Biodiversity and Ground-level Ozone

[1]Emberson, L.D., [2]Fuhrer, J., [3]Ainsworth, L., [1]Ashmore, M.R.

[1]Stockholm Environment Institute at York, Environment Dept. University of York, UK
[2]Bern University, Agroscope Reckenholz-Tänikon Research Station ART, Zürich, Switzerland
[3]USDA ARS Global Change and Photosynthesis Research Unit, Urbana, IL 61801, USA

This note is in response to a call to identify new and emerging issues that was placed by the CBD inviting further technical information on the impact of ground-level ozone (O_3) on biodiversity and about views on the scope and potential relevance of existing international scientific and regulatory mechanisms, including regional ones, on this issue. In this note we try to identify the ways in which ground level O_3 impact on biodiversity is relevant to the key criteria agreed by the CBD CoP.

(a) New evidence of unexpected and significant impacts on biodiversity;

Tropospheric ozone (O_3) is a global, secondary air pollutant impacting human health and ecosystems and an important greenhouse gas resulting in a direct radiative forcing of 0.35 - 0.37 W m^{-2} on climate (Foster et al., 2007; Shindell et al., 2009). The damaging effects of ground level O_3 on photosynthetic carbon assimilation, stomatal conductance, and plant growth negatively impact forests and natural ecosystems (Hayes et al., 2007; Wittig et al., 2009), which have downstream consequences for ecosystem goods and services (Royal Society, 2008).

Current O_3 concentrations are considerably higher in the Northern Hemisphere than the Southern Hemisphere, with background monthly mean O_3 in the Northern Hemisphere ranging from 35 to 50 ppb (Stevenson et al., 2006). In North America and Europe, higher O_3 occur in the summer with peak daily concentrations occurring in the late afternoon. Very high concentrations episodically occur with O_3 levels reaching 200-400 ppb in metropolitan areas or in more remote areas during heat waves (Royal Society, 2008).

The harmful effects of O_3 to vegetation have been well established through experimental studies, predominantly conducted in North America and Europe over the past 3 decades, but more recently in Asia. However, research has tended to focus on agricultural crops with fewer studies conducted on forest trees, and fewer again on grasslands. The vast majority of research investigating grassland responses to O_3 comes from Europe, with little experimentation done in the U.S., even less in Asia and none in the tropics. Thus, compared to trees and crops, much less is known about how grasslands are impacted by current and future O_3.

Seasonal O_3 profiles are also changing as hemispheric transport of O_3 affects the sources of O_3 and precursor emissions and hence the build up and destruction of the pollutant in the atmosphere. This has resulted in a strong shift in the seasonality of O_3 exposure, reflecting the stronger influence of northern hemisphere background concentrations which peak in the spring. This also suggests that early season species (such as the woodland bulb species) are at an increasing risk of adverse effects. To date the consequences of these changes in O_3 seasonality and associated impacts on biodiversity are poorly understood (HTAP, 2010).

Relevance of the issue to the implementation of the objectives of the Convention and its existing programmes of work;

In spite of the variability in global coverage of data describing O_3 effects on biodiversity there is substantial evidence from those studies that have been conducted showing that O_3 could be causing substantial damage to biodiversity, and the ecosystem services supported by biodiversity; these issues are explored further in this short technical note.

Ground level O_3 impacts on biodiversity

Recent meta-analyses comparing Northern temperate trees exposed to current ambient concentrations of O_3 compared to charcoal-filtered air suggest that currently O_3 is decreasing net photosynthesis of trees by 11% (Wittig et al. 2007) and a 7% decrease in tree biomass (Wittig et al. 2009). A limitation of extrapolating these data to mature forests is that the estimates are largely based on individual, young trees growing in a non-competitive environment, and extrapolation of results from seedlings may not be appropriate for predicting the response of mature trees and forests to O_3 (Chappelka & Samuelson 1998). However, since forest

vegetation and soils store more than 50% of terrestrial carbon (Dixon et al. 1994) the negative effects of O_3 on forest productivity have implications both for biodiversity as well as for the global carbon cycle and climate change (Felzer et al. 2005; Sitch et al. 2007).

Grasslands are highly diverse, multi-species communities, with a wide range of productivities. Therefore, predicting the response of grasslands to O_3 is complex, dependent upon both the sensitivities of individual species and the mutualistic interactions, competitive interactions, and specific microclimatic conditions, which may influence individual O_3 responses. While experiments have documented that elevated O_3 decreases grassland productivity (Volk et al., 2006, Bassin et al., 2007a), other experiments with established temperate (Volk et al., 2011), calcareous (Thwaites et al., 2006) and alpine grasslands (Bassin et al., 2007b) have shown that NPP of these systems is relatively resilient to rising O_3. Species also have been shown to respond differently to O_3 depending on competition (Scebba et al., 2006) and O_3 can have carry-over effects on growth and overwintering of grassland species (Hayes et al., 2006). Ozone also has more subtle changes in carbon assimilation, leaf longevity, and biomass partitioning of grassland species, suggesting that grassland productivity may decline in the longer term in response to O_3 (HTAP, 2010).

Ground level O_3 impacts on Ecosystem Services associated with biodiversity
Carbon sequestration
Semi-natural grassland ecosystems often host large species numbers, but are also known for high soil C-contents that may be sensitive to environmental disturbance. Ozone taken up by plant leaves alters the ecosystem C-balance directly through effects on photosynthetic C-fixation, plant respiratory C-loss and C-partitioning between different organs, and indirectly via changes in the degradation of plant-derived litter due to altered residue chemistry and changes in soil microbial activity. The net effect is often assumed to be a reduction in the C-balance indicating a loss of soil C sequestration, but experimental evidence obtained under realistic field conditions is scarce. In a long-term study in species-rich, low productivity mountain grassland with a high soil carbon content, it was observed that coupled effects of elevated O_3 on C-fixation and ecosystem respiration did not significantly alter seasonal C balance (Volk et al., 2011), but changes occurring beyond the duration of the experiment or in other grassland ecosystems cannot be excluded.

Empirical data have shown that plant response to O_3 is modified under other aspects of environmental change that stress plant systems, including other pollutants, atmospheric CO_2 concentrations, temperature, precipitation (or soil moisture availability) and N availability. The interactive effects of O_3 and atmospheric CO_2 concentrations on plants have received much attention (reviewed by Fuhrer 2009), although understanding is far from complete. Increased atmospheric CO_2 concentrations reduces stomatal conductance (Ainsworth & Rogers 2007), which subsequently decreases O_3 flux into plants (Fiscus et al. 2005). Such reductions in O_3 uptake would also lead to increased atmospheric O_3 concentrations in the boundary layer; in fact a doubling of CO_2 concentration was estimated to increase O_3 concentration over parts of Europe, Asia and the Americas by 4-8 ppb during the crop growing season (Sanderson et al. 2007). However, the relationship between stomatal conductance and CO_2 concentration may prove to be more complex than often assumed and elevated CO_2 may not completely alleviate the adverse effect of O_3 (Uddling et al., 2010). There is evidence from long-term field experiments that O_3 can significantly alter C cycling and reduce the increase in forest soil C sequestration caused by elevated $[CO_2]$ (Loya et al., 2003; Karnosky et al., 2005). However, the scant experimental data on the long-term effects of O_3 on soil C fluxes in a range of ecosystems is a major limitation to understanding the impacts of O_3 on global C fluxes (Andersen, 2003; Ashmore, 2005). Atmospheric CO_2 concentrations and O_3 concentrations also have the potential to alter N cycling in forest ecosystems through influences on plant growth and litter production. Generally, CO_2 stimulates photosynthesis, leaf and root litter production, while O_3 damages photosynthetic tissues and accelerates leaf senescence. The interactions between O_3, CO_2 and N are complex, and dependent on plant and soil microbial processes, which feedback on N availability (Holmes et al. 2006).

Hydrological cycle
As atmospheric CO_2 concentration increases in the future, global climate will change. In particular, temperature will increase and precipitation will change, and both are important determinants of stomatal conductance, NPP and uptake of O_3. As such, reduced stomatal conductance that occurs in response to elevated CO_2 concentrations may enhance water use efficiency of plants, which could help to partly alleviate the effects of reduced rainfall (Leakey et al. 2009). Increased water stress in a warmer climate may also be expected to decrease sensitivity to O_3 through reduced uptake (Fuhrer, 2009); however O_3 induced-damage to

stomatal functioning (Maier-Maercker, 1999; Mills et al., 2009; Wilkinson and Davies, 2009, 2010) might confound this effect. Understanding how combinations of increased temperature, drought and O_3 might interact to influence plant transpiration and hence water balance is complicated by our limited knowledge of the processes involved (Arneth et al. 2010). One of the few examples of observational data investigating responses to stress combinations is that collected for a mixed deciduous forest in eastern Tennessee, USA (McLaughlin et al., 2007a). These data suggest an increase in water use under warmer climates with high [O_3] with subsequent limitations of growth of mature forest trees and implications for the hydrology of forest watersheds (McLaughlin et al. 2007). There is also limited evidence to suggest that O_3 can affect CH_4 emissions from peatlands, possibly through O_3 causing plants to alter substrate availability to soil microbes or changes in transport of CH_4 through vascular plants with aerenchymatous tissue (Toet at el. 2011). The implications of such O_3 effects on CH_4 emissions could provide important feedbacks since CH_4 emissions themselves contribute significantly to predicted increases in global background O_3 concentrations (West & Fiore, 2005).

Urgency of addressing the issue/imminence of the risk caused by the issue to the effective implementation of the Convention as well as the magnitude of actual and potential impact on biodiversity;
Estimates of future O_3 vary widely depending on emissions and legislation scenarios. Projections from the HTAP 2010 assessment used mean O_3 concentration estimates from 6 global models to assess the implications of emission changes between 2000 and 2050 following the Representative Concentration Pathways (RCP) emission scenarios constructed for IPCC-AR5 (Figure 1). The results suggest changes in surface O_3 by 2030 over North America and Europe ranging from changes of about 1 ppb in the BAU RCP 8.5 scenario to reductions of about 5 ppb in the cleaner RCP 2.6 scenario. South Asia sees the greatest increases, ranging up to more than 5 ppb for RCP 8.5, while East Asia shows increases of about 2 ppb for RCP 8.5 and reductions of about 4 ppb for RCP 2.6. In summary, the future outlook for O_3 concentrations is strongly dependant on global and regional emission pathways and as such the urgency to take action to mitigate for O_3 impacts on biodiversity depends on which of these pathways of followed.

Figure 1. Mean surface O_3 changes over polluted regions of the Northern Hemisphere following the four RCP scenarios from 200 to 2050, for further details see HTAP, 2010.
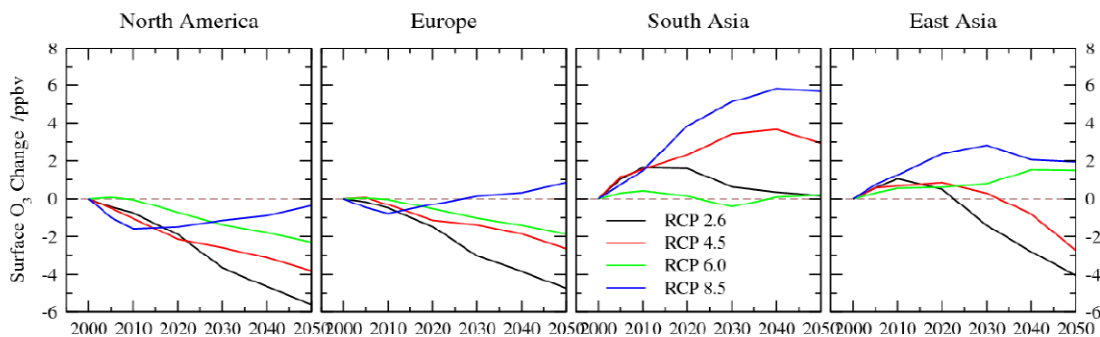

Evidence of the absence or limited availability of tools to limit or mitigate the negative impacts of the identified issue on the conservation and sustainable use of biodiversity;
Mitigation of O_3 precursor emissions (predominantly nitrogen oxides, carbon monoxide and volatile organic compounds including methane) requires changes in industrial, domestic and transport related emissions, often as part of international emission reduction programmes since O_3 is a transboundary pollutant. Importantly, the only world region that is making any concerted effort to control O_3 concentrations to limit vegetation damage is Europe through work under the UNECE Convention on Long Range Transboundary Air Pollution (http://unece.org/env/lrtap/) and various EU legislative directives. However, still thresholds and targets set by these bodies are exceeded in many locations across Europe with the likelihood that damage to vegetation resulting from O_3 exposures will be occurring across the region. The lack of similar international efforts to control O_3 precursor emissions in other parts of the world means that many ecosystems are completely unprotected from this strongly phyto-toxic pollutant.

Actual geographic coverage and potential spread, including rate of spread, of the identified issue relating to the conservation and sustainable use of biodiversity;

Experimental and modelling approaches are currently being used to understand plant responses to elevated O_3 and to predict their impacts on global net primary productivity (NPP); however significant gaps in knowledge remain about the interactions of rising tropospheric O_3 and other environmental factors including drought, soil nutrient status and variables associated with climate change (e.g., elevated CO_2 and rising temperature). While tropospheric O_3 is a driver of global warming, other climate changes over the next century have the potential to influence future O_3 by modifying the rates of O_3 production and destruction in the atmosphere and at the Earth's surface. For example, increasing atmospheric O_3 will negatively impact plant production, reducing the ability of ecosystems to sequester carbon, and thus indirectly feedback on atmospheric CO_2 concentrations, enhancing climate change (Sitch et al., 2007).
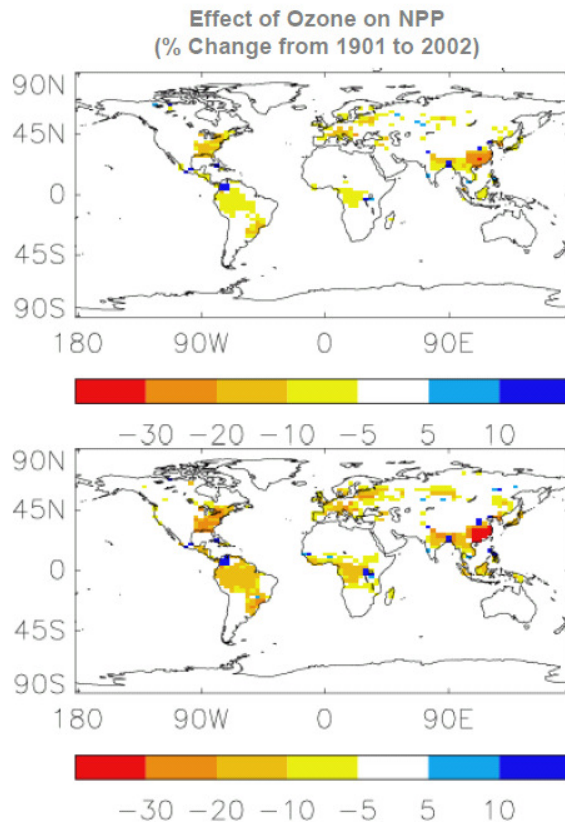
Figure 2 Simulated percentage change in net primary productivity (NPP) between 1901 and 2002 due to O_3 effects considering changes in atmospheric CO_2 concentration for 'lower'(upper panel) and 'high' (lower panel) O_3 plant sensitivity.

This model has also been used to estimate future impacts of O_3 on global productivity, and the results suggest that O_3 may offset potential gains in global GPP from rising atmospheric CO_2 concentrations by 18 – 34% (Sitch et al. 2007). These results were overlain with the World Wildlife Foundation G200 eco-regions to assess future threats of O_3 to biodiversity (Royal Society, 2008). Key biodiversity areas in south and east Asia, central Africa and Latin America were identified as being at risk from elevated O_3 concentrations (Figure 3).
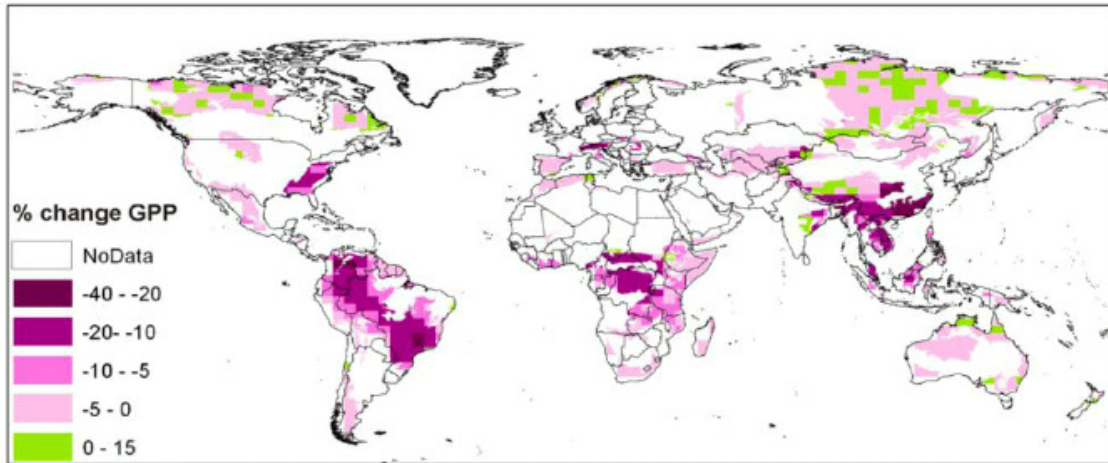
Figure 3. Global assessment of the projected percent decrease in gross primary productivity due to O3 under the IPCC A2 scenario in 2100 within the World Wildlife Foundation Global 200 priority conservation areas. From Royal Society (2008).

While the outputs from these modelling exercises offer the only global estimates for O_3 effects on NPP and associated impacts on ecosystem properties and services, there are limitations to these estimates. Still, the models support experimental findings that O_3 has had a significant negative impact on terrestrial NPP since the Industrial Revolution, which has important implications for terrestrial carbon storage and global radiative forcing (Sitch et al. 2007).

Magnitude of actual and potential impact of the identified issue on human well-being;
Affects on key ecosystems services will indirectly affect human well-being. There is some evidence that the cultural amenity value of conservation sites may be affected as O_3 can impact species of high conservation value (ROTAP, 2011). For example, much of the recent experimental work in the UK has focussed on semi-natural plant communities. The diversity of such communities, and the limited data available, make a detailed assessment of the national implications of these findings problematic. While the evidence base is too limited to provide clear conclusions on where ozone may pose the greatest threat to achieving targets for protection of biodiversity, there is an accumulating body of evidence that O_3 could have significant adverse effects on communities of high conservation value. BAP Priority Habitats were identified as being at greatest risk from O_3 with evidence of adverse effects on key indicator species (ROTAP, 2011). Analyses concluded that there was little evidence of adverse effects of season long exposure to O_3 on key species of montane, coastal wetland and heathland habitats although these did show sensitivity in a European assessment (Mills et al., 2007), but there was such evidence for UK woodland and grassland habitats. The information for these latter habitats is summarised in Table 1. For all four of the habitats in Table 1, the European threshold for adverse effects of O_3 is exceeded over a significant proportion of the UK area of the habitat, and there is experimental evidence to demonstrate that O_3, at relatively low concentrations, can have effects that would reduce the conservation value of the habitat. However, unlike nitrogen deposition, no spatial surveys exist to assess if species richness or species composition is different in areas of the country with higher ozone concentrations; this partly reflects the relatively small spatial gradients in O_3 across the countryside and partly the difficulty of defining appropriate O_3 exposure metrics (ROTAP, 2011).

Table 1. Summary of potential impacts of ozone on habitats of major conservation importance. The second column provides estimates of the proportion of the UK which is in exceedance of the critical level of an AOT40 of 5 ppm.h over six months (April-September).

Habitat	% of UK area of habitat above critical level	Effects on positive indicator species and functional groups	References
Calcareous grassland	71.5%	Reduced cover of dominant fine grass species and characteristic forb species	Thwaites et al., 2006
Acid grassland	25.9%	Decreased cover of characteristic grass species and forbs	Hayes et al, in prep
Mesotrophic grassland	21.8%	Reduced total productivity, Reduced cover of dominant fine grass species, and reduced cover of legume species Decreased cover of forbs, increased grass cover	Peacock et al., in prep Mills et al., in prep
Deciduous woodland	57.3%	Reduced flowering and bulb growth in characteristic woodland ground flora species Increased cover of shade intolerant woodland species	Peacock et al, in prep. Keelan (2008)

There may also be implications to human health resulting from enhanced atmospheric O_3 concentrations caused by reductions in the vegetative sink strength. Such reductions can occur as O_3 causes enhanced water loss from the system (see above), drying the soil and leading to a more rapid occurrence of water stress; this will cause the stomates to close reducing O_3 dry deposition and leading to a build up of atmospheric O_3 concentrations which may impact human health.

Magnitude of actual and potential impact of the identified issue on productive sectors and economic well-being as related to the conservation and sustainable use of biodiversity;

The evidence for negative effects of O_3 on fodder production is relatively strong, but it may depend on the type of plant community. Systems with high plant diversity are often low productivity systems due to climatic and edaphic conditions and the lack of nutrient inputs. Hence, reduced fodder production as observed by Volk et al. (2006) may be less important than in higher productivity systems with fewer species such as grass-legume pastures. In such systems significant losses in fodder production have been observed, although resistant species may benefit from the loss of more sensitive community components which compensates for the decline (e.g. Fuhrer et al. 1992). The more relevant observation thus may be a shift in plant species composition as this may have implications for both conservation and fodder quality. Long-term shifts in species composition in semi-natural grasslands with a high conservation value may be mediated through differential effects of O_3 on plant water status resulting from a negative effect of O_3 on leaf water diffusion, as indicated by results obtained under close-to-natural field conditions (Jäggi & Fuhrer, 2007). More subtle changes in diversity at the genetic level may be caused by micro-evolutionary processes (Kölliker et al., 2008), thus reflecting a possible slow adaptation of some species to O_3 stress.

In North America, experimental studies on semi-natural grasslands have focused on understanding O_3 impacts on nutritive quality of forage crops utilized in livestock production and/or as food and habitat for wildlife. These studies have used both FACE and chamber methods, that have exposed herbaceous vegetation (including fodder crops and naturally grown native grasses and forbs) to either ambient or elevated O_3 levels (comparing with filtered or ambient concentrations as appropriate). Most studies have been with improved, cool season C_3 grasses and legumes though a few studies have also investigated warm season and C4 grasses (Krupa et al. 2004). Results have found a variety of impacts on nutritive quality most commonly assessed in terms of altered concentrations of protein and /or cell-wall constituents such as lignin (e.g. Muntifering et al. 2006b). From such assessments, the forage value of species and communities can be derived using indices such as relative food value (RFV; Muntifering et al., 2006a) and consumable food value (CFV; cf. Krupa et al., 2004). These show that O_3 can reduce digestibility and nutritive food value though the metabolic processes underlying O_3-induced changes in nutritive quality are likely to be species-dependent, particularly in legumes adapted to a warm season and in C_4 grasses (Krupa et al. 2004).

Finally, as climate changes so can the incidence and distribution of pests and diseases; since studies have also shown that O_3 can mediate such impacts, either by causing toxicity to the secondary stress or by affecting the abundance and quality of the host plant (Flückiger et al., 2002; Fuhrer and Booker 2003; Fuhrer, 2009), interactions between climate and O_3 on the prevalence of such secondary stresses should also be considered. Interactions may also occur with increased N deposition to N limited ecosystems since insect herbivores are frequently limited by N availability. Additionally, rising atmospheric CO_2 concentrations may increase plant productivity at the expense of foliar N concentrations and may increase production of C based allelochemicals, both reducing the quality of the host plant (cf. Flückiger et al., 2002). Unfortunately, data for specific pest, disease and plant species competition interactions are often controversial (Fuhrer, 2009) complicating efforts to project parasite-host interactions under future environmental change.

References

Andersen CP. 2003. Source-sink balance and carbon allocation below ground in plants exposed to ozone. *New Phytol.* 157:213–228

Arneth A, Harrison SP, Zaehle S, Tsigaridis K, Menon S, et al. 2010. Terrestrial biogeochemical feedbacks in the climate system. *Nature Geosci.* 3:525-532

Ashmore MR. 2005. Assessing the future global impacts of ozone on vegetation. *Plant Cell Environ.* 28:949-964

Ainsworth EA, Rogers A. 2007. The response of photosynthesis and stomatal conductance to rising [CO2]: mechanisms and environmental interactions. *Plant Cell Environ.* 30:258-270

Bassin S, Volk M, Fuhrer J (2007a) Factors affecting the ozone sensitivity of temperate European grasslands: an overview. Env. Poll. 146:678–691

Bassin S, Volk M, Suter M, Buchmann N, Fuhrer J. 2007b. Nitrogen deposition but not ozone affects productivity and community composition of alpine grassland after 3 yr of treatment. *New Phytol.* 175:523–534

Chappelka AH, Sameulson LJ. 1998. Ambient ozone effects on forest trees of the eastern United States: a review. *New Phytol.* 139:91-108

Dixon RK, Brown S, Houghton RA, Solomon AM, Trexler MC, Wisniewski J. 1994. Carbon pools and flux of global forest ecosystems. *Science* 263:185-190

Felzer B, Reilly J, Melillo J, Kicklighter D, Sarofim M, Wang C, Prinn R, Zhuang Q. 2005. Future effects of ozone on carbon sequestration and climate change policy using a global biogeochemical model. *Climat. Change* 73:345-373

Fiscus EL, Booker FL, Burkey KO. 2005. Crop responses to ozone: uptake, modes of action, carbon assimilation and partitioning. *Plant Cell Environ.* 28:997-1011

Flückiger W, Braun S, Hiltbrunner E. 2002. Effects of air pollutants on biotic stress. In: *Air pollution and plant life*, eds. JN Bell, M Treshow, 20:379-406. Chichester: John Wiley & Sons, Ltd.

Fuhrer, J., Grandjean Grimm, A., Tschannen, W. & Shariat-Madari, H. (1992) The response of spring wheat (*Triticum aestivum* L.) to ozone at higher altitudes. II. Changes in yield, yield components and grain quality in response to ozone flux. New Phytologist 121, 211-219.

Forster P, Ramaswamy V, Artaxo P, Berntsen T, Betts R, et al. 2007. Changes in atmospheric constituents and in radiative forcing. In *Climate Change 2007: The Physical Science Basis*. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, ed. S Solomon, D Qin, M Manning, Z Chen, M Marquis, et al., pp. 129–234. Cambridge: Cambridge Univ. Press

Fuhrer, J., (2009) Ozone risk for crops and pastures in present and future climates. Naturwissenschaften 96: 173-194

Fuhrer J, Booker F. 2003. Ecological issues related to ozone: agricultural issues. *Environ. Int.* 29:141–154

Hayes F, Mills G, Williams P, Harmens H, Buker P. 2006. Impacts of summer ozone exposure on the growth and overwintering of UK upland vegetation. *Atmos. Environ.* 40:4088-4097

Hayes F, Jones MLM, Mills G, Ashmore M. 2007. Meta-analysis of the relative sensitivity of semi-natural vegetation species to ozone. *Environ. Pollut.* 146:754-762

Holmes WE, Zak DR, Pregitzer KS, King JS. 2006. Elevated CO2 and O3 alter soil nitrogen transformations beneath trembling aspen, paper birch, and sugar maple. *Ecosystems* 9:1354-1363

HTAP (2010) Dentener F, Keating T, Akimoto H, eds. 2010. *Hemispheric Transport of Air Pollution 2010. Part A: Ozone and Particulate Matter*, pp. 1-278. New York: United Nations

Jäggi, M. & Fuhrer, J.: Oxygen and carbon isotopic signatures reveal a long-term effect of free-air ozone enrichment on leaf conductance in semi-natural grassland. Atmospheric Environment 41, 8811-8817, 2007

Karnosky DF, Pregitzer KS, Zak DR, Kubiske ME, Hendrek GR, Weinstein D, Nosal M, Percy KE. 2005. Scaling ozone responses of forest trees to the ecosystem level in a changing climate. *Plant Cell Environ.* 28:965-981

Kölliker, R., Bassin, S., Schneider, D., Widmer, F. & Fuhrer, J. (2008) Elevated ozone affects the genetic composition of *Plantago lanceolata* L. populations. Environmental Pollution 152, 380-386

Krupa, S.V., Muntifering, R. & Chappelka, A.H. (2004). Effects of ozone on plant nutritive quality characteristics for ruminant animals. *The Botanica* **54,** 1-12.

Leakey ADB, Ainsworth EA, Bernacchi CJ, Rogers A, Long SP, Ort DR. 2009. Elevated CO2 effects on plant carbon, nitrogen, and water relations: six important lessons from FACE. *J. Exp. Bot.* 60:2859-2876

Loya WM, Pretgitzer KS, Karberg NJ, King JS, Giardina CP. 2003. Reduction of soil, carbon formation by tropospheric ozone under increased carbon dioxide levels. *Nature* 425:705–707

Maier-Maercker U. 1999. Predisposition of trees to drought stress by ozone. *Tree Physiol.* 19:71-78

McLaughlin SB, Wullschleger SD, Sun G, Nosal M. 2007. Interactive effects of ozone and climate on water use, soil moisture content and streamflow in a southern Appalachian forest in the USA. *New Phytol*. 174:125-136

Mills, G., Hayes, F., Jones, M.L.M. and Cinderby, S. (2007a) Identifying ozone-sensitive communities of (semi-) natural vegetation suitable for mapping exceedance of critical levels. *Environmental Pollution*, 146, 736-743.

Mills G, Hayes F, Wilkinson S, Davies WJ. 2009. Chronic exposure to increasing background ozone impairs stomatal functioning in grassland species. *Global Change Biol.* 15:1522-1533

Muntifering, R.B., Manning, W.J., Lin, J.C., Robinson, G.B. (2006a). Short-term exposure to ozone altered the relative feed value of an alfalfa cultivar. Environmental Pollution 140, 1-3.

Muntifering, R.B., Chappelka, A.H., Lin, J.C., Karnosky, D.F., Somers, G.L. (2006b). Chemical composition and digestibility of *Trifolium* exposed to elevated ozone and carbon dioxide in a free-air (FACE) fumigation system. Functional Ecology 20, 269-275.

Ren, W., Tian, H., Chen, G., Liu, M., Zhang, C., Cheppelka, H., Pan, S. (2007) Influence of ozone pollution and climate variability on net primary productivity and carbon storage in China's grassland ecosystems from 1961 to 2000 Env. Poll. 149: 327-335

ROTAP, 2011. http://www.rotap.ceh.ac.uk/

Royal Society. 2008. Ground-level ozone in the 21st century: future trends, impacts and policy implications. Science Report, Royal Society

Sanderson MG, Jones CD, Collins WJ, Johnson CE, Derwent RG. 2003. Effect of climate change on isoprene emissions and surface ozone levels. *Geophys. Res. Lett*. 30:1936

Scebba F, Canaccini F, Castagna A, Bender J, Weigel HJ, Ranieri A. 2006. Physiological and biochemical stress responses in grassland species are influenced by both early-season ozone exposure and interspecific competition. *Environ. Pollut.* 142:540-548

Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N, Bauer SE. 2009. Improved attribution of climate forcing to emissions. *Science* 326:716-718

Stevenson DS, Dentener FJ, Schultz MG, Ellingsen K, van Noije TPC, et al. 2006. Multimodel ensemble simulations of present-day and near-future tropospheric ozone. *J. Geophys. Res.* 111:D08301

Sitch S, Cox PM, Collins WJ, Huntingford C. 2007. Indirect radiative forcing of climate change through ozone effects on the land-carbon sink. *Nature* 448:791-795

Thwaites RH, Ashmore MR, Morton AJ, Pakeman RJ. 2006. The effects of tropospheric ozone on the species dynamics of calcareous grassland. *Environ. Pollut.* 144:500-509

Toet S, Ineson P, Peacock S, Ashmore M. 2011. Elevated ozone reduces methane emissions from peatland mesocosms. *Global Change Biol*. 17:288-296

Uddling J, Hogg AJ, Teclaw RM, Carroll MA, Ellsworth DS. 2010. Stomatal uptake of O3 in aspen and aspen-birch forests under free-air CO2 and O3 enrichment. *Environ. Pollut.* 158:2023-2031

Volk M, Bungener P, Contat F, Montani M, Fuhrer J. 2006. Grassland yield declined by a quarter in 5 years of free-air ozone fumigation. *Global Change Biol.* 12:74-83

Volk M, Obrist D, Novak K, Giger R, Bassin S, Fuhrer J. 2011. Subalpine grassland carbon dioxide fluxes indicate substantial carbon losses under increased nitrogen deposition, but not at elevated ozone. *Global Change Biol.* 17:366-376

West JJ, Fiore AM. 2005. Management of tropospheric ozone by reducing methane emissions. *Environ. Sci. Tech*. 39:4685-4691

Wilkinson S, Davies WJ. 2009. Ozone suppresses soil drying- and abscisic acid (ABA)-induced stomatal closure via an ethylene-dependent mechanism. *Plant Cell Environ.* 32:949-959

Wilkinson S, Davies WJ. 2010. Drought, ozone, ABA and ethylene: new insights from cell to plant to community. *Plant Cell Environ.* 33:510-525

Wittig VE, Ainsworth EA, Long SP. 2007. To what extent do current and projected increases in surface ozone affect photosynthesis and stomatal conductance of trees? A meta-analytic review of the last 3 decades of experiments. *Plant Cell Environ.* 30:1150-1162

Wittig VE, Ainsworth EA, Naidu SL, Karnosky DF, Long SP. 2009. Quantifying the impact of current and future tropospheric ozone on tree biomass, growth, physiology and biochemistry: a quantitative meta-analysis. *Global Change Biol.* 15:396-424