegetation to $O_3$ damage.

# 5. Future ozone trends and implications for vegetation

There are essentially two options available to reduce the damage to vegetation resulting from elevated $O_3$, the first is to reduce the concentrations of $O_3$ pollution in the atmosphere *via*

mitigation, i.e. a reduction in $O_3$ precursor emissions, and the second is to develop adaptation measures that reduce the adverse consequences of $O_3$ pollution.

## (a) Mitigation

The changes apparent in the global distribution of $O_3$ (see §3) clearly show a shift of $O_3$ precursor emissions towards Asia where the lower latitudes are expected to differentially increase the tropospheric $O_3$ burden due to the greater convection, reaction rates and NOx sensitivity of these regions [56]. It is also important to note that the particular precursor emissions driving $O_3$ formation vary globally depending upon the prevailing atmospheric pollutant composition. In polluted regions, $O_3$ formation is driven by the rapid photochemical oxidation of predominantly short-lived NMVOCs in the presence of NOx; $CH_4$ has little effect on the $O_3$ formed daily in urban plumes as it reacts very slowly (having a lifetime of 8–9 years). However, since $CH_4$ is well-mixed throughout the troposphere and is more abundant than all NMVOCs combined, anthropogenic $CH_4$ is estimated to contribute approximately seven times that of anthropogenic NMVOCs to the total tropospheric $O_3$ burden, being especially important in less polluted environments [104], and will result in an increase in background $O_3$ upon which local-to-regional $O_3$ builds. The interplay between $CH_4$ and $O_3$ is further complicated by the role that $O_3$ precursors play on $CH_4$ chemistry. NOx tends to increase hydroxyl radical (OH) concentrations, which reduce the lifetime of $CH_4$ and hence $CH_4$ concentrations. By contrast, CO, $CH_4$ and VOC emissions tend to reduce OH, increasing $CH_4$ concentrations. Understanding this chemistry, and how it varies geographically, seasonally and between polluted and non-polluted environments, is crucial to developing successful mitigation strategies. A source-attribution study investigated selected socioeconomic pathways (SSPs; [105]) and found that changes in $CH_4$ abundance, predominantly due to emissions from the energy, waste and agricultural sectors were the dominant drivers of changes in global surface $O_3$ (figure 3) [106]. By contrast, the study found that changes in emissions from energy, industry, transport and residential sectors were more important regionally [106]. This analysis highlights that local emission reductions are not always enough to reduce future regional surface $O_3$ concentrations and that hemispheric scale emission controls, particularly for $CH_4$, will be required to reduce long-range sources of $O_3$ and keep the regional surface $O_3$ below present-day concentrations.

This raises the question: What are the implications of different emission control options for vegetation damage? This is especially important given that the differential effects of $CH_4$ and NOx emission reductions on global versus regional-to-local $O_3$ concentrations will also affect the diurnal and seasonal $O_3$ concentration profiles. NOx controls will tend to reduce peak $O_3$ concentrations at the local scale due to the shorter lifetime of these chemical species in the atmosphere; such controls are often driven by the countries own self-interest; reductions in $CH_4$ will tend to reduce chronic (or background $O_3$ concentrations) [107]. It is also worth remembering that the longer lifetime of $CH_4$ leads to a slow $O_3$ response to control measures relative to NOx and NMVOC controls that would realize almost immediate effects. The removal of the entire anthropogenic $CH_4$ load by the year 2050 was found to reduce global $O_3$ crop damage (estimated using concentration-based metrics) by 26% leading to a 1% increase in global crop production of the four major staple crops (wheat, maize, rice and soya bean) [107]. These yield benefits correspond to a difference in global economic value for the four crops of US$ 4 to 7 billion, of which 40% is realized in East Asia, 20% in North America and 12% in Europe (based on 2000–2010 average crop production and producer prices). For such assessments, it is crucial that $O_3$ damage metrics are able to capture the influence of changing characteristics of $O_3$ profiles (diurnal, seasonal and spatial distribution). Key issues here are whether the $O_3$ metric has a threshold for damage and, if so, how close is the threshold to any changes in $O_3$ profile resulting from emission reductions. It is also important to know whether acute $O_3$ is more damaging than chronic $O_3$ when delivered as equivalent growing season $O_3$ exposures. It has been found that the AOT40 and PODy flux-based metrics respond quite differently to sets of changing $O_3$ profile over the course of 6 or more years [108]. The AOT40 metric, but not the PODy metric,
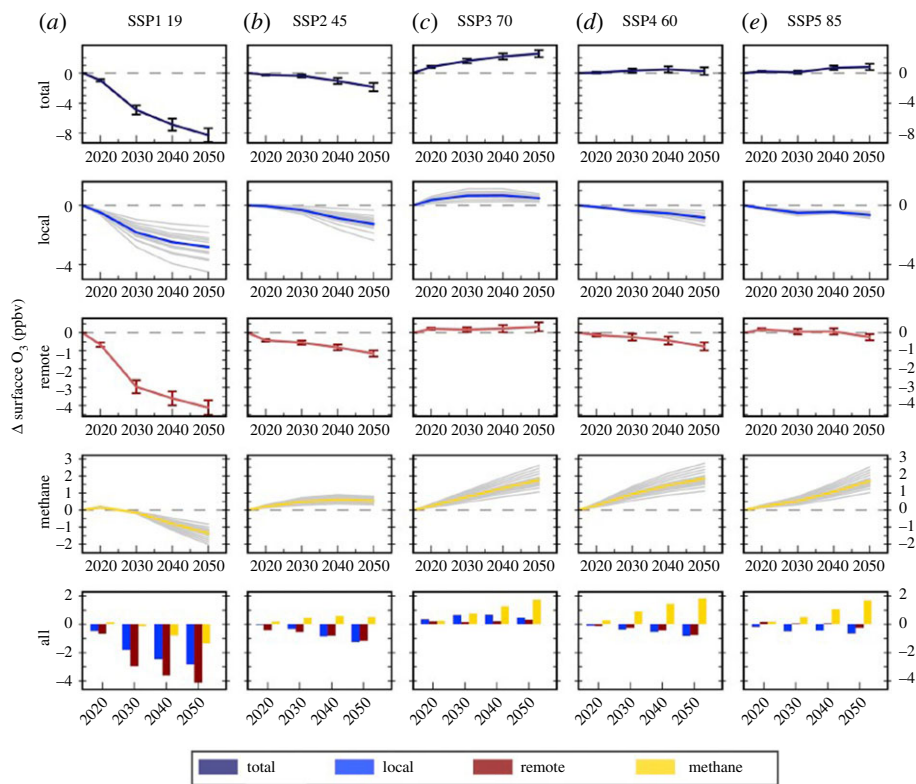
**Figure 3.** Total annual mean changes in regional surface $O_3$ concentrations over East Asia and the contribution of local (blue), remote (red) and methane (gold) sources between 2015 and 2050 from the parameterization for the CMIP6 emissions under the (*a*) SSP1 1.9, (*b*) SSP2 4.5, (*c*) SSP3 7.0, (*d*) SSP4 6.0 and (*e*) SSP5 8.5 scenarios. See [106] for further details. (Online version in colour.)

declined at a location (Harwell, UK) whose $O_3$ concentrations were driven by NOx emission reduction policy. By contrast, at a location more influenced by background $O_3$ concentrations (Auchencorth, UK), the PODy metric increased over time, an effect magnified for species with lower 'y' thresholds. The importance of the 'y' threshold level in determining the mitigation impact of global simulations of 50% emission reductions across all $O_3$ precursor source sectors has also been explored [109]. Larger benefits were found for C3 cropland, C3 grassland and C4 grassland (which have 'y' values of 5 nmol m$^{-2}$ s$^{-1}$) compared with deciduous broadleaf, evergreen needleleaf and shrub species with 'y' values of approximately 1.6 nmol m$^{-2}$ s$^{-1}$. These findings are particularly interesting when compared with the 'y' thresholds described in table 1 for the Asian species, which are often far higher (above 10 nmol m$^{-2}$ s$^{-1}$); using $O_3$ metrics with such high thresholds may reduce the perceived benefits of $CH_4$ emission reductions.

So which metric is most suitable for predicting damage for a wide variety of $O_3$ profiles? Evidence collected from wheat fumigation experiments found that PODy ERRs established under conditions of enhanced peak $O_3$ concentrations were also valid for higher background and lower peak concentrations, commonly associated with the current European $O_3$ profiles [110]. However, it has also been suggested that plants subjected to repeated exposures at low levels will become more resistant to later exposures [111], possibly due to changes in gene expression. It may also be that the longer the time period between high $O_3$ peaks, the more able the plant is to maintain normal plant growth and development. However, a long-term shift in energy allocation under continuous $O_3$ exposure may be less detrimental than long periods between acute temporary

exposures [1]. Further work is required to understand the influence of changing $O_3$ profiles in relation to detoxification thresholds and plant damage.

It is important to be aware that future $O_3$ concentrations will not only be dependent upon emission pathways. They will depend on changes in climate variables (particularly temperature, humidity and solar radiation) that will influence photochemical reaction rates, circulation and mixing of air masses [112]. Climate and land use-induced changes in biogenic VOC emissions as well as feedbacks caused by $O_3$ itself acting as a GHG will also influence $O_3$ production and loss in the atmosphere. As such, ecosystem geography and the meteorological and chemical atmospheric background composition in different global regions will all contribute to regional differences in mitigation impacts [109].

## (b) Adaptation

Adaptation options specifically designed to reduce $O_3$ impacts have not been widely investigated, most likely since $O_3$ also causes substantial damage to human health and is a GHG, so there are multiple benefits to be gained from mitigation control options [113]. In addition, adaptation is only really a feasible option for agricultural crops, which would leave forests and grasslands with no protection from prevailing $O_3$ concentrations. However, since evidence suggests that $O_3$ may cause substantial yield losses, especially in food-insecure regions in Asia, it is imperative to consider what options might be available or useful to enhance productivity while mitigation actions are implemented. Two types of adaptation options can be considered, technology options that might focus on crop breeding, for example of physiological traits that reduce $O_3$ sensitivity of different cultivars, and management practice options that would improve crop tolerance and avoidance of elevated $O_3$.

In relation to technology options, ERRs demonstrate the variation in sensitivity of cultivars of the same species to $O_3$ [20,21] and hence the potential to breed $O_3$-tolerant varieties. A recent review identified some challenges with two crop-breeding approaches considered suitable to provide $O_3$ tolerance in rice: marker-assisted selection and transgenic approaches [4]. The challenges identified were: $O_3$ heterogeneity across breeding trial sites, the 'small effect loci' genetic architecture of $O_3$ tolerance and the challenges in convincing farmers and breeders of the necessity of breeding for $O_3$ tolerance. However, ultimately the review emphasized that the substantial naturally occurring variability in $O_3$ tolerance of germplasm offered a very real possibility of breeding tolerant varieties. A number of plant traits have been identified that might contribute to improved $O_3$ tolerance, it is important to assess the synergies and trade-offs of such plant traits in relation to other well-known stressors that are likely to occur when $O_3$ levels are high (figure 4; [94]). Identified traits include those that reduce gas exchange (and hence $O_3$ uptake) while maintaining non-limiting levels of photosynthesis (i.e. traits that enhance water use efficiency (WUE)); such traits need to avoid trade-offs of reduced transpirational cooling (especially under co-occurring heat stress) and reduced soil nutrient uptake. Other traits might be those that enhance the detoxification capacity of plants while also minimizing any other gene-related trade-offs. Such traits could include breeding for high levels of antioxidants [114], for increased leaf mass per unit area (to lengthen the pathway and subsequent reaction time with apoplastic antioxidants and resistance to transport of $O_3$ (and its reactive oxygen species) to the cellular sites of damage [115]), and to increase functional redox balance [116], which may also help with defence against other abiotic stresses which cause damage through similar oxidative stress pathways [117]. Breeding plants to reduce the induction of programmed cell death, a key response to oxidative stress, could enhance $O_3$ tolerance [118] but would need to be balanced against unwanted interference with pathogen tolerance [94]. A focus on crop breeding to enhance root physiological traits to overcome the $O_3$ impact on root:shoot ratios supporting continued water and nutrient uptake ensuring high harvest indices and quality of harvestable products (e.g. sugar and protein contents) were also identified as important. Finally, phenology, that is already an important focus of many crop breeding programmes around the world [119], could help plants to avoid harmful $O_3$ exposures. For example, Indian cultivars with different heat
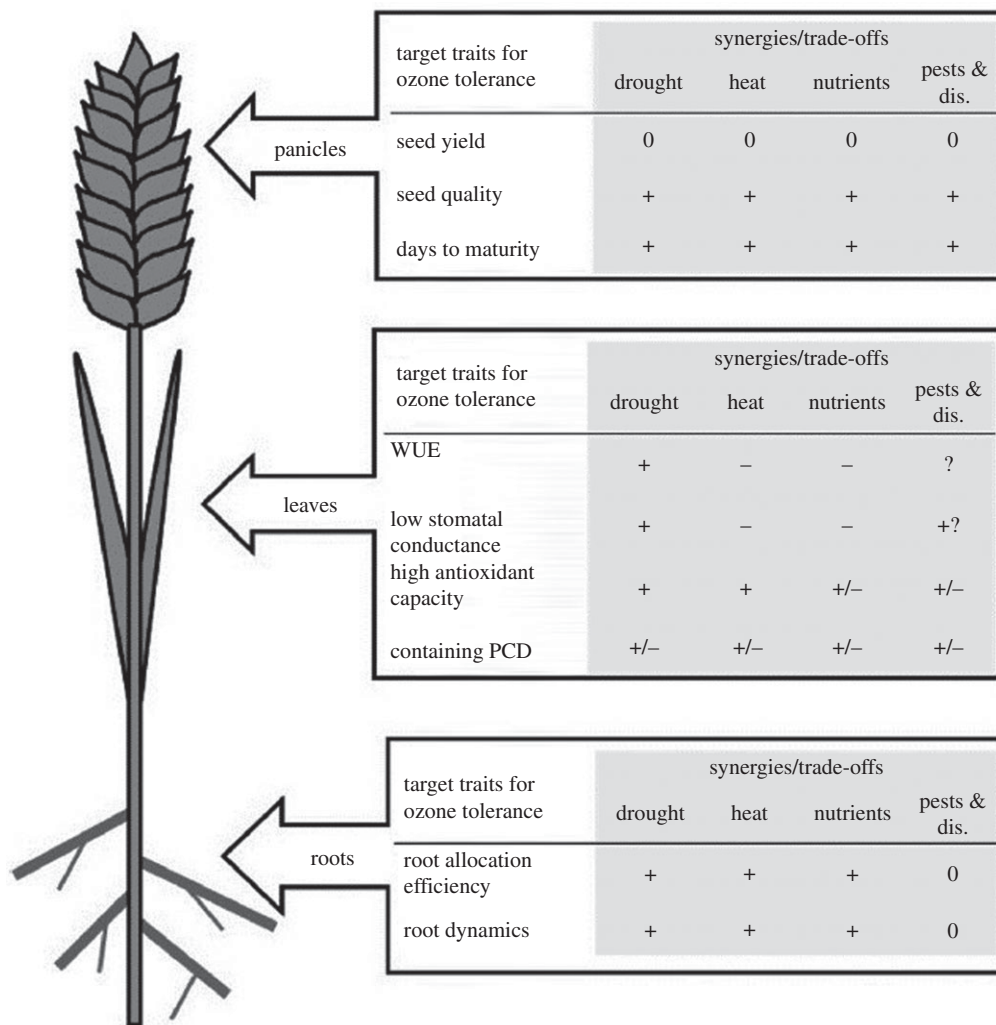
**Figure 4.** An ideotype for an $O_3$-tolerant crop. '+' indicates where there would be a benefit for other stresses of improving $O_3$ tolerance for the trait while '—' indicates a trade-off, and '0' indicates no effect. See [94] for further details.

stress traits including 'early maturing' heat avoidance varieties and 'late' or 'timely' sown heat-tolerant varieties were found to have different sensitivities to $O_3$ [120]. Such strategies need to balance the benefits of avoiding $O_3$ stress against stresses such as heat and water stress to ensure enough time for a productive grain-filling period.

A number of crop-management practices have been considered as potentially able to confer $O_3$ avoidance including changes to sowing date, irrigation scheduling and chemical protection [94]. For example, a global modelling study found that $O_3$-induced crop yield losses for irrigated crops are usually equal to or greater than for rain-fed crops, especially in India. This was due to irrigation allowing crop calendars to capture optimum radiation and temperature conditions, but also inadvertently causing co-occurrence with seasonal peaks in $O_3$ formation [121]. The study found that shifting crop calendars could reduce regional $O_3$ damage for specific crop-location combinations (e.g. up to 25% for rain-fed soya bean in India), but this had little impact at the global level.

# 6. Development of improved modelling approaches

A new generation of dynamic process-based models that rely on an understanding of the mechanisms by which $O_3$ causes damage rather than ERRs, are being developed and applied to better understand $O_3$ impacts on vegetation [23]. These models often differentiate between short-term effects of $O_3$ that are simulated as instantaneous effects on photosynthesis, usually modelled as a reduction in the plants maximum carboxylation capacity (Vcmax) [64], and long-term effects of accumulated $O_3$ dose that will cause an earlier and enhanced onset of senescence [122]. These types of modelling approaches have been developed and scaled to estimate consequent effects on C assimilation for both crops (e.g. [122–124] and forests [125,126]). These process-based models rely to some extent on empirical relationships but it is possible to confine these to fundamental plant processes to allow more integrated modelling of $O_3$ impacts. By focusing on leaf-level photosynthesis, and the coupling of photosynthesis to gsto, the assessment of $O_3$ flux can be intrinsically linked to the fundamental processes that determine C assimilation and subsequent allocation that supports plant metabolism, respiration, growth and productivity. However, care should be taken to consider and allow for modification to the coupling (or indeed decoupling) of photosynthesis to gsto that might occur on exposure to $O_3$ [70,126]. A robust mechanistic understanding of how these fundamental plant physiology processes are impacted by $O_3$ should allow the incorporation of the influence of climate variables and plant characteristics (i.e. those associated with both species and genotype as well as environment such as elevation, geographical location, soil textures, etc.) on $O_3$ damage.

Figure 5 provides a conceptual overview of key mechanisms involved in two key resource use efficiencies—WUE and nitrogen use efficiency (NUE)—and how modelling could incorporate the effect of $O_3$ damage on these processes. The focus on resource-use efficiency provides a useful way of integrating the effect of $O_3$ on a variety of processes that combine to influence an overarching aspect of plant physiology. Ozone pollution will influence WUE through changes in gsto (#1; [69]) and ultimately transpiration [127]. This will occur either by directly impairing stomatal functioning (through damage to guard cells [128]) or indirectly through reductions in photosynthesis (caused by damage to photosynthetic machinery) leading to an increase in sub-stomatal $CO_2$ concentrations (Ci; #2) and closure of stomata [23]. Ozone may also reduce root:shoot biomass ratios [11] leading to reduced soil water uptake by roots (#8) and can accelerate leaf senescence (#7; [129], reducing plant water utilization. These effects will influence transpiration (#11; [130]) and have implications for C assimilation (#5), allocation (#6) and ultimately crop growth and yield [11].

Ozone can cause changes in N uptake and utilization *via* the following mechanisms: through early senescence (#7; [129]), which will shorten the crop development period and duration of grain filling leading to reduced N uptake (#8; [22]), and effects on N remobilization altering protein and starch contents of grain yield (#9; [22]); by reduced root:shoot ratio and root activity through altered allocation patterns (#6; [11]) causing reduced N uptake (#8; [22]); by reduced transpiration (#4) due to stomatal closure, which would lead to lower N translocation to the shoots and roots (#9; [27]); and finally by reduced C assimilation (#5) leading to reduced total plant growth (biomass) causing reduced total plant N demand and hence uptake (#9; [22]). Photosynthetic NUE is also important and dependent upon the $CO_2$ saturation of Rubisco (#2, [75]). Understanding the relationship between gross photosynthetic capacity, chlorophyll degradation during leaf senescence (#7) and the shift from N assimilation to N remobilization are all important in the assessment of $O_3$ effects on NUE.

Robust process-based models capable of incorporating $O_3$ damage require specific empirical data (e.g. that describe $O_3$ effects on key physiological processes such as respiration, gsto and photosynthesis and how these vary within canopies and across growing seasons). These data would help define key physiological, developmental, resource-use and growth processes and their parameterization for particular species and genotypes. One way to achieve better-targeted data collection and subsequent analysis is to increase the collaboration between experimentalists and modellers to improve understanding, and hence modelling of $O_3$ effects for a range of
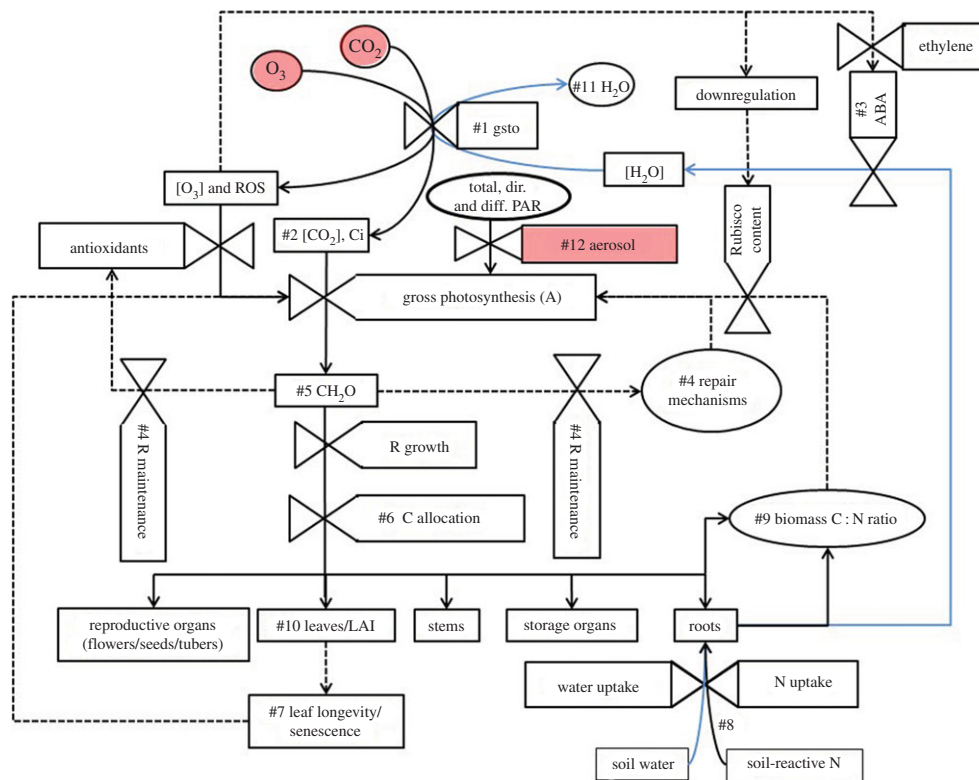
**Figure 5.** A conceptual overview of the mechanisms by which pollution ($O_3$ and aerosols) and elevated $CO_2$ (shaded) will influence WUE and NUE. This overview describes the stomatal uptake of $O_3$ pollution and impairment of radiation by aerosol pollution and the consequent effects on C assimilation, allocation and the crop's ability to take up nutrients and water from the soil. Also shown are feedbacks (dashed lines) that will alter the uptake of $O_3$ (e.g. through changes in stomatal conductance (gsto)) and modification of C assimilation (*via* changes in respiration (R), photosynthetic capacity and leaf longevity). Modified from Emberson *et al.* [23]. (Online version in colour.)

environmental stress conditions; such an approach is currently underway in an AgMIP-Ozone initiative [23]. Such collaborative efforts could also inform the development of ecosystem models that are included in land-surface exchange schemes. Currently, some of these land surface models may lack the finer detailed aspects of crop modelling (e.g. developmental stage, C allocation algorithms) and still rely indirectly on empirical ERRs that integrate biomass and yield responses. However, these models do offer the opportunity to simulate a wider range of ecosystems and the exchange of gases ($CO_2$, $H_2O$ and potentially $O_3$) at various scales from cellular, to leaf, canopy and ecosystem levels incorporating the influence of multiple global changes including $O_3$. Future innovations of these ecosystem models will also be important for the development of the new generation of earth system models [131] that would eventually enable holistic assessments of the exchange and impacts of pollution within the context of the entire earth system. Here, one of the key challenges has been to identify how best to model the interface between the atmosphere and land surface. The tight coupling between stomatal $O_3$ deposition and $O_3$ effects [132,133] would suggest that efforts to further develop $O_3$ deposition schemes to use coupled photosynthesis-gsto approaches may help to align the air quality community with the land-surface and earth system modelling community. This could provide opportunities to compare and contrast approaches for assessing the risk of pollution to ecosystems and to work together to develop improved and more powerful modelling tools that can support both air quality and climate policy.

# 7. Conclusion

Current levels of $O_3$ concentration are known to be causing damage to sensitive genotypes, species and species groups in North America, Europe and Asia. Future $O_3$ concentrations, even under optimistic emission scenario pathways, will continue to cause damage to vegetation, particularly across many parts of South and East Asia with additional yield losses for wheat, soya bean and maize of between 0.1 and 11% globally by 2030. Concentration-based $O_3$ risk assessment methods based on empirically derived ERRs for whole plant biomass and yield have limitations since they are unable to incorporate environmental conditions that we know will influence $O_3$ damage. Even where concentration-based ERRs are coupled with process-based models, inconsistencies between the ERR and process-based modelling may produce misleading results in terms of $O_3$ interactions with other stressors and hence risk and damage estimates. The use of flux-based ERRs has identified the global climate variable conditions likely to cause the highest yield losses in wheat as being the warm-temperate-moist, tropical-moist and tropical-wet climates of the NH (with mean yield losses of between 12 and 17%); further work is required to understand impacts on forests and grasslands and how elevated $CO_2$, N and management practices might also influence $O_3$ damage. These flux-based ERRs use a detoxification threshold; it will be crucial to understand how such damage thresholds might influence the efficacy of global versus local to regional emission reduction strategies that will differentially alter the diurnal amplitude and seasonality of $O_3$ profiles. An alternative dynamic process-based modelling approach would be useful to gain a fuller understanding of the interactions between $O_3$ and other stresses related to changes in climate, N deposition and hydrology thereby supporting the development of both mitigation and adaptation options to confer $O_3$ tolerance and avoidance. Such approaches would require the collection of targeted empirical data and improved dialogue between experimentalists and modellers, which should lead to improved scientific knowledge to support air quality, climate change and land-use policymaking.

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