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REVIEW

Ozone risk for crops and pastures in present and future climates

Jürg Fuhrer

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Abstract Ozone is the most important regional-scale air pollutant causing risks for vegetation and human health in many parts of the world. Ozone impacts on yield and quality of crops and pastures depend on precursor emissions, atmospheric transport and leaf uptake and on the plant's biochemical defence capacity, all of which are influenced by changing climatic conditions, increasing atmospheric CO_2 and altered emission patterns. In this article, recent findings about ozone effects under current conditions and trends in regional ozone levels and in climatic factors affecting the plant's sensitivity to ozone are reviewed in order to assess implications of these developments for future regional ozone risks. Based on pessimistic IPCC emission scenarios for many cropland regions elevated mean ozone levels in surface air are projected for 2050 and beyond as a result of both increasing emissions and positive effects of climate change on ozone formation and higher cumulative ozone exposure during an extended growing season resulting from increasing length and frequency of ozone episodes. At the same time, crop sensitivity may decline in areas where warming is accompanied by drying, such as southern and central Europe, in contrast to areas at higher latitudes where rapid warming is projected to occur in the absence of declining air and soil moisture. In regions with rapid industrialisation and population growth and with little regulatory action, ozone risks are projected to increase most dramatically, thus causing negative impacts major staple crops such as rice and wheat and, consequently, on food security. Crop improvement may be a way to increase crop cross-tolerance to co-occurring stresses from heat, drought and ozone. However, the review reveals that besides uncertainties in climate projections, parameters in models for ozone risk assessment are also uncertain and model improvements are necessary to better define specific targets for crop improvements, to identify regions most at risk from ozone in a future climate and to set robust effect-based ozone standards.

Keywords Ozone · Crops · Pastures · Climate change · Yield loss

Introduction

Increasing food demand for a growing world population combined with changing consumption patterns causes concern about the future availability of food and animal feed (Schmidhuber and Tubiello 2007). Many environmental factors, including climate change and air pollution, which influence crop productivity both directly and indirectly, are additional threats. Increasing temperatures, altered rainfall and more frequent extreme weather events will change production potentials with some regions benefiting and others being affected negatively (Parry et al. 2004; Tubiello et al. 2007). Among air pollutants, ozone is most important because of the widespread occurrence of this secondary pollutant and its known risk for effects on vegetation and human health (Akimoto 2003). Current levels in surface air are often sufficiently high to reduce yields of major staple crops such as rice (*Oryza sativa*), wheat (*Triticum aestivum*), corn (*Zea mays*) and potato (*Solanum tuberosum*), which is a priority issue for food insecure regions (Ashmore 2005; Ashmore et al. 2006).

J. Fuhrer (✉)
Air Pollution/Climate Group, Agroscope Research Station ART,
Reckenholzstrasse 191,
CH-8046 Zurich, Switzerland
e-mail: juerg.fuhrer@art.admin.ch

Moreover, ozone is a potent greenhouse gas and contributes to the greenhouse effect (Denman et al. 2007).

Global climate change and ozone pollution share some of the anthropogenic causes, but because of the differences in their properties, the timeframe for impacts differs. Due to the long-lived nature of the major greenhouse gases CO_2, N_2O or CH_4, climate change impacts are typically studied over 50–100 years. In contrast, ozone and its reactive precursors such as oxidised nitrogen and volatile organic compounds (VOCs) are short-lived and, therefore, ozone has more immediate impacts on crops and pastures. These impacts will persist, but they could be influenced by changing climatic conditions due to altered characteristics of the receptors and changes in atmospheric reactions and transport characteristics. Hence, assessments of future ozone risks should not depend exclusively on information obtained under the current climate. But, given the complexity of the interactions between vegetation, climate and ozone (Fig. 1), more comprehensive assessments are still lacking. Moreover, as a result of agro-technological developments with the introduction of new crops and varieties, partly in response to climate change, future agroecosystems will likely differ in terms of their sensitivity to ozone and other stresses thus making realistic projections difficult.

This review addresses the question of ozone risks for crops and pastures today and how such risks could be influenced by the changing climate. A simple conceptual framework is used that links (1) ozone production, distribution and ozone exposure; (2) ozone transfer and plant uptake and (3) vegetation responses to the amount of absorbed ozone, including detoxification and repair and cellular damage (Fig. 2).

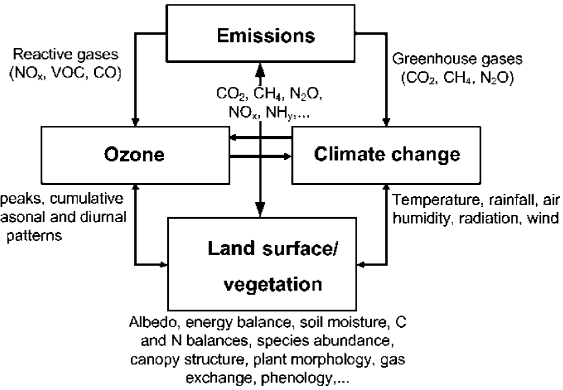

Fig. 1 Scheme of interactions between vegetation, climate and ozone pollution. Anthropogenic and natural emissions of reactive gases and greenhouse gases are the cause of both ozone formation in the troposphere and climate change, which interact through the radiative forcing caused by ozone, and the effect of climate parameters on ozone formation and destruction. Climate change and ozone further interact as they both affect vegetation and land surface properties. The outcome of this interaction determines vegetation responses to ozone in a future climate

Observed effects of ozone

Crops

Yield loss and shifts in crop quality are key aspects of this review. Many years of research in Europe and North America using the open-top chamber (OTC) technique with charcoal-filtered air, non-filtered ambient air and ozone-enriched air have produced a wealth of data and exposure-yield relationships (Ashmore 2002), which were used as input to economic crop loss assessments (Mauzerall and Wang 2001). Depending on crop and genotype, yield responds differently. Mills et al. (2007) classified wheat, watermelon, pulses, cotton, turnip, tomato, onion, soybean and lettuce as the most ozone-sensitive crops; sugar beet, potato, oilseed rape, tobacco, rice, maize, grape and broccoli as moderately ozone-sensitive and barley and fruit represented by plum and strawberry as ozone-tolerant.

Ozone affects many determinants of yield including photosynthesis, biomass, leaf area index (LAI), grain number and grain mass, as shown for rice (Ainsworth et al. 2008). In earlier reviews by Fuhrer and Booker (2003), Fiscus et al. (2005) and others, mechanisms behind the effect of long-term ozone exposure on yield have been presented and discussed. In essence, ozone penetrates leaves through the stomata. Via the production of reactive oxygen species (ROS), it impairs photosynthetic CO_2 fixation by impairing rubisco activity or stomatal functioning, and/or indirectly via acceleration of leaf senescence and thus protein (rubisco) and chlorophyll degradation, particularly in leaves formed during flowering (Morgan et al. 2004). This latter effect can be measured as reduced light interception and light-to-biomass conversion efficiency (Dermody et al. 2008). Ozone can inhibit reproduction by affecting pollen germination and tube growth, fertilisation and abscission or abortion of flowers, pods and individual ovules or seeds (Black et al. 2000). Finally, ozone impairs phloem loading and assimilate partitioning to roots and grain is often reduced while carbohydrates are retained in leaves (*cf.* Fuhrer and Booker 2003). In turn, this contributes to (1) higher shoot/root biomass ratio, (2) lower harvest index (together with the effect of a reduced length of grain filling period) and (3) altered leaf chemistry. According to Grantz et al. (2006) inhibition of allocation to roots can occur in the absence of changes in growth rate and McKee and Long (2001) suggested that ozone effects on allocation and development are more important for reductions in final yield than effects on photosynthesis and biomass accumulation. Decreased allocation below ground alters the carbon (C) flux to soils, leading to effects on soil processes (Andersen 2003) and the long-term system C balance (Felzer et al. 2005) (see below).

When elevated ozone is combined with elevated CO_2, yield loss is typically considerably less than with ozone

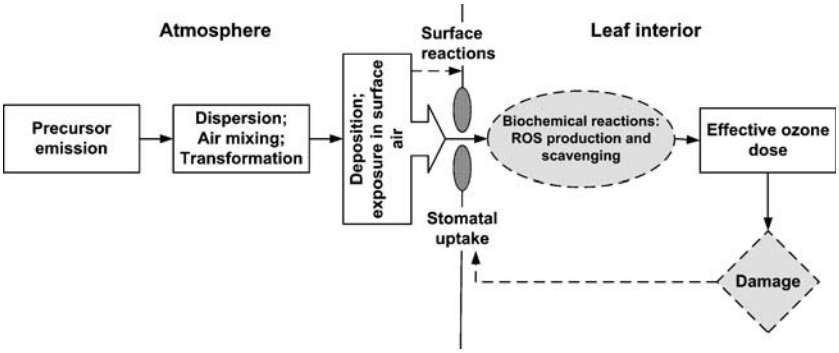

Fig. 2 Elements of ozone a simplified risk assessment approach. Ozone effects on plants are dependent on leaf uptake through stomata, which is influenced by the concentration in the air near the leaf surface (exposure), and leaf conductance to gas diffusion. Exposure concentration results from ozone formation, atmospheric transport and turbulent diffusion in the boundary layer, and is influenced by surface destruction. The effective dose, which causes damage to cellular components and may feed back to the functioning of stomata, finally depends on the rate of reactions with biomolecules. (*ROS* reactive oxygen species)

alone. For instance, a meta-analysis of data from a range of experiments revealed that in soybean (*Glycine max*) seed yield decreased in elevated ozone and elevated CO_2 by only half on the average, as compared to the decrease observed in ambient CO_2 and elevated ozone (Morgan et al. 2003). Mechanisms involved in this protective effect of CO_2, including reduced stomatal conductance, were discussed before (Fuhrer and Booker 2003) and are addressed in the section “Ozone risk determinants and their response to climate change”. Conversely, ozone can also diminish the stimulating effect on yield of elevated CO_2 (Fiscus et al. 2002). Similarly, fertilisation benefits are largely cancelled out by yield losses caused by increased temperature in most C3 plants such as wheat (Amthor 2001) and rice (Ainsworth 2008). This negative effect of warming is mainly due to the acceleration of development in determined crops which reduces the post-flowering period. Thus it can be assumed that CO_2 protection from ozone effects also becomes less effective with increasing temperature (*cf.* Fuhrer 2003), but further studies on the interactive effects of ozone, elevated CO_2 and temperature for the most important crops are needed in order to project future yields in regions with different rates of warming (Ainsworth 2008).

The response of crop quality to increasing ozone is not straightforward. An analysis by Pleijel et al. (1999) for wheat revealed that the loss in grain yield is accompanied by increased grain quality. A more comprehensive analysis for wheat by Piikki et al. (2008) confirmed that ozone increases grain protein concentration while decreasing protein yield and that the effect of elevated CO_2 on grain quality is opposite to that of ozone. In potato, reducing sugar and starch content of tubers decreased significantly with increased ozone, while at the same time ascorbic acid concentrations increased (Vorne et al. 2002). Vandermeiren et al. (2005) suggested that any increase in ozone would likely reduce potato tuber yield, but that season-long exposure to elevated ozone could have both beneficial and detrimental effects on tuber quality. No effect of increasing ozone on seed composition and quality was observed in peanut (*Arachis hypogaea*) (Burkey et al. (2007).

Increasing attention is being paid to impacts of ozone on crops in regions characterised by rapid urbanisation and industrialisation (Emberson et al. 2001b). For China, Chameides et al. (1999), Aunan et al. (2000) and others suggested that crop yields may already be affected today and that further reductions are expected in the future. Wheat, soybean and corn were identified as especially sensitive to ozone due to the likely co-occurrence of peak levels of ozone and the growing season of these crops (Emberson et al. 2003). Using an integrated assessment approach, Wang and Mauzerall (2004) calculated that in China, Japan and South Korea 1–9% of wheat, rice and corn yields and 23–27% of soybean yield were lost due to 1990 levels of ozone and that losses may exceed 30% by 2020. In the Yangtze River Delta, one of leading regions in economic growth in China, declining grain yield were observed with increasing ozone in an OTC study with winter wheat and rice suggesting that observed 1999 levels of ozone caused significant crop loss (Feng et al. 2003). Exposure–response relationships from studies in the United States and Europe suggested that crop loss in wheat was 20% to 30% in 1999/2000 (Huixiang et al. 2005) and Chen et al. (2008) confirmed reduced grain yield relative to the filtered-air control at concentrations above current ambient levels (i.e., in treatments with ozone added to non-filtered air). Wang et al. (2008) reported that effects on oilseed rape *(Brassica napus*) were largest when treatments were characterised by diurnal variations in ozone instead of constant exposure. Using foliar application of an ozone-protectant (ethylenediurea, EDU), Wang et al. (2007a, b) comparing EDU-treated with untreated plants concluded that local ambient levels of ozone with an annual mean concentrations of 74 ppb mainly affect wheat but not rice. However, from effects of ozone observed in experimental exposure–response studies, it could be expected that rice yield would decrease significantly at this level of ozone (Ainsworth 2008).

Near Varansi city in India, Agrawal et al. (2003) observed negative effects of ambient air pollution containing ozone in a mixture with other pollutants on yield of mung bean (*Vigna radiata*) and palak (*Beta vulgaris*) during summer and of wheat (*Triticum aestivum*) and mustard (*Brassica campestris*) during winter. Later, Agrawal et al. (2006) showed that also seed quality in mung bean declined due to the combined effect of ozone and other pollutants, with potential consequences for the nutrition of the urban population. Yield of tropical wheat in a suburban area in the eastern Gangetic Plain was strongly reduced in non-filtered ambient air with a mean ozone concentration of 40 ppb as compared to charcoal-filtered air with 90% less ozone (Rai et al. 2007). The authors suggested that the combination of ozone and NO_2 was mainly responsible for the effect at sub-urban sites and ozone alone at rural sites. Significant combined pollutant impacts on wheat varieties were found in Lahore, Pakistan (Wahid 2006).

Less attention has been paid so far to potential ozone risks to crops in Africa. Yet, there is evidence of ozone effects based on the yield ratio in EDU-treated vs. non-treated plants in rural areas of the Nile Delta for potato (Hassan 2006) and for soybean (Ali and Abdel-Fattah 2006). From measured and modelled ozone levels, in combination with exposure–response information derived for wheat in Europe, Van Tienhoven et al. (2006) concluded that agricultural production in southern Africa could be at risk, particularly in Zimbabwe.

Many estimates of crop losses involved exposure–response functions from OTC studies. Their direct application in yield loss and economic studies has caused considerable debate because of possible confounding effects of the chamber environment, which could lead to an overestimation of impacts (Musselman et al. 2006). But in a free-air ozone enrichment system (SoyFACE) significant yield loss in soybean at a mean ozone level as projected for 2050 in many world regions, was comparable—or even larger—to that expected from results obtained in earlier OTC experiments (Morgan et al. 2006), thus confirming the threat of increasing ozone levels for the yield of major crops.

Pastures

Compared to arable crops, pasture responses to ozone are arguably more complex. Bassin et al. (2007a) concluded that results for simple, young mixtures are not directly comparable with those for established communities and that results from OTC studies differ systematically from those in free-air fumigation experiments. Pastures are typically mixtures of species ranging from monocultures to bi-species mixtures and to multi-species communities and ranging from low to high productivity depending on site conditions and management. Results from several experiments with productive grass/clover mixtures showed that the high-protein legume fraction declined with increasing ozone, with negative effects for forage quality, because clover (*Trifolium* spp.) as the most important legume in temperate pastures appeared in most cases to be less tolerant to ozone than the grasses (*cf.* Fuhrer 1997). Nussbaum et al. (1995) found that the white clover fraction (*Trifolium repens*) declined in response to long-term treatments with low peak concentrations, whereas the companion grass *Lolium perenne* was affected in treatments characterised by episodic peak concentrations. Early-season ozone exposure decreased relative food value of *Poa pratensis* (Bender et al. 2006) and possibly in alfalfa (*Medicago sativa*) (Muntifering et al. 2006) leading to nutritional implications for its utilisation by herbivores.

More recently, interest has shifted towards less productive, multi-species communities with a high conservation value. But changes in yield and species composition in temperate old grasslands (Volk et al. 2006), calcareous grassland (Thwaites et al. 2006) or alpine grasslands (Bassin et al. 2007b) were difficult to detect against a background of natural variability. In temperate and alpine grassland, subtle changes in C-assimilation and water economy were inferred from shifts in stable C and O isotopic signatures (Jäggi and Fuhrer 2007; Bassin et al. 2008) and reduced leaf longevity from normalised difference vegetation index (NDVI) measurements (Bassin et al. 2007b). Thus, in the longer run lower productivity and altered species dominance may appear. After 5 years of exposure to elevated ozone, Kölliker et al. (2008) reported small shifts at the genetic level in *Plantago major*, a key species in temperate semi-natural grasslands. Clearly, more experiments using free-air ozone enrichment as described by Volk et al. (2003) will be needed across different habitats, climates and productivity levels before generalisations about the sensitivity of pastures to ozone can be made.

Current ozone exposure, trends and projections

In risk assessments, ozone exposure is typically summarised by suitable statistical indices based on measured concentrations. These can be characteristics of the frequency distribution of hourly concentrations measured near the surface in ppm (parts-per-million by volume) or ppb (parts-per-billion by volume) such as mean, median, maximum or percentiles. To be more receptor-specific, calculations are limited to the relevant time of the year, i.e. the growing season, and specified periods during the day, e.g. daylight hours. Results from OTC studies suggested that indices that give greater weight to peak concentrations and those accumulating exposure were best related to yield changes (Musselman et al. 1994). Examples of cumulative indices in units of ppm h (or ppb h, using hourly means) are:

$$\mathrm{AOT40} = \sum([\mathrm{O}_3] - 40) \text{ for } [\mathrm{O}_3] > 40\,\text{ppb during daylight hours})$$

$$\mathrm{SUM06} = \sum[\mathrm{O}_3] \text{ for } [\mathrm{O}_3] \geq 60\,\text{ppb}.$$

An index involving a continuous weighting function is:

$$\mathrm{W126} = \sum([\mathrm{O}_3]\,W,$$

With the sigmoidal weighting function W=1/(1+4403(exp (−0.126 [O_3]))). While SUM06 and W126, which were not used later in this review, are mostly used in the USA (USEPA 2006), AOT40 has been adopted by the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP, www.unece.org, last accessed Oct 2008) (UNECE 2004). For wheat under non-limiting conditions yield loss was directly related to AOT40 (Fuhrer et al. 1997) and, consequently, the index was used for spatial and temporal ozone risk assessments in Europe (UNECE 2004). However, the discussion about pros and cons of different concentration-based indices to predict vegetation effects is ongoing (Musselman et al. 2006) and indices based on stomatal ozone flux are now being developed and used (see the following section).

Current levels of ozone

Ozone is photo-chemically produced from natural and anthropogenic precursors, mainly nitrogen oxides (NO_x), volatile organic compounds (VOCs), methane (CH_4) and carbon monoxide (CO) (*cf.* Staehelin 2001). Levels measured in surface air depend on the balance between formation and destruction of ozone and are influenced by physical factors such as radiation, temperature and humidity and on air mixing. In the northern hemisphere ozone is also influenced by the influx from the stratosphere (Lefohn et al. 2001; Grewe 2007). In the course of the year, concentrations vary strongly with episodic peak concentrations in the most polluted regions during the warmest months in summer and maxima during spring prevailing at background sites (Vingarzan 2004; Jonson et al. 2006). In regions such as East Asia exposed to summer monsoon which transports oceanic air with less ozone, ozone seasonal patterns show a peak during pre- and post-monsoon periods (He et al. 2008). Similarly, ozone depletion during the specific monsoon season was observed in other regions.

During the day, ozone concentration pattern depends on elevation and shows strong diurnal variations at lowland sites where ozone destruction dominates during the night and vertical mixing together with photo-chemical activity causes highest levels in the afternoon. At higher elevation sites, diurnal profiles of ozone are less variable and concentrations remain high during the night due to mixing and coupling to the free troposphere. A similar damped diurnal cycle can be observed at coastal sites (e.g., Parrish et al. 2008).

From spring to summer, mean concentrations in rural areas of Europe reach 40 to 50 ppb, and average (1997–2001) levels of AOT40 calculated for May, June and July range from less than 3 ppm h in northern Scandinavia to values >10 ppm h in southern Europe (EMEP 2004). At individual sites, maximum values of around 30 ppm h (2003) were recorded in southern Switzerland and around 20 ppm h at sites in Italy (ICP Vegetation 2007). Similar AOT40 levels were reported to occur frequently in other densely populated regions such as the northeast of India with the Indo-Gangetic plain (Mittal et al. 2007; Engardt 2008). In rural agricultural areas of the USA, mean ozone concentrations reach between 50 and 60 ppb (90th percentile) (USEPA 2006).

Observed trends in ozone

During the last century, annual mean surface concentrations of ozone at mid to high latitudes have more than doubled (Hough and Derwent 1990). Concentrations over the mid- and high-latitude of the Eurasian and North American continents were 15–25 ppb in 1860 but increased to between 40 and 50 ppb even in remote areas and from 10–15 ppb to 20–30 ppb over the mid- and high-latitude Pacific Ocean (Lelieveld and Dentener 2000). Due to efforts to reduce precursor emissions, ozone levels in many rural and urban areas of Europe, North America and Japan have been changing recently such that the frequency of the highest values shows a declining trend, while minima are increasing (Jonson et al. 2006; Oltmans et al. 2006; Jenkin 2008). Trends at more than 300 sites in Germany between 1990 and 2000 showed a decline in the 99 percentile by ca. 1.6 ppb year^{-1} (Beilke and Walasch 2000). An important contribution to the upward trend in the low percentiles mainly during winter is a reduction in the titration by the ozone–NO reaction due to regionally reduced NO_x emissions (Jonson et al. 2006). In other regions such as Southeast Asia trends differ. For instance, in the Yangtze Delta region of China, Xu et al. (2008) observed a decrease in the average concentration, but an increase in the daily amplitude of the diurnal variation due to increasing frequencies at both high and low ends of the ozone distribution, and the most likely cause was believed to be an increase in NO_x concentrations.

Opposite to trends in more polluted areas, annual mean concentrations at background sites at mid-latitudes of the northern hemisphere have been increasing at about 0.5–2% per year, presumably due to rising NO_x emissions on a global scale, and by intercontinental transport of pollutants

(Auvray and Bey 2005; Derwent et al. 2006; Derwent 2008). From 1987–2003, the increase in mean ozone concentration measured at an Atlantic costal station (Mace Head) in Ireland has increased by 0.49 ppb year^{-1} (Simmonds et al. 2004) and by 0.31 ppb year^{-1} from 1987 to 2007 (Derwent et al. 2007). A similar average trend in mean annual ozone concentration of 0.34 ppb year^{-1} was determined for the North American west coast, although at a 7 ppb lower mean concentration level (Parrish et al. 2008). At seven out of nine rural and remote sites in the western USA, there was a significant increase in ozone with a mean trend of 0.26 ppb year^{-1}, corresponding to an average increase of 5 ppb between 1987 and 2004 (Jaffe and Ray 2007). Current levels at background sites range between 20–45 ppb, depending on location, elevation and distance to emission sources (Vingarzan 2004). The comparison between recent ozone concentrations and those of the last decade at Pic du Midi (2,877 m), as well as trends calculated over 14-year data series at three high-altitude sites in the Alps (Jungfraujoch, Sonnblick and Zugspitze) revealed that background ozone is still increasing but at a slower rate than in the 1980s and 1990s (Chevalier et al. 2007). Regional studies suggested that the influence of an increasing background concentration in Europe differs between seasons; for instance in Switzerland, where summer peak concentrations declined from 1992 to 2002 while the seasonal median remained stable, median concentrations increased by 0.69 and 0.58 ppb year^{-1} in winter and autumn, but only by 0.35 and 0.11 ppb year^{-1} in spring an summer, respectively (Ordóñez et al. 2005).

Projections of future ozone levels

Future trends in ozone will depend on the anthropogenic emission path of precursors and on trends in temperature, humidity and solar radiation. By 2030, average ozone in surface air over much of the northern hemisphere could increase by 2 to 7 ppb across the range of IPCC SRES emission scenarios described in Nakicenovic and Swart (2000). By 2100 the two more extreme scenarios projected baseline ozone increases of >20 ppb, while the other four scenarios yielded changes of −4 to +10 ppb (Prather et al. 2003). More recently, multi-model simulations for 2030 projected that with current air quality legislation implemented worldwide global surface ozone would increase by 1.5±1.2 ppb on average, but by 4.3±2.2 ppb for the IPCC SRES A2 scenario (Dentener et al. 2006), with the strongest increase in South Asia, Southeast Asia and the Middle East (Gauss et al. 2007). Using 26 different models, projections for 2030 resulted in an ensemble mean change in tropospheric ozone burden ranging from a 5% decrease to an increase by 6% and 15%, depending on the emission scenario (Stevenson et al. 2006). A reduction in future ozone levels results from a scenario with maximum feasible reductions (MFR), whereas an intermediate increase by 6 ppb results from the scenario with current legislation (CLE) and a stronger mean increase by 6–10 ppb from the A2 scenario (IPCC 2007). Hence, only with the assumption of best available technology in place globally, surface ozone levels may generally decrease, but this assumption seems to be too optimistic (Derwent 2008). Hence, the more likely development is an increase in mean ozone worldwide, even including Europe where precursor emissions are expected to decline due to efforts under the UNECE CLRTAP because of growing hemispheric influence of emissions in parts of Asia, Latin America and Africa.

Although anthropogenic emissions cause the largest response in ozone, a major factor influencing future trends in ozone is climate change, but the effect of both factors vary in space (Zeng et al. 2008). Separate effects of emissions and climate change on the global distribution of ozone in two selected months are shown in Fig. 3. The plots show that emissions affect ozone levels mainly in the mid-latitudes, while climate change effects are strongest in land areas with the strongest warming.

Shifts in climate have diverse and complex impacts on ozone through changes in circulation and meteorological conditions affecting ozone production and destruction. IPCC SRES emission scenarios consistently indicate an increase in global mean temperature with the most pronounced warming at mid to higher latitudes and associated shifts in precipitation with some regions getting wetter and some regions getting drier (IPCC 2007). Generally, warming in regions at higher latitudes tends to be accompanied by increasing annual precipitation, whereas those at lower latitudes receive progressively less precipitation.

The change in surface temperature is associated with increased atmospheric humidity (see the following section), which again has an impact on ozone levels. While increasing temperature, together with more radiation due to decreasing cloudiness, favours ozone formation, several studies suggested that a warmer and more humid climate would slow down the increase in ozone because of the positive effect of increased humidity on ozone destruction (*cf.* Zeng et al. 2008). The relative contribution of factors favouring ozone formation vs. those favouring ozone degradation may change with region, as shown for the United States (Racherla and Adams 2008), with the main positive impact of future climate change centred over the eastern United States. For the second part of the twenty-first century, Vautard and Hauglustaine (2007) analysing results of a number of simulations studies concluded that surface ozone would increase by 5–15 ppb at mid-latitudes where the impact of increased radiation, temperature and more stagnant conditions dominate over the effect of increased water vapour, in contrast to tropical/equatorial areas where ozone destruction

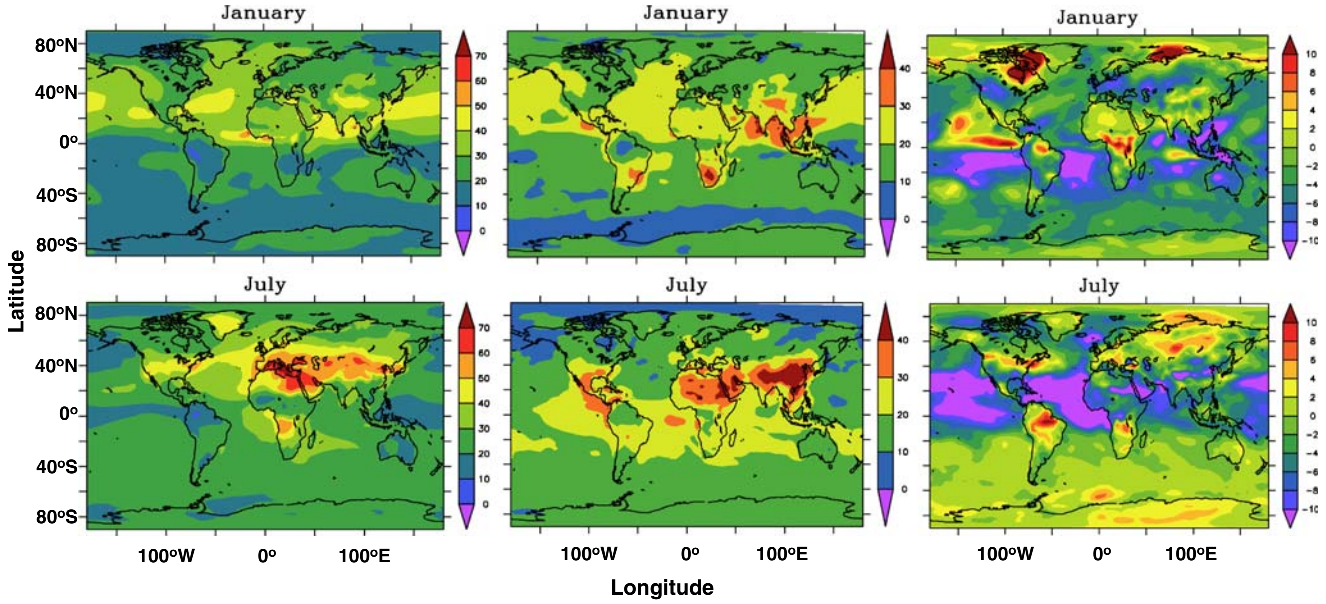

Fig. 3 Modelled surface ozone (ppb) in January and July from the present-day simulation (*left*), changes in surface ozone (ppb) between 2000 and 2100 due to anthropogenic emission changes (*middle*) and due to climate change (*right*) (reprinted from Zeng et al. 2008, with permission from the author)

will be favoured by higher humidity and less warming. Without considering trends in precursor emissions, Kunkel et al. (2008) in a study for the northeast of the United States quantified the effect of reduced cloudiness using two different cumulus parameterisations. Resulting increases in daily mean concentration ranged between 12% and 27% for a scenario with high anthropogenic emissions. Zeng et al. (2008) and others pointed to the important role of increasing biogenic emissions of reactive species, which favours ozone production. Biogenic emissions are generally thought to increase with temperature as, for instance, emissions of VOCs such as isoprene or terpene from forest trees are highly temperature-dependent. According to IPCC (2007), under the A2 scenario, biogenic hydrocarbons are projected to increase by between 27% (Sanderson et al. 2003) and 59% (Hauglustaine et al. 2007) contributing to a 30% to 50% increase in ozone formation over northern continental regions. Increasing CO_2 in the atmosphere could stimulate total leaf surface area in forests leading to even larger hydrocarbon emissions (Arneth et al. 2008), but this effect may be limited because of a reduction in emission rates per unit leaf area (Calfapietra et al. 2008). Therefore, the quantitative contribution of these processes to ozone production on larger scales remains uncertain (Racherla and Adams 2008).

Extremely warm years can serve as a model case for future conditions and measurements during such years can help validate projections for future trends in ozone. 2003 was a year that is often seen as an analogue of typical future climatic conditions in Europe with long periods of heat and low precipitation (Beniston et al. 2004). Blocking anticyclonic conditions are likely becoming more frequent in Europe (Schär et al. 2004), and also in other mid-latitude continental regions (Vautard et al. 2007), and the frequency of ‘hot’ days with temperatures above 30°C could increase progressively over the next decades (Beniston et al. 2007). From this it may be expected that the length of ozone episodes may increase due to longer warm and dry periods. In 2003, the average daily maximum ozone concentration in summer in Switzerland was 15 ppb or nearly 29% higher than during the period 1992–2002 (Ordóñez et al. 2005). Using the meteorology of 2003, Szopa and Hauglustaine (2007) projected for 2030 the strongest absolute increase in ozone in the northern and eastern regions of Europe and a smaller increase in more southern parts.

Increasing temperature will extend the ozone season both into the late spring and early fall (Racherla and Adams 2008). Together with longer episodes with favourable conditions for ozone formation this trend is likely to increase the ozone accumulated exposure over the potential growing season, although for specific crops cumulative exposure may decline due to an accelerated development. When using cumulative indices involving a cut-off concentration such as AOT40, even more pronounced changes in exposure than in mean concentrations are expected (Reilly et al. 2007). This is because the increase in baseline ozone leads to more frequent exceedance of the cut-off. Using 18 atmospheric models, Ellingsen et al. (2008), for the CLE scenario (current legislation in place), obtained an increase in AOT40 by 21–38% by 2030 over the northern hemisphere, relative to 2000 and by 50% on the Indian subcontinent, but a decrease with current regional legislation in Europe. For the A2 scenario, the largest increase in AOT40 (80–100%) was found for India and Southeast Asia. With respect to the effect of climate change by 2030, the latter study provided inconclusive results because of the short time horizon. Using MATCH (http://www.mpch-mainz.mpg.de/~lawrence/MATCH/match_overview.html, last accessed Oct 2008), a global 3-dimensional model of atmospheric transport and chemistry AOT40 could increase across much of the mid-latitude temperate regions by as much as a factor of about 4 and 6 by 2050 and 2100, respectively, for an emission scenario without pollution control, but a decline for scenarios with pollutant emissions capped at 2005 level and greenhouse gas emissions reduced to stabilise CO_2 concentrations at 550 ppm by 2100 (Reilly et al. 2007). Giorgi and Meleux (2007), using the IPCC A2 scenario, projected the strongest increase in AOT40 by the end of this century (>50% relative to 1961–1990) over France, England, Belgium, the Netherlands, south-western Germany and north-eastern Switzerland. Using regional models, Meleux et al. (2007) for Europe and Forkel and Knoche (2006) for southern Germany consistently projected increasing frequencies of ozone episodes by 2030 leading to substantial increases in seasonal cumulative ozone exposure.

Overall, climate change, together with increasing baseline ozone levels due to altered large-scale emission patterns, could cause an increase in the frequency of years with higher cumulative ozone exposures in Europe, as compared to today, with a stronger trend in north-western as compared to southern Europe. This is in spite of current regional emission control measures. In most regions, ozone risks for vegetation based on AOT40 show moderate deteriorations by 2030 if current emissions legislation is followed and slight improvements if current emissions reduction technology is used optimally. In the case of a pessimistic 'business-as-usual' scenario (A2) substantially higher ozone levels by 2030/2050 must expected worldwide, in particular on the Indian subcontinent, in Southeast Asia and in some African regions. However, apart from uncertain emission projections, uncertainties in the model outputs remain; for instance with respect to effects of climate-chemistry feedbacks (Stevenson et al. 2005) and of land surface–climate interactions (Seneviratne et al. 2006; Sitch et al. 2007).

Ozone risk determinants and their response to climate change

Leaf uptake

The risk for ozone effects on plants not only depends on the ozone concentration in the surface boundary layer, but also on (1) the rate at which ozone penetrates leaves through stomata and (2) the capacity of the leaves to tolerate ozone and its derivatives present in the leaf interior (*cf.* Fuhrer and Booker 2003). Hence, ozone damage is a function of the balance between the rate of uptake at a given point in time, $F_{\mathrm{st}}(t)$ and the plant's defence reaction at that time, $D(t)$, i.e. the 'effective flux' ($\mathrm{EF_{st}}$) (Musselman et al. 2006):

$$\mathrm{EF_{st}} = F_{\mathrm{st}}(t) - D(t) \tag{1}$$

$\mathrm{EF_{st}}$ can be integrated over time to yield the cumulative effective loading ($\mathrm{AF_{st}}$). Rates of D are temporally variable and depend on energy-consuming biochemical processes removing ozone or its products in the leaf interior, for which a general process-based representation in models is still lacking (Matyssek et al. 2008) (see below). In the absence of a mechanistic formulation, a constant value of D is used. $\mathrm{AF_{st}}$ with D=6 nmol m^{-2} project leaf area is referred to as $\mathrm{AF_{st}}6$ (UNECE 2004), with the value for D derived by best-fit regression using data from OTC studies. Pleijel et al. (2007) and others provided empirical evidence that modelling $\mathrm{AF_{st}}6$ yields better statistical relationships to yield of wheat and potato than can be obtained with concentration-based indices (e.g., AOT40). The difference is likely due to the better capturing of the effect of environmental conditions on F_{st} or more specifically leaf conductance to ozone diffusion (g_s) (see below). Figure 4 shows the relationships for $\mathrm{AF_{st}}6$ vs. relative yield for wheat and potato. The improved relationship between $\mathrm{AF_{st}}$ and yield loss has stimulated the development of a flux-based approach for ozone risk analysis in Europe to replace the exposure-based assessment (Fuhrer 2000).

Factors affecting leaf uptake

Central to models of F_{st} is g_s which together with the ozone concentration gradient across the stomata determines the rate of ozone diffusion into a leaf:

$$F_{\mathrm{st}} = g_s\,\Delta[O_3] \tag{2}$$

From measured rates of water vapour diffusion, g_s for ozone can be estimated by accounting for the difference in molecular diffusivity between ozone and water vapour. It is often assumed that the ozone concentration inside the leaves is zero; hence ozone uptake can be calculated from external concentrations multiplied by g_s. However, as pointed out by Paoletti and Manning (2007), this assumption must be questioned because experimental evidence suggests that internal concentrations may be larger (Moldau and Bichele 2002). Under steady-state conditions, the ozone flux into the leaves also depends on ozone removal by reaction with apoplastic components, mainly ascorbate (asc) (see below). Eller and Sparks (2006) showed a direct relationship between symplastic asc and ozone influx. In their experiment, the

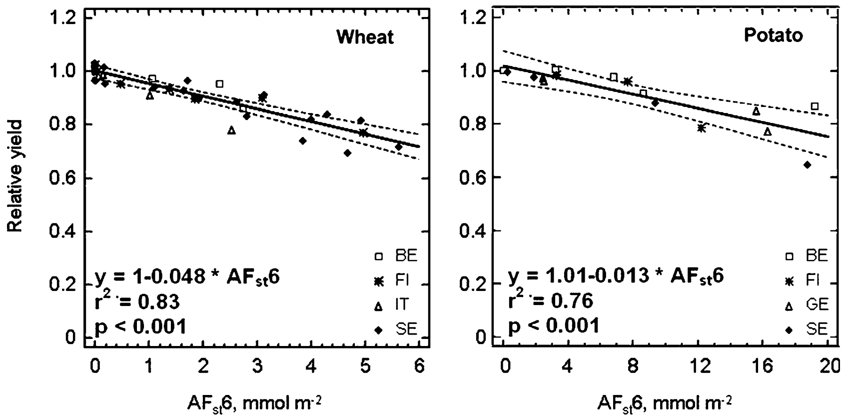

Fig. 4 Relationship between relative yield and the modelled, accumulated stomatal uptake of ozone, per unit projected sunlit leaf area, above an ozone uptake rate threshold of 6 nmol O_3 m^{-2} s^{-1} (AF$_{st}$6) for wheat (13 experiments from Belgium, *BE*, Finland, *FI*, Italy, *IT* and Sweden, *SE* and potato (seven experiments from Belgium, *BE*, Finland, *FI*, Germany, *GE* and Sweden, *SE*. The integration period for AF$_{st}$6 was from 270°C days before anthesis until 700°C days after anthesis for wheat and from plant emergence until 1,130°C days after emergence for potato (reprinted from Pleijel et al. (2007), Copyright (2007), with permission from Elsevier)

concentration of asc together with g_s explained 66% of the variation in ozone flux. Additional factors such as reaction with glutathione or the strength of the external surface sink for ozone may explain the remaining variability.

Because ozone flux to leaves is partitioned to stomata and to external surfaces, F_{st} is influenced by surface destruction of ozone, which depends on leaf surface characteristics and surface conditions such as wetness (Zhang et al. 2006) and temperature (Fowler et al. 2001), although the interactions are variable and may differ with climate and plant species (Altimir et al. 2006). Unless droplets block stomatal openings (Grantz et al. 1997), surface wetness generally acts to enhance total ozone flux to foliage, although a mechanistic understanding of how surface moisture affects ozone deposition is lacking (Altimir et al. 2006). This may significantly increase the fraction of non-stomatal ozone flux and thus may prevent a certain portion of stomatal uptake.

In a changing climate, changes in surface wetness are complex as they depend both on night-time temperature and on evaporative conditions during daytime. During extremely warm periods favourable for high ozone levels, it seems likely that surface wetness declines and surface temperature increases, which leads to increased surface destruction with no known biological consequence, and, consequently, to a reduction in the fractional stomatal ozone flux.

Climate change effects on stomatal uptake

There are several important environmental factors controlling g_s under natural conditions: solar radiation (PPFD), air temperature (T_a) and leaf-to-air vapour pressure deficit (D_s), ambient CO_2 concentration (C_a) and soil water potential (ψ) and g_s, which varies with phenological stage (*phen*). Following Jarvis (1976), actual values of g_s are often modelled from species-specific maximum conductance g_{max} under non-limiting conditions modified by coefficients or scalars (*f*) accounting for the relative influence of each of the above factors. In addition, g_s responds to ozone due to direct effects on guard cell functioning (Torsethaugen et al. 1999; Grulke et al. 2007) or indirectly to an increased ratio of internal to external [CO_2] resulting from reduced photosynthetic CO_2 assimilation or changes on stomatal aperture and density (Elagöz et al. 2006). The effect of ozone on stomatal behaviour and thus on g_s is difficult to quantify; in tree species, it was estimated at −12% on the average for current ambient ozone relative to the concentration in charcoal-filtered air (Wittig et al. 2007). This negative effect of ozone can be considered by introducing an additional scalar, f_{O3}. However, using the Jarvis-type model strongly depends on the quality of the g_{max} estimate and results may only be accurate when applied under conditions representative of those under which the parameterisation was performed. This limits application of the Jarvis-type approach to estimate F_{st} across larger scales covering different climates and to extrapolate F_{st} from current climatic conditions to the future with different climatic conditions and higher CO_2 concentrations. Moreover, estimates of g_{max} and of the various functional relationships are available only for a small number of species in temperate climates and data for species in Mediterranean and other non-temperate environments are lacking (Alonso et al. 2007).

An alternative, semi-empirical method which does not depend on g_{max} was proposed by Ball et al. (1987) (often referred to as the Ball–Berry model) by introducing a relationship between relative humidity (h_s), air CO_2 concentration (C_a) and photosynthetic rate (A). Later, Leuning (1995) suggested replacing h_s by the leaf-to-air vapour pressure deficit (D_s) in the Ball–Berry model and

Yu et al. (2001) proposed gross assimilation rate (A_g) be used instead of A. The resulting equation is then:

$$g_s = a\frac{A_g}{C_a(1 + D_S/D_0)}, \tag{3}$$

where a is a constant and D_0 is a parameter reflecting characteristics of response of stomata to D_s, i.e. the curvature of the humidity response curve of g_s. But like the Jarvis-type approach, application of this model is limited by uncertainties in the parameter values.

In the framework of the UNECE CLRTAP, ozone deposition modelling at the continental scale applies the deposition of ozone and stomatal exchange model (DO$_3$SE, Emberson et al. 2001a), which involves the multiplicative Jarvis-type algorithm for g_s:

$$g_s = g_{\max}*\left[\min\left(f_{\text{phen}}, f_{\text{O3}}\right)\right]*f_{\text{PPFD}} \\ *\max\left\{f_{\min}, \left(f_{\text{T}}*f_{\text{Ds}}*f\psi\right)\right\} \tag{4}$$

with $f_{\min}$ defining a fixed minimum value of g_s (typically 1% of $g_{\max}$).

Using this model, Harmens et al. (2007) simulated a lower potential ozone risk for winter wheat under conditions of +3°C, as compared to current climatic conditions, in spite of an assumed increase in ozone concentration by a constant amount of 5 ppb. The lower risk inferred from a lower F_{st} could be expected from the assumed CO$_2$-dependent 35% reduction in $g_{\max}$ and the assumed decrease in g_s as a function of increasing leaf-to-air vapour pressure deficit, D_s. Using a similar ozone flux model (ozone deposition model, ODEM; Nussbaum et al. 2003; Bassin et al. 2004), Keller et al. (2007) simulated AF$_{st}$ in wheat and grassland in 2 years greatly differing in ozone levels and in climatic conditions (2000 vs. 2003) and found only small differences in AF$_{st}$, indicating that the hot and dry conditions on the Swiss Central Plateau in 2003 limited g_s and thus counteracted the effect of higher ozone concentrations (Fig. 5). These examples illustrate that using g_s-based models may be attractive to assess current and future potential ozone risks of their sensitivity to changes in the main climatic factors, but validation of the model with respect to AF$_{st}$ remains difficult.

Under changing climatic conditions, the behaviour of stomata, including the response to increased levels of CO$_2$, plays a central role for ozone risk to plants. A meta-analysis of results from Free Air CO$_2$ Enrichment (FACE) studies revealed an average reduction in g_s by elevated CO$_2$ (475–600 ppm) by 20% (Ainsworth and Long 2005), a concentration that could be reached around 2050 (IPCC 2007), with the largest response in C3 and C4 grasses and herbaceous crops (Ainsworth and Rogers 2007). A general reduction in g_s due to elevated CO$_2$ concentration would reduce the ozone flux from the atmosphere to the plant interior and consequently would reduce ozone depletion in surface air. It was estimated that under doubled CO$_2$ concentration this effect could increase ozone levels throughout the year by 5–20% over large parts of the northern hemisphere (Sanderson et al. 2007). Additionally, g_s is influenced by D_s, which depends on air temperature, T_a, and the air vapour pressure deficit, D_a. Once D_s approaches a critical value above which the evaporative demand of the atmosphere exceeds the plant's water transport capacity, g_s decreases and the sensitivity of g_s to T_a becomes small (Dai et al. 1992). At low D_s, g_s increases with increasing T_a. When g_s declines, the evaporative cooling of the leaf is reduced. This, in turn, leads to moderately higher leaf temperatures (T_l) and to a change in the difference between T_l and T_a (T_l-T_a). With an increasing difference T_l-T_a, g_s declines linearly (Baker et al. 2007; Fig. 6), which can be considered an indirect response to warming via changes in D_s. Hence, the response of g_s to D_s is critical in predicting physiological responses to changing T_a in species adapted to cool-temperate conditions (Sinclair et al. 2007).

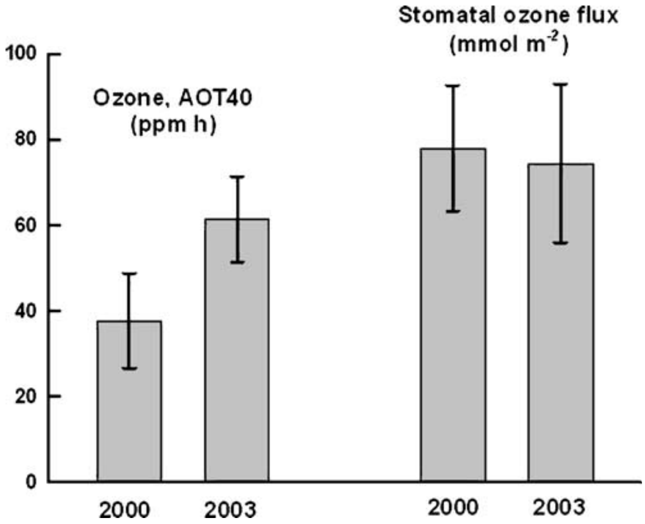

Fig. 5 Comparison between the level of ozone in the air (expressed as accumulated exposure above 0.04 ppm) in 2000 and 2003 and in cumulative stomatal ozone flux to grasslands in Switzerland (plot produced with data from Keller et al. 2007)

The response of g_s to D_s depends on species and it is directly related to specific g_s at low D_s (≤1 kPa) (Oren et al. 1999):

$$g_s = -m \times \ln D_s + b \tag{5}$$

where m is the stomatal sensitivity to D, or $-dg_s/d\ln D_s$, and b is defined as the reference g_s at 1 kPa. Both parameters can be generated by least-squares regression. The relationship suggests that the sensitivity to changes in D_s is largest in species characterised by high g_s at low D_s (i.e., high $g_{\max}$). This could contribute to the difference between

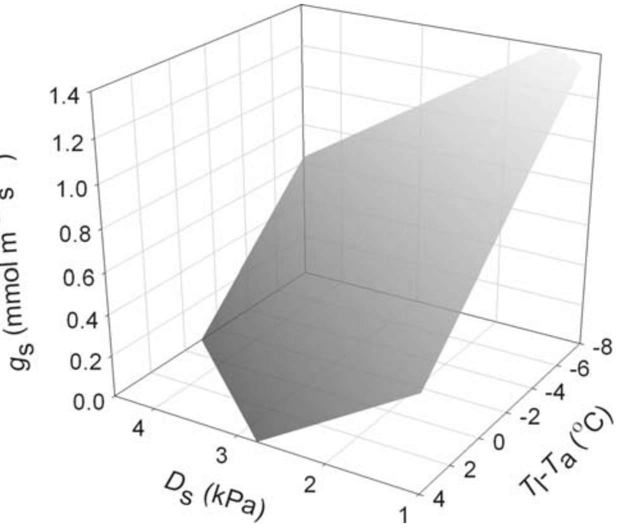

Fig. 6 Three dimensional response surface of stomatal conductance (g_s) measured at a photosynthetic photon flux density (PPFD) of 1,500 μmoles (photons) m^{-2} s^{-1} *vs.* leaf minus air temperature differential ($T_l - T_a$) and leaf-to-air vapour pressure deficit (D_s). Equation for the fitted plane is $y = 1.08 – 0.09(T_l - T_a) - 0.26(D_s)$ (redrawn from Baker et al. 2007)

grassland species in terms of the level of ozone necessary to elicit visible leaf injury at varying levels of D_s (Bungener et al. 1999). With changing climatic conditions, this difference in specific responses to D_s could affect plant–plant interactions in multi-species communities, and hence their responses to ozone stress, an effect which is not currently taken into account in ozone risk evaluations.

Specific humidity in surface air currently increases by about 4.9% °C^{-1}, with differences between regions and between day and night (IPCC 2007). Philipona et al. (2004) and Auer et al. (2007) documented rapid increases in moisture over central Europe over the period 1995 to 2003, coupled to increasing T_a (Philipona et al. 2005). The analysis of a global dataset revealed that during 1976–2004 large increases in moisture occurred over the central and eastern United States, India and western China, with the largest increases over Eurasia where the strongest warming (~0.2° to 0.7°C decade^{-1}) occurred (Dai 2006).

While atmospheric moisture increased with recent climate warming (Willett et al. 2007), D_a changed very little during the past 50 years of observation across the United States (Szilagyi et al. 2001). For D_a to increase, air warming would need to be faster during the day than during the night, thus increasing the diurnal range in T_a, which may be the case in some regions (e.g. Mediterranean region in Europe), but not in others (IPCC 2007). Hence, whether D_a remains stable or will change in the future depends on the changes in specific humidity relative to the increase in daily maximum T_a. Periodically, during periods with restrictive surface boundary conditions for evapotranspiration (i.e., heatwaves), reduced air humidity at high T_a will lead to increased D_a, especially in regions such as Europe with a strong land surface–atmosphere coupling (Seneviratne et al. 2006). Only under these dry conditions, direct effects of T_a and increasing D_a can be expected to strengthen the effect of D_s to reduce g_s and hence AF$_{st}$.

This overview suggests that the behaviour of g_s will mainly depend on the ability of the plants to extract soil water and to maintain high g_s, particularly in regions where the evaporative demand increases. If g_s remains high, potential productivity is sustained, but also AF$_{st}$ and the associated risk for ozone impacts remains high. Therefore, consideration of the availability and plant extraction of soil water is crucial for estimating the response of stomata to changes in temperature and humidity. Projections of moisture in the upper soil layers have been presented recently (IPCC 2007; Bates et al. 2008). Decreasing average soil moisture is expected in the subtropics and in the Mediterranean region and increases in East Africa, central Asia and some other regions where precipitation is expected to increase with climate change, including high latitudes and some wet tropics. In dry tropics and much of the mid-latitudes, including central and southern Europe, the projected decrease in summer precipitation and a higher evaporative demand would reduce soil moisture. Implications of these trends for ozone risks depend on the degree of synergy between future crop growing periods and climate-induced soil moisture changes and the presence or absence of irrigation.

Factors affecting canopy uptake

The variables linking climate to g_s are mainly based on leaf-scale data, although some of the principles apply equally to canopy conductance, g_c. In optimal conditions, leaf g_s correlates well with g_c over a wide range of vegetation types. But at the canopy level, the situation can be complicated by two inter-related factors: (1) canopy architecture and (2) species composition. In pastures, both of these may change in a changing climate through shifts in species dominance (see below) and/or formation of gaps resulting from the effect of drought (Lüscher et al. 2005).

Exposure to ozone varies vertically because ozone penetration into the canopy depends on atmospheric turbulence and leaf area distribution (Jäggi et al. 2006). In monocultures of cereals this should be less important since activity of the topmost leaves is most important for final grain yield and ozone depletion inside the canopy is less relevant. Nevertheless, in rice, Reid and Fiscus (2008) found decreasing ozone effects on yield with increasing plant density. In mixed grasslands, the effect of canopy structure maybe even more pronounced as different species occupy different canopy layers. Jäggi et al. (2006) showed that ozone exposure of clover plants in the lower part of the canopy is only about half the exposure of the taller grasses at the top. Also, g_s varies across the canopy due to gradients in D_a, T_a and photosynthetically active radiation (PAR). Davison et al. (2003) found much greater reductions in PAR than in ozone in a canopy of *Rudbeckia laciniata*. At 50 cm above ground, the ozone concentration varied from only 15% to 90% of ambient levels, whereas PAR was consistently below 10%. It was concluded that uptake of ozone by low leaves was limited by PAR rather than by ozone. In contrast, Jäggi et al. (2006) found a moderate PAR reduction throughout the canopy in a two-layered grass canopy with less than 20% of total LAI in the upper half. As a result, g_s in leaves of *T. repens* at 50% of the maximum canopy height were similar to g_s in *Alopecurus pratensis* leaves at canopy top. During daytime, leaves of *A. pratensis* were exposed to 92% while leaves of *T. repens* were exposed to only 64% of the reference ozone concentration above the canopy. Consequently, species occupying the lower part of the canopy had reduced ozone uptake as compared with taller companion species in spite of similar g_s.

In the context of climate change and increasing CO_2, the effect of a changing canopy structure on microclimate is relevant because elevated CO_2 may cause a modest increase in LAI (Ainsworth and Long 2005; Dermody et al. 2008). In a field experiment with *L. perenne*, where T_l was raised over T_a by 3°C, Nijs et al. (1997) observed a decrease in g_s relative to the ambient air control, but only in the top leaves and not in leaves at lower canopy positions. In the same experiment, interaction between C_a and T_a on g_s was observed, i.e. elevated CO_2 decreased g_s and reduced the sensitivity of g_s to T_a even in the most exposed leaves. Similarly, the sensitivity to D_s can be reduced at high CO_2 (e.g., Maherali et al. 2003). Vice versa, the effect of elevated CO_2 declines with increasing T_l (Allen et al. 2003).

As a result of cutting or grazing, gradients of ozone in pasture canopies are temporarily removed and species at lower canopy positions become exposed to higher ozone levels and more light during the initial phase of re-growth. Thus, more frequent management interventions in response to climate-induced changes in phenology could increase the ozone sensitivity of productive grassland systems (Ashmore and Ainsworth 1995).

Defence reactions

Ozone dissolves in the apoplastic fluid where it decomposes to hydrogen peroxide, singlet oxygen and hydroxyl radicals (ROS) (Sandermann 2008). A complex system of protection from oxidative damage operates in the extracellular and intracellular space, as recently reviewed by Tausz et al. (2007), Sandermann (2008), Heath (2008) and Matyssek et al. (2008). Reaction with asc has long been recognised as a key process for the detoxification of secondary ROS, and extracellular asc is believed to be the first line of defence against ozone and its decomposition products (Dizengremel et al. 2008), although antioxidants other than asc may be involved (D'Haese et al. 2005; Burkey et al. 2006). However, direct experimental evidence for specific compounds remains scarce. Reactions of asc with ozone proceeds via ozonolysis with the production of zwitter ions and of singlet oxygen, which is toxic and needs to react again with asc (for details, see Sandermann 2008). End products of the electron transfer reactions are monodehydroascorbate and dehydroascorbate (dha). After transport through the plasmalemma, these compounds are regenerated and reduced asc is re-translocated to the extracellular space (Sanmartin et al. 2003) (Fig. 7). Using plants over-expressing dehydrascorbate reductase, Chen and Gallie (2005) and Eltayeb et al. (2006) provided direct evidence for improved protection against oxidative damage via enhanced recycling of asc and Eltayeb et al. (2007) observed increased ozone tolerance in plants over-expressing

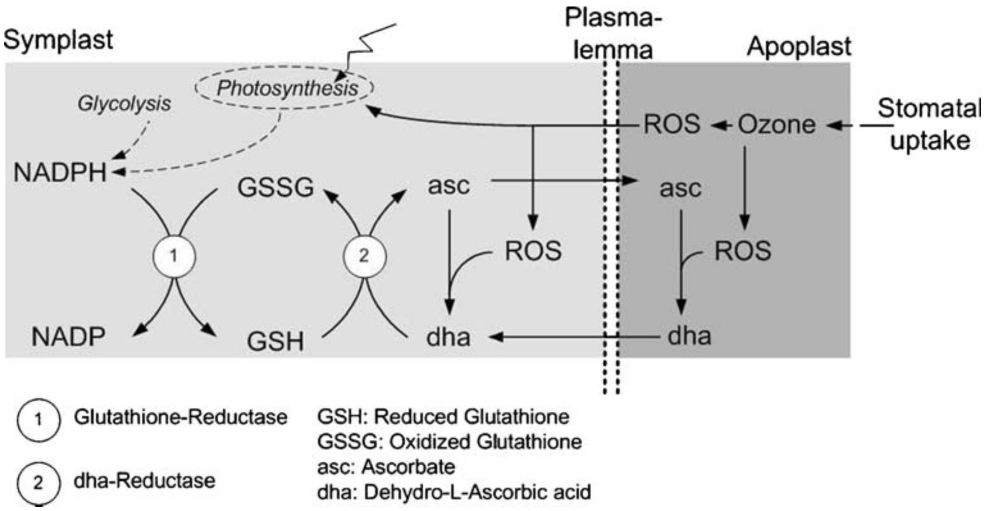

Fig. 7 Simplified scheme of antioxidative defence systems in green cells based on the recycling of ascorbate (asc), which in the apoplast captures ROS produced by penetrating ozone. (*ROS* reactive oxygen species) (see Fuhrer and Booker 2003 for more details)

mono-dehydrascorbate reductase. Further enzymes involved are glutathione peroxidase, superoxide dismutase and catalase (Heath 2008).

Similar reactions involving antioxidants to avoid oxidative stress operate in cellular organelles to protect from ROS produced during photo-chemical reactions. This ‘photo-protection’ is particularly important during periods of photo-oxidative stress caused by the combination of intensive radiation, drought and heat (Reynolds et al. 2005). This could enable cross-tolerance to stresses imposed by combinations of extreme weather and ozone, but the timing, intensity and order of exposure would be crucial (Tausz et al. 2007). Alternatively, under conditions of extremely warm and dry weather, the antioxidant system may not be as effective in removing ROS because of competing intercellular reactions. Detoxification processes require reducing power (NADPH) and C skeletons for the regeneration and de novo synthesis of the antioxidants involved (Dizengremel et al. 2008). Hence, the defence capacity may decline when the supply of assimilates becomes insufficient due to limited available energy (Wieser and Matyssek 2007).

The situation is equally ambiguous with respect to the effect of elevated CO_2. In leaves of alfalfa (*Medicago sativa*) CO_2 enrichment reduced the activity of several antioxidant enzymes (catalase, superoxide dismutase and glutathione reductase and asc peroxidase), suggesting a lower basal rate of oxygen activation and H_2O_2 formation, leading to a relaxation of the antioxidant system (Erice et al. 2007). Hence under less stressful climatic conditions elevated CO_2 could be beneficial for detoxification, as reported for poplar plants (*Populus alba* x *tremula*) (Schwanz and Polle 2001). Moreover, elevated CO_2 was found to increase antioxidant levels in leaves due to the positive effect on photosynthesis and assimilate availability. Nevertheless, in their review, Tausz et al. (2007) concluded that although elevated CO_2 increases different defence metabolites the available information concerning CO_2 effects on the efficiency of the antioxidant defence systems remains inconclusive.

Detoxification capacity may be linked to the internal structure of leaves. Leaves with a smaller intercellular air space volume may be more tolerant to ozone, as shown for strawberry cultivars (*Fraxinus* x *ananassa*) (Keutgen and Pawelzik 2008). Cell density and mesophyll resistance can be negatively correlated with specific leaf area (SLA) or leaf area ratio (LAR) ($cm^2\ g^{-1}$), and thus ozone tolerance may decrease with increasing SLA, as suggested by Bassin et al. (2007a) and Matyssek et al. (2008). Thicker cell walls could have more detoxification capacity due to longer residence times of ROS and thus a higher probability of interactions with antioxidants (Plöchl et al. 2000; Rinnan and Holopainen 2004).

Morphological traits of leaves could be altered by climate change. For instance, interactive effects of increased temperature, drought and elevated CO_2 on leaf morphology were studied in canola (*Brassica napus*) (Qaderi et al. 2006). The study showed that specific leaf weight (SLW, $g\ m^{-2}$) and LAR increased in response to drought and higher temperature thus indicating the formation of thicker leaves, while elevated CO_2 partially reversed the effect. Changes in leaf structure may reflect adaptation to reduce water loss under dry and warm conditions, which would imply increased tolerance to ozone.

Shifts in crop phenology

The largest influence of environmental stresses on final cereal yield in terms of number of kernels head^{-1} and individual kernel weight occurs during the stages of booting through heading and anthesis to grain filling (Klepper et al. 1998). Pleijel et al. (1998) showed that ozone exposure is much more effective in decreasing the grain yield of wheat between anthesis and end of grain filling than ozone exposure before anthesis. Soja et al. (2000) identified for wheat that the most sensitive period was defined as starting 2 months before and ending 1 month after anthesis, with the month in the middle as the most relevant one, and for bean during post-anthesis, i.e. during pot-setting and pot-filling. For bean (*Phaseolus vulgaris*), Tingey et al. (2002) suggested that ozone-sensitivity was greatest during pod filling and maturation because of reduced energy levels available for repair. In plantain (*Plantago lanceolata*), as in other native species, maximum sensitivity to ozone likely occurs during early developmental stages (Soja et al. 2000). Later in the season, g_s and ozone uptake decline (Jaudé et al. 2008; Bergweiler et al. 2008). But Soja et al. (2000) argued that periods of maximum ozone uptake may not coincide with periods of highest sensitivity with respect to crop yield because of diurnal variations in leaf defence capacity. For potato, Hacour et al. (2002) concluded that the most distinct effects of long-term exposure to ozone were only apparent at full canopy, but even more significant during crop senescence. Similarly, a meta-analysis of data for soybean (*Glycine max*) revealed increasing impact of ozone with developmental stage with the greatest effect evident at completion of seed filling (Morgan et al. 2003).

With increasing temperature, phenology will change. A national survey of the phenology of 78 agricultural and horticultural events in Germany spanning the years 1951–2004 revealed that perennial crops exhibited a significantly higher response to mean spring temperature than the annual crops, and that the mean response lies around 4 d $°C^{-1}$ (Estrella et al. 2007). Also, elevated CO_2 was generally found to accelerate crop development (*cf.* Cleland et al. 2007). With this shift in development, most sensitive stages will occur earlier during the year. Also, with warmer spring temperatures farmers will likely advance planting dates. Hence, with climate change the phenological calendar of crops and the seasonal pattern of high ozone levels could become separated, particularly in the more polluted regions where highest levels of ozone occur during the warmest part of the year. Conversely, in more remote regions with early springtime peaks in ozone, together with conditions favouring high g_s, the situation may be worse as the advancement of plant development may lead more frequent co-occurrence of sensitive stages and early-season ozone stress (Karlsson et al. 2007). Thus, studies of future ozone risk for vegetation need to take account of shifting crop phenology, in relation to changing seasonal patterns of microclimatic conditions.

Shifts in pasture community characteristics

Climate change and elevated CO_2 will affect the productivity and species composition of pastures (Lüscher et al. 2005). Hence, effects of ozone on future pasture communities cannot be assessed without considering species changes. Provided that with increasing T_a and less rainfall during the growing season, species with xeromorphic characteristics such as dense leaves, succulence, dense hairiness or a thick cuticle may be favoured (see the previous section). These species are likely more tolerant to ozone due to reduced g_s and lower mesophyll conductance. But in areas with increasing dryness, more sparse canopies may develop providing improved penetration of ozone and enhanced ozone exposure across the entire canopy.

Secondary effects

Pests, diseases and weeds

Ozone can have secondary effects on crops by affecting the incidence of pests and diseases and by altering crop–weed competition (*cf.* Fuhrer and Booker 2003). However, little is known about how the effect of ozone may be modified in a future climate with elevated CO_2 in specific host–pathogen or crop–weed systems. The outcome of environment–plant–pathogen or plant–pest interactions may strongly vary with timing, stage of plant development, predisposing factors and environmental conditions thus making generalised predictions for future conditions very difficult (*cf.* Fuhrer 2003). In one of the rare studies under realistic field conditions, elevated ozone in combination with elevated CO_2 had no effect on adult female density but stimulated egg-laying by a variant of the western corn rootworm (Coleoptera: Chrysomelidae) suggesting increased population density and risk of damage to the subsequent corn crop (Schroeder et al. 2006). Climate change is likely to modify the disease spectrum in some regions and pathogens or pests considered unimportant today may turn out to be potential new threats in future (Chakraborty et al. 2000), but this issue is beyond the scope of this review. An important role is played by the onset of senescence in ozone-exposed plants and the declining quality of the leaves, for instance in relation to aphid infestation. Since ozone accelerates leaf senescence, it can be expected that pests and diseases which depend on a high quality diet will decline, while those primarily affecting weakened plants will increase. However, data for specific pests and diseases are often controversial. As an example, for aphids there are nearly equal numbers of reports indicating increased, reduced or no effect of ozone on performance (Holopainen 2002). According to Pritchard et al. (2007) it is unreasonable to expect that a single plant component can predict the general response of aphids to climate change, and the same may apply to ozone.

Similarly, little is known about crop–weed interactions, but differential ozone tolerance of crops and weeds could alter the competitive outcome. For instance, tomato (*Lycopersicon esculentum*) was more sensitive to ozone than nutsedge (*Cyperus esculentus*), which reduced tomato productivity under low and moderate ozone concentrations; thus, control of this weed may become more difficult with increasing ambient ozone levels (Shrestha and Grantz 2005). Ozone may also affect the effectiveness of herbicides. In the San Joaquin Valley (California), Grantz et al. (2008) found that a glyphosate-resistant biotype of horseweed (*Conyza canadensis*) may lose its competitive advantage in polluted environments.

Soil C sequestration

Effects of ozone on residue mass and on the concentration of secondary metabolites, lignification and/or the C/N ratio of above- and below-ground plant parts may change decomposition processes in the soil (Booker et al. 2005). This aspect must be considered in the context of reduced transfer of C to roots and the soil and soil C turnover. Data from a study with blackberry (*Rubus cuneifolus* Pursh.) and broomsedge bluestem (*Andropogon virginicus*) indicated that ozone influences substrate quality and soil microbial activity, resulting in reduced rates of litter decomposition (Kim et al. 1998). The effects of ozone on plant and residue quality may translate into lasting changes in soil chemical and microbiological properties. In aspen (*Populus tremuloides*) and in mixed aspen-birch (*Betula papyrifera*) stands, Loya et al. (2003) observed that after 4 years of exposure, ozone strongly inhibited extra stable soil C formation from elevated CO_2. Under wheat and soybean, elevated ozone caused a change in soil C quality towards high molecular weight and more aromatic components, in contrast to elevated CO_2 (Islam et al. 1999). Highly relevant in a global change context is the effect of ozone on C pools in grassland soils, which probably contribute >10% of the total biosphere C store (*cf.* Jones and Donnelly 2004). Volk et al. (2006) reported decreasing productivity in semi-natural grasslands after 5 years of elevated ozone, suggesting reduced C transfer to soil. In meadows at a northern European site, Kanerva et al. (2008) observed changes in biomass and composition of microbial communities, which may affect soil processes. Thus improved estimates of potential soil C sequestration under different management regimes and climate scenarios need to take into account the effects of ozone, as suggested by simulation with biogechemical models (Ren et al. 2007a; Sitch et al. 2007). However, there are great uncertainties associated with model parameters (Ren et al. 2007b). In most studies, effects of ozone are simulated from direct effects on photosynthesis and indirect effects on g_s by changing intercellular CO_2 concentration. Possible changes in residue quality, which may affect carbon cycling and stabilisation in the soil, are often ignored due to uncertain effects of ozone on this parameter. Moreover, effects of fertilisation, irrigation tillage and differences between different crop types are not usually taken into account.

The negative impact of ozone on stable soil C pools could be aggravated by higher T_a. In modelling studies, increasing temperatures could favour net soil C losses in arable and grassland soils (Smith et al. 2008), but the issue is still controversial (Davidson and Janssens 2006). It has been stated that rates of soil C loss through soil respiration could acclimate to higher T_a and would decline after a period of treatment at elevated T_a (Luo and Zhou 2006). Moreover, effects of climate change, CO_2 and ozone on soil C overlaps with strong effects of soil use and management (Dawson and Smith 2007).

Crop improvement

Crop improvement could help to limit crop losses due to changing climatic conditions with more frequent periods of stress such as heat and drought and, hence, to increase food security. One way of achieving this would be to create varieties with improved tolerance to oxidative stress caused by ozone, based on the current understanding of the underlying mechanisms (see above). Comparative studies reveal considerable variation between genotypes in ozone tolerance, such as in snap bean (*Phaseolus vulgaris*) (Flowers et al. 2007). Although the more tolerant genotypes were not found to have significantly higher leaf antioxidant levels (Burkey et al. 2000), ozone tolerance can be associated with elevated extracellular asc contents at low ozone concentrations (Burkey and Eason 2002). Suitable varieties could be identified through rapid selection based on molecular genetic approaches to identify discrete traits and by quantitative trait locus (QTL) mapping for complex traits (Takeda and Matsuoka 2008), particularly if these traits are generic across differently stressed environments (Reynolds et al. 2007). Given that oxygen toxicity plays an important role not only with respect to ozone but also to other abiotic stresses (Reynolds et al. 2005), ozone-tolerant varieties may be among those varieties selected for tolerance to other stresses such as drought, heat or salt. Moreover, older varieties could be a source of more ozone-tolerant material due to lower g_s (Pleijel et al. 2006), higher antioxidative capacity and higher levels of dark respiration leading to lower oxidative damage to proteins and integrity of cellular membranes (Biswas et al. 2008).

One of the most important effects of ozone is a reduction of leaf lifespan. In cereals, accelerated senescence shortens the period of grain filling and grain ripening, leading to reduced grain weight. Drought has a similar effect and crops with pronounced drought tolerance such as sorghum (*Sorghum bicolor*) are characterised by their capacity to delay senescence during dry periods, i.e. the ‘stay green’ trait. The underlying mechanisms have been discussed extensively by Takeda and Matsuoka (2008). It needs to be assessed whether the genetically controlled mechanisms behind improved grain filling under drought could also confer tolerance to ozone through the reduction of ozone effects on leaf senescence, which again could be tied to the role of asc in determining the onset of senescence (Conklin and Barth 2004).

Conclusions

Ozone risks for crops and pastures depend on exposure, leaf uptake and the plant’s defence capacity. These components are likely to change with changing anthropogenic emissions of precursor gases and climatic conditions. Largest effects of increasing emissions on ozone levels are expected in region with rapid industrialisation and population growth and limited regulations, while modifying effects of climate change on both ozone levels and plant sensitivity are likely largest in areas experiencing the strongest warming. Properties of leaves determining the rate of absorption such as g_{max} and actual g_s, and the defence capacity can be modified by temperature, air and soil moisture, increasing C_a and altered radiation, all of which are undergoing changes with distinct regional patterns. In areas where the frequency of hot/dry periods is projected to increase such as much of the Mediterranean and central Europe, ozone episodes may become more frequent and cumulative exposures will grow, but leaf uptake of ozone will decline. In contrast, in more remote rural areas with rapid warming and less drying, for instance at northern latitudes, ozone risks are likely to grow because of increasing hemispheric transport of pollution leading to peak ozone levels at times when plant sensitivity is high. Excess ozone uptake not only reduces crop growth and yield and alters crop quality but in the longer term may also lead to changes in species and genetic composition of semi-natural plant communities and the ecosystem, water, economy and carbon stocks. However, uncertainties in climate projections and in model parameters make projections for future risks of increasing ozone difficult. Empirical information obtained under current climatic conditions should not be extrapolated in time because of changing functional relationships and because plant traits will change in response to climate change and technological developments. Thus, studies on interactions of different factors and more mechanistic models than those currently used for ozone risk assessments are needed in order to determine future stocks at risks and the regions where ozone may impair food security. This information would be necessary to identify targets for crop improvements and for regulatory purposes.

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